Koninklijke Akademie van Wetenschappen
te Amsterdam.

PROCEEDINGS

OF THE

SECTION OF SCIENCES.

VOLUME V.

AMSTERDAM,
JOHANNES MÜLLER.
June 1903.

(Translated from: Verslagen van de Gewone Vergaderingen der Wis- en Natuurkundige Afdeeling van 31 Mei 1902 tot 24 April 1903. Dl. XI).

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(1st PART)

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December 1902.

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CONTENTS.

KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN TE AMSTERDAM.

PROCEEDINGS OF THE MEETING

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CONTENTS.

The following papers were read:

Physics. — "*Ternary systems.*" IV. By Prof. J. D. van der Waals. (Continued from Vol. IV pag. 694).

B. If we put $T =$ constant in equation I of our previous communication, we find the relation between dp, dx_1 and dy_1 at constant temperature in the following form:

$$v_{21}\, dp = \left\{ (x_2 - x_1) \frac{\partial^2 \zeta}{\partial x_1^2} + (y_2 - y_1) \frac{\partial^2 \zeta}{\partial x_1 \partial y_1} \right\} dx_1 + $$
$$+ \left\{ (x_2 - x_1) \frac{\partial^2 \zeta}{\partial x_1 \partial y_1} + (y_2 - y_1) \frac{\partial^2 \zeta}{\partial y_1^2} \right\} dy_1 \quad . \quad . \quad . \quad . \quad . \quad (II)$$

For a binary system this relation is simplified to:

$$v_{21}\, dp = (x_2 - x_1) \frac{\partial^2 \zeta}{\partial x_1{}^2}\, dx_1$$

We know from the properties of a binary system, that we have then a curve $p = f(x_1)$ and a curve $p = f(x_2)$, and that the branch representing liquid phases is always found higher than the one representing vapour phases. Both curves start at the point representing the vapour-tension of the first component, and finish at the corresponding point for the second component. This however is only true if the temperature is lower than T_{cr} of that component. If $T > (T_{cr})_2$ then the two curves are joined fluently so that they form a single one.

For a ternary system we have to deal with two surfaces $p = f(x_1, y_1)$ and $p = f(x_2, y_2)$ instead of the curves $p = f(x_1)$ and $p = f(x_2)$. We will use as a rule the index 1 for a liquid phasis, the index 2 for a vapour phasis. These surfaces cover the rectangular triangle OXY, and above the angles of this triangle they have points in common. The common ordinates represent the maximum tensions of the three components. This holds good, if the temperature is lower than T_{cr} of each of the components. In some cases these sheets may have still another point in common, just as is the case with the two branches for a binary mixture if a maximum pressure occurs. But for the present we will disregard the existence of such a maximum pressure. If $T < T_{cr}$ of one of the components then the two sheets of the p-surface do not cover any longer the whole rectangular triangle, but they have joined fluently to one surface.

In the above equation II the properties of these two sheets of the p-surface are expressed in the form of a differential equation; — we will now proceed to deduce the principal properties from this equation. Even for the pressure-curves of a binary mixture the number of these properties is already considerable. For a ternary system they will of course be still much more numerous, and even properties occur which have no analogon for a binary system. But many of the properties of the pressure-curves of a binary mixture may directly be extended to the corresponding ones for the pressure surfaces of a ternary mixture. Such properties need hardly be treated here, as we suppose the properties of a binary mixture to be known. Accordingly I will limit myself in the main to treating those properties that are proper to ternary systems but not to binary systems. The study of the ternary systems however has induced me, to give a more detailed discussion of some equations, given in Cont. II for a binary mixture, from a more general point of view. And in some cases this detailed discussion has enabled me to give a more precise and accurate form to some of the equations and to some of the quantities occurring in them. In these cases I shall discuss some properties more extensively, concerning which I had else confined myself to refer to Cont. II.

From a theoretical point of view the relation between p, x_1 and y_1 at given temperature is not more important than that between v_1, x_1 and y_1 or between v_2, x_1 and y_1. But even for a simple substance the experimental investigation concerning the maximum pressure has first been executed, and only in these later years it has been followed by an investigation concerning the densities. In the same way we may expect, that also for a ternary system the experiment will occupy itself in the first place with the determination of the pressure, and that the investigation as to the densities of the phases coexisting with other phases, will follow later. The surface representing for all temperatures the pressure as function of the composition of a binary mixture has been called by me "surface of saturation". We might call for a ternary system the surface whose properties we are about to investigate "surface of saturation for a given temperature". Wherever it is not ambiguous I shall speak simply of "surface of saturation".

In the following considerations we will take triangle OXY in a horizontal plane; the direction in which the pressure is laid off is then vertical. We represent the maximum pressures of the three components by p_1, p_2 and p_3 where we choose the indices in such a way that

$$p_1 < p_2 < p_3.$$

If $T > T_{cr}$ for one of the components, then the surface of saturation does not reach the corresponding angle and the corresponding maximum pressure does not exist any longer.

a. Curves of equal pressure.

For curves of equal pressure, we have $dp = 0$, and equation II is reduced to:

$$\left\{(x_2-x_1)\frac{\partial^2\zeta}{\partial x_1^2} + (y_2-y_1)\frac{\partial^2\zeta}{\partial x_1 \partial y_1}\right\} dx_1 +$$
$$+\left\{(x_2-x_1)\frac{\partial^2\zeta}{\partial x_1 \partial y_1} + (y_2-y_1)\frac{\partial^2\zeta}{\partial y_1^2}\right\} dy_1 = 0.$$

The projection of these curves is of course the same as the projection of the connodal curve of the ζ-surface construed for this pressure. We have discussed this projection in our first communication p. 461. If p is chosen such that $p_1 < p < p_2$, the two branches of this projection cut the two sides of the triangle adjacent to the right angle. If $p_2 < p < p_3$ then they cut the hypothenuse and the other side corresponding with the third component. If $p = p_2$ then the two branches cut one another in the angle of the second component. We might find the equation of these curves if we could express x_2 and y_2 in x_1 and y_1, and if $\frac{\partial^2 \zeta}{\partial x_1{}^2}$, $\frac{\partial^2 \zeta}{\partial x_1 \partial y_1}$ and $\frac{\partial^2 \zeta}{\partial y_1{}^2}$ were known. And though this is not completely possible in all cases, yet in some cases we may find the equation approximately. A digression in order to discuss these quantities cannot be left out here; else we shall always be confronted with the same unanswered questions in all subsequent problems.

The value of ζ is given p. 449, vol. IV, in the following form:

$$\zeta = MRT\{(1-x-y)\,log\,(1-x-y) + x\,log\,x + y\,log\,y\} + pv - \int pdv.$$

We omit the linear function of x and y, as it has no influence on the phenomena of equilibrium. So the value of ζ consists of a pure function of x and y, and of another part which fulfils the well known condition:

$$(d\zeta)_{xyT} = vdp.$$

This second part is known if the equation of state is known. In fig. 1, p. 450 I have represented graphically this second part such as we may conclude its course to be if we only assume the principle of continuity. In what follows we will extend the principle of continuity so far, that we assume the equation of state to vary fluently if x and y vary fluently. We now imagine the second part of ζ to be construed for all mixtures, i. e. for all values of x and y, and for all values of p. If we now put $p =$ constant, then we have an auxiliary quantity, which varies with x and y, and the knowledge of whose properties is the condition for the solving of all questions relating to the equilibrium, either of a binary, or of a ternary mixture, or of any system of still more components. As we have already stated the knowledge of this quantity depends on the knowledge of the equation of state. From this appears, how absurd the opinion is, that knowledge of the equation of state would not be required for the knowledge of these systems. Yet we find this opinion often expressed. For the knowledge of the equilibrium of a simple substance it would be required, but for much more complicated systems it would be totally superfluous! I have introduced this auxiliary quantity already before (see i. a. Cont. II, p. 147); I shall represent by μ the quotient, obtained by dividing it by MRT. Now we have:

$$\zeta = MRT\{(1-x-y)\, log\,(1-x-y) + x\, log\, x + y\, log\, y + \mu\}.$$

From this follows

$$\left(\frac{d\zeta}{dx}\right)_{p,T,y} = MRT\left\{ log\, \frac{x}{1-x-y} + \left(\frac{d\mu}{dx}\right)_{p,T,y} \right\}$$

$$\left(\frac{d\zeta}{dy}\right)_{p,T,x} = MRT\left\{ log\, \frac{y}{1-x-y} + \left(\frac{d\mu}{dy}\right)_{p,T,x} \right\}$$

$$\left(\frac{d^2\zeta}{dx^2}\right)_{p,T,y} = MRT\left\{ \frac{1-y}{x(1-x-y)} + \left(\frac{d^2\mu}{dx^2}\right)_{p,T,y} \right\}$$

$$\left(\frac{d^2\zeta}{dxdy}\right)_{p,T} = MRT\left\{ \frac{1}{1-x-y} + \left(\frac{d^2\mu}{dxdy}\right)_{p,T} \right\}$$

$$\left(\frac{d^2\zeta}{dy^2}\right)_{p,T,x} = MRT\left\{ \frac{1-x}{y(1-x-y)} + \left(\frac{d^2\mu}{dy^2}\right)_{p,T,x} \right\}.$$

For brevity's sake I shall represent $\left(\frac{d\mu}{dx}\right)_{p,T,y}$ by μ'_x. With analogous signification the symbols μ'_y, μ''_x, μ''_{xy} and μ''_y will be used.

We deduce from the conditions of coexistence (see p. 551, 553 and 554 Vol. IV) the following relations.

From $\left(\frac{d\zeta}{dx}\right)_1 = \left(\frac{d\zeta}{dx}\right)_2$ follows $\frac{x_1}{1-x_1-y_1}\, e^{\mu'x_1} = \frac{x_2}{1-x_2-y_2}\, e^{\mu'x_2}$ . . (1)

From $\left(\frac{d\zeta}{dy}\right)_1 = \left(\frac{d\zeta}{dy}\right)_2$ follows $\frac{y_1}{1-x_1-y_1}\, e^{\mu' y_1} = \frac{y_2}{1-x_2-y_2}\, e^{\mu' y_2}$ . . (2)

And from $\left\{\zeta - x\frac{d\zeta}{dx} - y\frac{d\zeta}{dy}\right\}_1 = \left\{\zeta - x\frac{d\zeta}{dx} - y\frac{d\zeta}{dy}\right\}_2$ follows:

$$\{log\,(1-x_1-y_1) + \mu_1 - x_1\, \mu'_{x_1} - y_1\, \mu_{y_1}\} = \{log\,(1-x_2-y_2) + \mu_2 - x_2\, \mu'_{x_2} - y_2\, \mu'_{y_2}\}\ (3).$$

From these equations (1), (2) and (3) again follows, that we can express the relation between the composition of the coexisting phases only then, if we know what variation in the equation of state is caused by the substitution of one of the components by another. So we find e. g. for the determination of the limiting value of the ratio of x_1 and x_2 in the case that x_1 and y_1 are infinitely small the equation:

$$log\, \frac{x_2}{x_1} = \mu'_{x_1} - \mu'_{x_2}\ .$$

If we exclude the knowledge of the equation of state, we can in nowise account for the considerable differences which this ratio shows in different cases, and we have to consider it as a primary datum without any relation to other properties of the solvent or of the solved substance. Neither can we account for the value of this ratio, if we think that the application of the law of Boyle is sufficient for the theory of mixtures; for this law is the same for all substances and cannot therefore account for the different values which this ratio has in different cases. Therefore it appears convincibly that a closer investigation of the quantities μ, μ'_x, μ'_y, μ''_x, μ''_{xy} and μ''_y is required. I pass now to this investigation.

We start from the following equation, which may be considered as the definition of the quantity under consideration:

$$MRT\mu = \int_0^p v\,dp$$

So in the first place this quantity depends on p, but as the equation of state for a mixture depends on the composition, it also depends on x and y. We deduce from this equation:

$$MRT\left(\frac{d\mu}{dx}\right)_{pTy} = MRT\mu'_x = \int_0^p \left(\frac{dv}{dx}\right)_{pTv_1} dp$$

If we write $\left(\frac{dv}{dx}\right)_p = -\left(\frac{\partial p}{\partial x}\right)_v \left(\frac{\partial v}{\partial p}\right)_x$, we find also:

$$MRT\mu'_x = -\int \left(\frac{\partial p}{\partial x}\right)_v \left(\frac{\partial v}{\partial p}\right)_x dp = -\int_{v=\infty}^{v} \left(\frac{\partial p}{\partial x}\right)_v dv$$

or $MRT\mu'_x = \left(\frac{\partial \psi}{\partial x}\right)_v$

In Cont. II, p. 9 and p. 19 I have started from this last equation, and making use of the form of the equation of state given there, I have obtained the result, that for low temperatures μ'_{x_2} may be neglected and μ'_{x_1} may be put approximately proportional to $-\frac{dT_{cr}}{dx}$, if by the symbol T_{cr} we represent the temperature which would be the critical temperature of a liquid mixture, if this mixture might be considered as a simple substance; or, what comes to the same, T_{cr} represents that temperature for which the theoretical isothermal of that mixture which we think always homogeneous, presents only one horizontal tangent, and for which therefore maximum- and minimum-pressure have coincided.

It is true that this quantity T_{cr} is no experimental quantity, and that we therefore might superficially think, that the introduction of T_{cr} is of no use; but in the first place in very many cases the critical temperatures, found experimentally, do not differ much from this quantity and in the second place even the simple assumption, that this quantity varies fluently with the composition, will yield many conclusions, confirmed by the experiments. As an instance I mention the connection of the fact, that if a mixture has a minimum critical temperature, a maximum-pressure is found on the connodal curve. A closer investigation of the signification of the quantity μ itself will however enable us to give a still more exact form to all further conclusions which have been deduced in this way, and to all further deductions which are important for the theory of mixtures. For the present I shall occupy myself only with the case that one of the coexisting phases is a rarefied gas-phasis. In this case μ'_{x_2} and μ'_{y_2} may be neglected. For in the equation:

$$MRT\mu = \int^{p} vdp$$

the value of v may be represented by $\frac{MRT}{p}$ if the phases are very rare, and this holds for every mixture whatever its composition may be. Therefore we get by integration:

$$MRT\mu = MRT\,l\,p + \varphi(T) \ .$$

In order to remain in accordance with the form of p. 450, I will determine $\varphi(T)$ such, that we may write:

$$\mu = log\frac{p}{MRT} + 1.$$

This signifies in fig. 1 that the vapour branches coincide, whatever the value of x, y and $1-x-y$ may be.

In all such cases the equations (1) and (2) may be simplified as follows:

$$\frac{x_2}{1-x_2-y_2} = \frac{x_1}{1-x_1-y_1}e^{\mu'_{x_1}}$$

and

$$\frac{y_2}{1-x_2-y_2} = \frac{y_1}{1-x_1-y_1}e^{\mu'_{y_1}}$$

If the pressure increases μ'_x and μ'_y begin to differ from zero, and properly speaking these quantities always differ from zero. This is to be ascribed to the deviation from the law of Boyle which occurs in a different degree for different mixtures. But just as we do not commit considerable errors if we neglect the deviation from the law of BOYLE for rare vapours, but obtain utterly absurd results, if we neglect this deviation for liquids, in the same way we may neglect the difference in the degree of this deviation according to the different composition, if we are treating of a rare vapour phasis, but if we should disregard this difference in the case of a liquid phasis it would lead to absurdities.

Let us now imagine for the different mixtures the pressure to be so far increased, that the double point in fig. 1, p. 450 is reached Experimentally this can of course not be performed without disturbing. the homogeinity, and without condensation of a part of the vapour phasis, which is compressed. But though what we imagine cannot be realised, yet we may put the question, what would happen with the quantity under consideration, if we according to the principle of continuity, should imagine the homogeneity to continue to exist. Then we find the value of μ for the liquid phasis in that double point, and we may write the equation:

$$\mu_l = log \frac{p'}{MRT} + 1. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

The pressure p' in this equation is that one, which we have before called coincidence-pressure. As has already been observed this state cannot be realised. Such a liquid, coexisting with such a vapour would be a state of equilibrium; but an unstable one, or one that is metastable. It is however possible by increasing the pressure still more to get in this way a homogeneous liquid which differs only slightly from the one under consideration and which in fact can be realised as a homogeneous phasis. It appears from fig. (1) that μ for this more compressed liquid is somewhat greater than the value written down in the last equation. But again that surplus of the amount of μ may be neglected. For we have always:

$$MRT\, d\mu = vdp.$$

But if we calculate the surplus of μ, v represents the liquid-volume. And unless the increase of the pressure should be excessive $\frac{vdp}{MRT}$ is a quantity without significance, if v is a volume of a liquid. From this follows that the quantity which we have represented by μ'_{x_1} may be found approximately in differentiating the above equation (4) and therefore may be represented by:

$$\mu'_{x_1} = \frac{1}{p'} \frac{dp'}{dx_1}.$$

In the same way we have:

$$\mu'_{y_1} = \frac{1}{p'}\frac{dp'}{dy_1},$$

so the dependence of μ'_{x_1} and μ'_{y_1} on the coordinates x_1 and y_1 is reduced to the dependence of the coincidence-pressure on x_1 and y_1. The coincidence-pressures would be the maximum-pressures of the different mixtures, if they behaved like simple substances. The following relation exists for the coincidence pressures, at least approximately:

$$-\log\frac{p'}{p_{cr}} = f\frac{T_{cr}-T}{T}.$$

Consequently we find:

$$\mu'_{x_1} = -\frac{f}{T}\frac{dT_{cr}}{dx_1} + \frac{d\log p_{cr}}{dx_1}$$

and

$$\mu'_{y_1} = -\frac{f}{T}\frac{dT_{cr}}{dy_1} + \frac{d\log p_{cr}}{dy_1}$$

or

$$\mu'_{x_1} = -f\frac{T_{cr}}{T}\frac{d\log T_{cr}}{dx_1} + \frac{d\log p_{cr}}{dx_1} \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

and

$$\mu'_{y_1} = -f\frac{T_{cr}}{T}\frac{d\log T_{cr}}{dy_1} + \frac{d\log p_{cr}}{dy_1} \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

It is clear from the deduction that these formulae may only be considered as an approximation for the case, that the vapour-pressure is low, and therefore T much lower than T_{cr}. Putting $f=7$ we may put the factor of the first term at a value of about 12 or 14, and the factor of the second term is unity. If therefore the values of $\frac{d\log T_{cr}}{dx_1}$ and $\frac{d\log T_{cr}}{dy_1}$ have moderate ratios to those of $\frac{d\log p_{cr}}{dx_1}$ and $\frac{d\log p_{cr}}{dy_1}$ we find for μ a course not differing much from proportionality to $-\frac{dT_{cr}}{dx_1}$. So we obtain a result in a way, totally differing from that in which I had obtained it before (Cont. II, p. 148 etc.) But in the way we have now followed we are enabled to add a correction term. Of course these equations (5) and (6) are only approximations, and that, for several reasons. But we must distinguish between the character of these approximations. In the first place we have assumed that μ'_{x_2} and μ'_{y_2} vanish for a vapour phasis, and so that μ for different mixtures at the same pressure has the same value. If the density of the vapour phases is so small, that they do not perceptibly deviate from the laws of Boyle and Gay-Lussac everyone will agree that this approximation may be admitted. In the second place we have ascribed to μ for the liquid state the value which it has in the double-point, though the pressure exceeds that of the double-point. This approximation comes to the same as to say that we neglect the volume of the liquid compared with that of the vapour; and also this approximation is of no signification if the gases are very rare. But the chief reason, for which we have to consider these equations (4) and (5) only as approximations is that we make use of the following relation for the pressure of the double-point:

$$-\log \frac{p'}{p_{cr}} = f\left(\frac{T_{cr}}{T} - 1\right)$$

if we suppose in this equation f for all substances and so also for all mixtures to be the same and independent of the temperature. Therefore if we set:

$$\mu'_{x_1} = \frac{1}{p'}\frac{dp'}{dx_1},$$

we assume a relation, which is incontestable in all those cases, in which the vapour-phasis may be considered as a perfect gas. But if we do more and if we assume a peculiar property of the equation of state, as that one assumed in the formula for the pressure p' of the double-point, the decision of the question, whether the equations (5) and (6) are contestable or not depends upon the question whether the relation used is accurate. Therefore in applying the equations (5) and (6) it is not our aim to obtain numerically perfectly reliable results, but only to get an idea of the course of the coexistence pressure for different mixtures which is in the main reliable, and which makes us understand the phenomena.

According to these considerations, knowledge of the pressure of the double-points is required for the determination of the shape of the surface of saturation. If we introduce this pressure also into the graphical representation, we add a third surface to the two surfaces, liquid sheet and vapour sheet. The third sheet is found between the first and the second one, and the only points which it has in common with them are those above the angles of the rightangled triangle. In the case, that points of maximum pressure occur, in which points the liquid sheet and the vapour sheet touch each other, this third sheet also will touch both of them. If we cut these three sheets by a plane $p = C$, we get three sections and the projections of these sections are the curves, which we have already mentioned in (a) p. 3 as curves of equal pressure; to these however is added the curve of equal coincidence pressure. After this expatiation on the signification of the quantities occurring in formula II, p. 3, we will return to the question if we can determine the shape of these projections. In these calculations we confine ourselves to the case of small vapour pressure.

We may put (see p. 7):

$$\frac{x_2}{1-x_2-y_2}=\frac{x_1}{1-x_1-x_1}\,e^{\mu'_{x_1}}$$

and

$$\frac{y_2}{1-x_2-y_2}=\frac{y_1}{1-x_1-y_1}\,e^{\mu'_{y_1}}$$

Adding these equations we get.:

$$-1+\frac{1}{1-x_2-y_2}=\frac{x_1\,e^{\mu'_{x_1}}+y_1\,e^{\mu'_{y_1}}}{1-x_1-y_1}\,.$$

or

$$\frac{1}{1-x_2-y_2}=\frac{1+x_1(e^{\mu'_{x_1}}-1)+y_1(e^{\mu'_{y_1}}-1)}{1-x_1-y_1}$$

Hence also:

$$\frac{x_2}{x_1}=\frac{e^{\mu'_{x_1}}}{1+x_1\,(e^{\mu'_{x_1}}-1)+y_1(e^{\mu'_{y_1}}-1)}$$

and

$$\frac{y_2}{y_1}=\frac{e^{\mu'_{y_1}}}{1+x_1\,(e^{\mu'_{x_1}}-1)+y_1(e^{\mu'_{y_1}}-1)}$$

In the same way: $$\frac{x_2-x_1}{x_1}=\frac{(1-x_1)(e^{\mu'_{x_1}}-1)-y_1(e^{\mu'_{y_1}}-1)}{1+x_1\,(e^{\mu'_{x_1}}-1)+y_1(e^{\mu'_{y_1}}-1)}$$

and

$$\frac{y_2-y_1}{y_1}=\frac{(1-y_1)(e^{\mu'_{y_1}}-1)-x_1(e^{\mu'_{x_1}}-1)}{1+x_1\,(e^{\mu'_{x_1}}-1)+y_1(e^{\mu'_{y_1}}-1)}$$

If we substitute in equation II these values of x_2-x_1 and of y_2-y_1, and the values of $\frac{\partial^2\zeta}{\partial x_1{}^2}$, $\frac{\partial^2\zeta}{\partial x_1\partial y_1}$ and $\frac{\partial^2\zeta}{\partial y_1{}^2}$ found on page 5 and if we divide by MRT then we find the following differential equations, where we denote for brevity's sake by N the nominator of the fractions indicating the values of x_2-x_1, and y_2-y_1

$$0=\frac{(1-x_1)(e^{\mu'_{x_1}}-1)-y_1(e^{\mu'_{y_1}}-1)}{N}\left\{\frac{1-y_1}{1-x_1-y_1}+x_1\mu''_{x_1}\right\}dx_1+$$

$$+\frac{(1-y_1)(e^{\mu'_{y_1}}-1)-x_1(e^{\mu'_{x_1}}-1)}{N}\left\{\frac{y_1}{1\quad x_1-y_1}+y_1\mu''_{x_1y_1}\right\}dx_1+$$

$$+\frac{(1-x_1)(e^{\mu'_{x_1}}-1)-y_1(e^{\mu'_{y_1}}-1)}{N}\left\{\frac{x_1}{1-x_1-y_1}+x_1\mu''_{x_1y_1}\right\}dy_1+$$

$$+\frac{(1-y_1)(e^{\mu'_{y_1}}-1)-x_1(e^{\mu'_{x_1}}-1)}{N}\left\{\frac{1-x_1}{1-x_1-y_1}+y_1\mu''_{y_1}\right\}dy_1\,.$$

If we put: $\mu''_{x_1} dx_1 + \mu''_{x_1 y_1} dy_1 = d\mu'_{x_1}$ and $\mu''_{x_1 y_1} dx_1 + \mu''_{y_1} dy_1 = d\mu'_{y_1}$, then we may write this equation in the following form:

$$0 = d\, log \{1 + x_1 (e^{\mu'_{x_1}} - 1) + y_1 (e^{\mu'_{y_1}} - 1)\} - x_1 d\mu'_{x_1} - y_1 d\mu'_{y_1}$$

$$\text{or } C = \ log \{1 + x_1 (e^{\mu'_{x_1}} - 1) + y_1 (e^{\mu'_{y_1}} - 1)\} + \quad \mu_{x_1 y_1} - x_1 \mu'_{x_1} - y_1 \mu'_{y_1}$$

Applying equation (3) of p. 5 it would have been possible to obtain this integral for the projection of the curves of equal pressure in a simpler way. In this equation, where the index 2 indicates again a rare vapour phasis, we equate μ'_{x_2} and μ'_{y_2} to zero and μ_2 to $log \dfrac{p}{MRT} + 1$; so we get:

$$log\,(1 - x_1 - y_1) + \mu_{x_1, y_1} - x_1\, \mu'_{x_1} - y_1\, \mu'_{y_1} = log\,(1 - x_2 - y_2) + log \frac{p}{MRT} + 1,$$

from which follows:

$$log \frac{p}{MRT} = log \frac{1 - x_1 - y_1}{1 - x_2 - y_2} + \mu_{x_1 y_1} - x_1 \mu'_{x_1} - y_1 \mu'_{y_1} - 1$$

In connection with the value I have given before

$$log \frac{p}{MRT} = \frac{1 - x_1 - y_1}{1 - x_2 - y_2} = 1 + x_1 (e^{\mu'_{x_1}} - 1) + y_1 (e^{\mu'_{y_1}} - 1)$$

This equation may be written in the following form:

$$log \frac{p}{MRT} = log \{1 + x_1 (e^{\mu'_{x_1}} - 1) + y_1 (e^{\mu'_{y_1}} - 1)\} + \mu_{x_1 y_1} - x_1 \mu'_{x_1} - y_1 \mu'_{y_1} - 1. \quad (7)$$

Already long ago I have given a corresponding equation for a binary system. It may also be found Cont. II, p. 146, though in a somewhat modified form. I have shown for the case of a binary mixture, that such an equation in some cases may represent a straight line, but that it in other cases represents a curve, which at certain values of x_1 presents a maximum value for p. The intermediate forms may also occur of course. The course of the function μ being at least approximately determined by that of the functions T_{cr} and p_{cr}, knowledge of the dependence of these functions on x and y would be required for an adequate discussion of equation (7). This would be possible according to my equation of state putting

$$T_{cr} = \frac{8}{27} \frac{a}{b} \quad \text{and} \quad p_{cr} = \frac{1}{27} \frac{a}{b^2}.$$

But as the quantities $\dfrac{a}{b}$ and $\dfrac{a}{b^2}$ depend rather intricately on x and y this would lead to an elaborate discussion, and I have not yet suc ceeded in drawing simple conclusions from it in a concise manner and to formulate them sharply. In the formula

$$\mu = -f\left(\frac{T_{cr}}{T} - 1\right) + log\, p_{cr}$$

the discussion of the term T_{cr} and of its first and second derivative function according to x and y would already require extensive calculations, and the discussion of $log\, p_{cr}$ and its derivatives would still augment the difficulties considerably. And though it is true, as we have observed above, that generally the influence of $log\, p_{cr}$ is not great, yet some cases occur, namely those, in which $\frac{dT_{cr}}{dx}$ and $\frac{dT_{cr}}{dy}$ are small, in which this influence is decisive. Therefore for the present I will not enter into an accurate discussion, and only investigate some peculiar cases.

So as first case we may suppose that the three components have been chosen in such a way, that the course of p will be represented by a straight line for each of the three pairs, which may be formed from the components of the ternary system. This may be the case if the difference of the critical temperatures of the components of these pairs is considerable and the critical pressures either differ but slightly or have such values that the expression:

$$-f\frac{dT_{cr}}{Tdx} + \frac{dp_{cr}}{p_{cr}\, dx}$$

may be considered to be constant for each of the three pairs. Then we may expect that for the ternary system μ'_{x_1} and μ'_{y_1} will be everywhere constant or nearly constant, from which follows that $d\mu'_{x_1}$ and $d\mu'_{y_1}$ may be neglected compared with μ'_{x_1} and μ'_{y_1}. If we in fact neglect the values of $d\mu'_{x_1}$ and $d\mu'_{y_1}$ the differential equation of the curves of equal pressure assumes the following form:

$$0 = d\, log \{1 + x_1 (e^{\mu' x_1} - 1) + y_1 (e^{\mu' y_1} - 1)\}.$$

And we get for the equation of the projection of these curves:

$$C = 1 + x_1 (e^{\mu' x_1} - 1) + y_1 (e^{\mu' y_1} - 1).$$

And we find for the value of p from equation (7)

$$p = MRT\, e^{\mu_0 - 1} \{1 + x_1 (e^{\mu' x_1} - 1) + y_1 (e^{\mu' y_1} - 1)\}.$$

The supposition namely that $d\mu'_{x_1}$ and $d\mu'_{y_1}$ are zero comes to the same as to take two different constants for μ'_{x_1} and μ'_{y_1}. But then we have also:

$$\mu_{x_1 y_1} = \mu_0 + x_1 c_1 + y_1 c_2 ,$$

where μ_0 denotes the value of $\mu_{x_1 y_1}$ for the first component.

From this we deduce that the liquid sheet of the saturation surface is a plane, and so that:

$$p = p_1 (1 - x_1 - y_1) + p_2 x_1 + p_3 y_1 \quad . \quad . \quad . \quad . \quad . \quad (8)$$

We deduce this form for p by making use of the relations for each of the components:

$$p_1 = MRT\, e^{\mu_0 - 1}$$

$$p_2 = MRT\, e^{\mu_0 + \mu'_{x_1} - 1}$$

$$p_3 = MRT\, e^{\mu_0 + \mu'_{y_1} - 1}$$

The value $e^{\mu'_{x_1}}$ which is constant in this case, is equal to $\frac{p_2}{p_1}$ and the value of $e^{\mu'_{y_1}}$ is equal to $\frac{p_3}{p_1}$.

The lines of equal pressure for liquids are therefore all parallel to each other. If $p = p_2$ the projection of such a line is:

$$1 - x - \frac{p_3 - p_1}{p_2 - p_1} y = 0$$

It cuts therefore the Y-axis at the point $y = \frac{p_2 - p_1}{p_3 - p_1}$. It appears that in this case we have the interesting circumstance, that the addition of a substance with a given maximum tension to a binary mixture whose vapour pressure is equal to that maximum tension, does not bring about any variation of that pressure, however great or small the added quantity may be.

The other line of equal pressure, the section of the vapour sheet, lying at the same height of p, and representing phases coexisting with those of the first line, may be deduced from:

$$p = p_1 (1 - x_1 - y_1) + p_2 x_1 + p_3 y_1$$

if we express in this equation x_1 and y_1 in x_2 and y_2; and this may be easily done if μ'_{x_2} and μ'_{y_2} vanish, and μ'_{x_1} and μ'_{y_1} may be considered as constants. We write then:

$$\frac{x_1}{1 - x_1 - y_1} = \frac{x_2}{1 - x_2 - y_2} e^{-\mu'_{x_1}}$$

and

$$\frac{y_1}{1 - x_1 - y_1} = \frac{y_2}{1 - x_2 - y_2} e^{-\mu'_{y_1}}$$

These equations would also hold, if μ'_{x_1} and μ'_{y_1} still depended on x_1 and y_1, but then it would not be possible to express x_1 and y_1 in x_2 and y_2. Performing the substitutions mentioned we get:

$$\frac{1}{p} = \frac{1-x_2-y_2}{p_1} + \frac{x_2}{p_2} + \frac{y_2}{p_3} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (9)$$

As it is however not only our aim to obtain the results, but as we also wish to interpret the equations given before, we return to equation II in order to determine the line of equal pressure for the vapour phases.

If we continue to use the index 2 for the vapour phasis, and the index 1 for the liquid phasis, but if we now apply equation II to the vapour phases, it assumes the following form:

$$v_{12}\, dp = \left\{ (x_1 - x_2) \frac{\partial^2 \zeta}{\partial x_2^{\,2}} + (y_1 - y_2) \frac{\partial^2 \zeta}{\partial x_2 \partial y_2} \right\} dx_2 + $$
$$+ \left\{ (x_1 - x_2) \frac{\partial^2 \zeta}{\partial x_2 \partial y_2} + (y_1 - y_2) \frac{\partial^2 \zeta}{\partial y_2^{\,2}} \right\} dy_2 .$$

As we may neglect μ'_{x_2} and μ'_{y_2} for the vapour phases, we may also neglect the second derivatives of μ; and we may put:

$$\frac{\partial^2 \zeta}{\partial x_2^{\,2}} = MRT \frac{1-y_2}{x_2(1-x_2-y_2)} , \quad \frac{\partial^2 \zeta}{\partial x_2 \partial y_2} = MRT \frac{1}{1-x_2-y_2}$$

and $$\frac{\partial^2 \zeta}{\partial y_2^{\,2}} = MRT \frac{1-x_2}{y_2(1-x_2-y_2)} .$$

We have $v_{12} = v_1 - v_2 - (x_1 - x_2)\left(\frac{dv}{dx_2}\right)_p - (y_1 - y_2)\left(\frac{dv}{dy_2}\right)_p$; and $\left(\frac{dv}{dx_2}\right)_p$ and $\left(\frac{dv}{dy_2}\right)_p$ are zero for the vapour which we assume to follow the law of Boyle, and so to occupy the same volume, if the pressure and the number of molecules are constant. If we neglect moreover the volume v_1 of the liquid compared with v_2 the volume of the vapour, then we get after division by MRT:

$$-\frac{dp}{p} = \left\{ (x_1 - x_2) \frac{1-y_2}{x_2(1-x_2-y_2)} + \frac{y_1 - y_2}{1-x_2-y_2} \right\} dx_2 + $$
$$+ \left\{ \frac{x_1 - x_2}{1-x_2-y_2} + (y_1 - y_2) \frac{1-x_2}{y_2(1-x_2-y_2)} \right\} dy_2 .$$

For a binary system this yields the well known equation:

$$\frac{dp}{p} = \frac{x_2 - x_1}{x_2(1-x_2)} dx_2 .$$

If further we substitute for $x_1 - x_2$ and $y_1 - y_2$ the values:

$$x_1 - x_2 = x_2 \frac{(1-x_2)(e^{-\mu' x_1}-1) - y_2(e^{-\mu' y_1}-1)}{(1-x_2-y_2) + x_2 e^{-\mu' x_1} + y_2 e^{-\mu' y_1}}$$

and

$$y_1 - y_2 = y_2 \frac{(1-y_2)(e^{-\mu' y_1}-1) - x_2(e^{-\mu' x_1}-1)}{(1-x_2-y_2) + x_2 e^{-\mu' x_1} + y_2 e^{-\mu' y_1}},$$

then we get by integration:

$$p = \frac{C}{(1-x_2-y_2) + x_2 e^{-\mu' x_1} + y_2 e^{\mu' y_1}}.$$

or in connection with the value of $e^{-\mu' x_1}$ and $e^{-\mu' y_1}$ given before:

$$p = \frac{C}{(1-x_2-y_2) + x_2 \frac{p_1}{p_2} + y_2 \frac{p_1}{p_3}}$$

The constant C is of course the pressure for the case that x_2 and y_2 are equal to zero, so it is equal to p_1, and we find again equation (9). If we now give to p the same value as for the liquid sheet, we find the second branch of the curve of equal pressure. So we find for $p = p_2$:

$$1 - x_2 = \frac{p_2}{p_3} \, \frac{p_3 - p_1}{p_2 - p_1} \, y_2,$$

a line which yields $y_2 = 1$ for $x_2 = 0$ and:

$$y_2 = \frac{p_3}{p_2} \, \frac{p_2 - p_1}{p_3 - p_1}$$

for the point of intersection with the axis for the third component. This value is of course the value of y_2 for the pressure p_2 of the vapour phasis of the binary system consisting of the first and the third component. The projections of these vapour lines of equal pressure are again parallel.

The line:

$$\frac{1}{p} - \frac{1}{p_1} = x_2 \left(\frac{1}{p_2} - \frac{1}{p_1}\right) + y_2 \left(\frac{1}{p_3} - \frac{1}{p_1}\right)$$

is displaced parallel to itself, when the value of p varies. The vapour sheet consists therefore of parallel lines and may be considered as a cylindrical surface. The section with the POX plane is a hyperbola, and also that with the POY plane.

If we cut the sheet of the coincidence pressures also at the same height, we get a third line, which lies between the two former ones, and which we have already mentioned in our first communication as the projection of the line of the double-points. The equation of this line may be found from the equations of p. 8 and 9 namely from:

$$\frac{1}{p'}\frac{dp'}{dx} = \mu'_{x_1}$$

and

$$\frac{1}{p'}\frac{dp'}{dy} = \mu'_{y_1} \, .$$

In this case we have $\mu'_{x_1} = log\frac{p_2}{p_1}$ and $\mu'_{y_1} = log\frac{p_3}{p_1}$; integrating we find for the equation of this curve:

$$log\, p' = c + x\, log\frac{p_2}{p_1} + y\, log\frac{p_3}{p_1} \, .$$

If x and $y = 0$, this third sheet coincides with the two others, and $p' = p_1$; from this the value of C may be calculated. We may also write this equation in the following form:

$$p' = p_1{}^{(1-x-y)}\, p_2{}^x\, p_3{}^y$$

or

$$log\, p' = (1-x-y)\, log\, p_1 + x\, log\, p_2 + y\, log\, p_3 \, .$$

This equation also represents a right line, which is displaced parallel to itself, if p' varies.

So we find very simple lines for the three curves, which we get in this case for a binary system, namely a right line, a hyperbola, and between them an exponential curve.

We shall now discuss the case which differs most from that which we have treated, namely that, in which each of the pairs that may be formed from the components of the ternary system, presents a maximum pressure. The critical temperatures of the components do not differ much in this case, and for each pair a composition may be found, for which the function μ' vanishes. Then we may expect, that for the ternary system a value for x_1 and for y_1 may be found for which the values of μ'_{x_1} and μ'_{y_1} are equal to zero. If the function μ' depended only on T_{cr}, then we might simply express this in properties of T_{cr}, and we might say: for each of the pairs a minimum critical temperature occurs, so we may also expect a minimum value for T_{cr} for the ternary system. As μ still contains the term $log\, p_{cr}$, the same set of values of x_1 and y_1 which yields the minimum value of T_{cr} will not make μ'_{x_1} and μ'_{y_1} vanish. This agrees indeed with the considerations for a binary mixture, given in Cont. II.

For values of x_1 and y_1 differing only slightly from those, for which

μ'_{x_1} and μ'_{y_1} vanish, the first derivatives of μ may be considered to be small in this case but the second derivatives on the other hand will be decisive for the course.

In order to determine for this case also the projection of the curves of constant pressure we will make use of equation (7):

$$\log\frac{p}{p_m}=\log\{1+x_1(e^{\mu'_{x_1}}-1)+y_1(e^{\mu'_{y_1}}-1)\}+\mu_{x_1y_1}-x_1\mu'_{x_1}-y_1\mu'_{y_1}-1.$$

If we call the values of x_1 and y_1, for which μ'_{x_1} and μ'_{y_1} vanish, x_m and y_m and the corresponding pressure p_m, then we have:

$\log\frac{p_m}{MRT}=\mu_m-1$ hence also:

$$\log\frac{p}{p_m}=\log\{1+x_1(e^{\mu'_{x_1}}-1)+y_1(e^{\mu'_{y_1}}-1)\}+\mu_{x_1y_1}-x_1\mu'_{x_1}-y_1\mu'_{y_1}-\mu_m.$$

It appears already from this form of p_m that this pressure of this system may be considered as a coincidence pressure, and as this system can be realised, it may be considered as an ordinary maximum tension. If we now consider μ'_{x_1} and μ'_{y_1} to be small, so that we may put $e^{\mu'_{x_1}}-1=\mu'_{x_1}$ and $e^{\mu'_{y_1}}-1=\mu'_{y_1}$ and

$$\log\{1+x_1\,\mu'_{x_1}+y_1\,\mu'_{y_1}\}=x_1\,\mu'_{x_1}+y_1\,\mu'_{y_1},$$

then we find for mixtures, whose composition does not differ much from x_m and y_m:

$$\log\frac{p}{p_m}=\mu_{x_1y_1}-\mu_m\ .$$

If we write:

$$\mu_{x_1y_1}=\mu_m+\tfrac{1}{2}\{(x_1-x_m)^2\,\mu''_{xm}+2\,(x_1-x_m)\,(y_1-y_m)\,\mu''_{x_my_m}+(y_1-y_m)^2\,\mu''_{ym}\}$$

we may write the last equation:

$$\log\frac{p}{p_m}=\tfrac{1}{2}\{(x_1-x_m)^2\,\mu''_{xm}+2\,(x_1-x_m)\,(y_1-y_m)\,\mu''_{x_my_m}+(y_1-y_m)^2\,\mu''_{ym}\}.$$

If we only inquire into the mathematical consequences of this last equation, without trying to answer the question, if the suppositions as to the values, which we have ascribed to μ''_{xm}, $\mu''_{x_my_m}$ and μ''_{ym}, may be found in nature, we may only say, that if μ'_{xm} and μ'_{ym} vanish, the curves of equal pressure in the immediate neighbourhood of this singular point will be conic sections. In order that p_m may be really a maximum pressure, the first member must be negative for all real values of x_1-x_m and y_1-y_m and this requires, that μ''_{xm} and μ''_{ym} are both negative and that $(\mu''_{x_my_m})^2<\mu''_{xm}\,\mu''_{ym}$. Then the curves of equal pressure are ellipses whose centre is the singular point. For a binary mixture the quantity μ''_x has always appeared to be negative in accordance with this theory, when the components were substances, which do not exercise any chemical action upon one another, for which therefore the molecules in the mixture may be considered to be simply mixed, without suffering any internal modification. For such binary mixtures minimum critical temperatures have actually been found, — and the chief term of μ being $-f\left(\frac{T_{cr}}{T}-1\right)$ a minimum value of T_{cr} corresponds to a negative value of μ''_x, — but never with certainty maximum critical temperatures. If μ''_{xm} and μ''_{ym} could be positive, and $\mu''_{xm}\mu''_{ym}>(\mu''_{xmym})^2$, then we should also get ellipses for the curves of equal pressure, but then we should have $p>p_m$, and the ternary system would present a minimum pressure, which would also lead to minimum pressures for the pairs of which the system consists. If maximum critical temperature for a binary system should really occur in nature, and if we then formed a ternary system, of which one pair of components presented a maximum and another pair a minimum value of T_{cr}, then μ''_{xm} and μ''_{ym} might have opposite signs, and the point for which μ'_{xm} and μ'_{ym} vanish would be a stationary point as to the pressure, and the curves of equal pressure would intersect in that point.

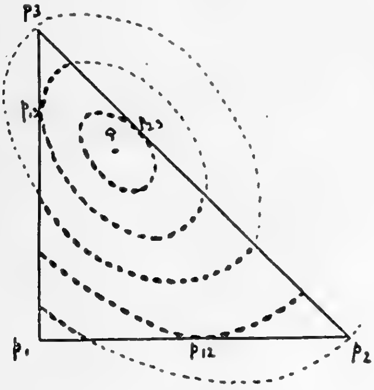

Fig. 12.

In figure 12 the course of the curves of equal pressure has been represented schematically for the case of maximum pressure for the three pairs of components and for maximum pressure for a point of the system. The succession of the values of the pressure is then:

$$p_1 < p_2 < p_{12} < p_3 < p_{13} < p_{23} < p_m,$$

only the order of succession of p_{12} and p_3 and of p_{13} and p_{23} may be reversed. The figure does not require any further explanation.

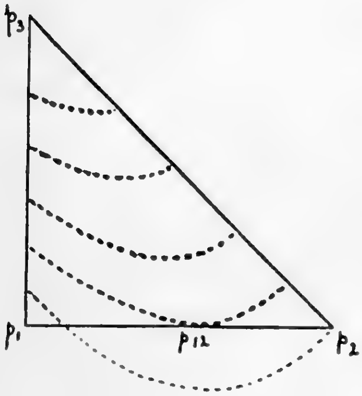

Fig. 13.

As intermediate case for the course of the curves of equal pressure, we assume a system, in which for two of the pairs the pressure increases or decreases regularly, but the third pair has a maximum pressure. So in fig. 13 the pressures follow each other in this way: $p_1 < p_2 < p_{12} < p_3$. One of the curves of equal pressure, namely that one for which $p = p_{12}$, touches the OX-axis.

In the following chapter we will give some indications concerning the course of the curves of constant pressure for the vapour phases in this case, and in the general case. Let us return to that purpose to equation II of p. 3 of this communication.

b. Displacement of the curves of equal pressure with variation of the pressure.

We have already observed that the projection of the connodal curve of a ζ-surface, construed for a certain value of p coincides with the projection of the curves, for which the pressure is equal to p, and that therefore all laws, which hold for the connodal curve, also apply to the curves of equal pressure.

If in the equation:

$$v_{21}\, dp = \left\{(x_2-x_1)\frac{\partial^2\zeta}{\partial x_1^{\,2}} + (y_2-y_1)\frac{\partial^2\zeta}{\partial x_1 \partial y_1}\right\} dx_1 + \\ + \left\{(x_2-x_1)\frac{\partial^2\zeta}{\partial x_1 \partial y_1} + (y_2-y_1)\frac{\partial^2\zeta}{\partial y_1^{\,2}}\right\} dy_1$$

we choose the values of dx_1 and dy_1 such, that

$$\frac{dx_1}{x_2-x_1} = \frac{dy_1}{y_2-y_1} = \frac{dl}{L}$$

where L represents the length of a line, connecting the point P_1, whose coordinates are x_1 and y_1 with the point P_2, representing the phasis coexisting with P_1 and whose coordinates are x_2 and y_2.. Be further dl the length of a line, whose projections are dx_1 and dy_1, then the point $x_1 + dx_1, y_1 + dy_1$ lies between the points P_1 and P_2. It lies therefore in what we may call the heterogeneous region. The above equation may then be written:

$$v_{21}\frac{dp}{dl} = L\left\{\frac{\partial^2\zeta}{\partial x_1^{\,2}}\left(\frac{dx_1}{dl}\right)^2 + 2\frac{\partial^2\zeta}{\partial x_1 \partial y_1}\left(\frac{\partial x_1}{dl}\right)\left(\frac{dy_1}{dl}\right) + \frac{\partial^2\zeta}{\partial y_1^{\,2}}\left(\frac{dy_1}{dl}\right)^2\right\}.$$

The second member of this equation is positive for the points of the connodal curve, as the ζ-surface lies above the tangent plane for all phases which may be realised. If the point P_1 represents a liquid phasis, then v_{21} is positive, and therefore $\frac{dp}{dl}$ also positive. When the pressure increases the liquid branch is displaced in such a way, that it moves towards the side of what was before the heterogeneous region. This rule for a ternary system is equivalent to the rule of KONOWALOW for a binary system, if this latter rule is duly extended. If on the other hand P_1 lies on the liquid sheet, then v_{21} and therefore also $\frac{dp}{dl}$ is negative. This signifies that the vapour branch of the curves of equal pressure moves on towards the heterogeneous region if the pressure *decreases,* and on the other hand towards the region which at constant pressure belonged to the homogeneous region, if the temperature *increases.* If the pressure is varied the two branches move, in such a way, that one of the branches retreats for the other. If there is not yet question of critical phenomena, a point for which $v_{21} = 0$ does not yet exist, and the given rule holds without exceptions. For the case that no maximum pressure exists, the two branches of the projection of the curves of equal pressure consist of two curves, originating both in the same side of the rightangled triangle, and ending again in the same side. Every point on one of the branches has a conjugated point on the other branch. We will call the lines joining such a pair of conjugated points (coexisting phases) *chords.* The first of these chords have the direction of one of the sides of the rightangled triangle and the last the direction of the other side. If these two sides are the sides containing the right angle, then the chord turns over an angle of 90°. It occurs however only as an exception that the chord is directed towards the origin in other points than the extremities. Afterwards we will return to this question.

If a maximum pressure exists, the branches of the curves of equal pressure form closed curves near the phasis, whose pressure is maximum. The liquid branch contracts if the pressure increases, and according to the rule, deduced above, it moves towards the branch of the vapour phases. This branch therefore must also form a closed curve round the point of maximum pressure and that a smaller one. For the limiting case, the curve for the liquid phases is an ellipse the curve for the vapour phases is also closed, but has other dimensions, and its axes have other directions and another ratio, in the limiting case, however, it must coincide with the ellipse of the liquid phases. At any rate therefore, the position of the liquid branches being given for increasing pressure we may immediately conclude to the relative position of the vapour branches.

(To be continued.)

Physics. — *"Statistical Electro-mechanics."* By Dr. J. D. VAN DER WAALS Jr. (Communicated by Prof. VAN DER WAALS).

Prof. GIBBS has newly published a treatise entitled "Elementary principles in statistical mechanics", in which he communicates some considerations, belonging to a science, which he calls "Statistical mechanics," and of which he states that "on account of the elegance and simplicity of its principles" it is eminently worthy that the laws to which it is subjected, are studied. The laws relate to the behaviour of a great number of systems, whose motions are mutually independent. These systems quite agree with one another as to their nature, and only differ in so far, that the integration constants of the differential equations of motion have different values, or, what comes to the same, that the values of the generalized coördinates and of the generalized velocities at an arbitrary moment (e. g. at the moment $t = 0$) differ for different systems. The laws, which hold for such ensembles of systems have a very general character, as GIBBS shows; yet in their application they are confined to systems, consisting exclusively of ordinary matter. Now the question arises whether such like considerations might be applied to electro-magnetic systems, and whether in doing so we might extend our very limited knowledge of the phenomena of radiation in connection with the laws of thermodynamics.

We cannot deny however that we must not expect *too much* from these considerations. The greater part of the theses deduced by GIBBS are exclusively or principally applicable to ensembles of systems which he calls canonical and which have such an important phace in his considerations, because they represent the simplest law possible of the distribution of the systems over the different "phases" [1]). Mathematical simplicity, however, is not a trustworthy criterion, when we want to investigate, what is actually to be found in nature. For our mathematical representation e. g. the simplest motion, a vibrating string can perform, is an harmonic motion, yet we should be utterly mistaken if we should assume, that every vibrating string would execute such a motion. Perhaps we run the risk of making similar mistakes if we assume, that all systems in nature will follow the laws which we have deduced on the supposition of a canonical distribution of the systems of an ensemble.

It is true that GIBBS shows in his chapters XI—XIII that the cano-

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[1]) Two systems are considered to be in the same phase when they are to be found in the same element of extension in phase.

nical distribution is the most probable one, provided the only condition, to which the ensemble is subjected, be that the mean value of the energy of the systems is a prescribed quantity; but the main difficulty happens to be to answer the question whether this is indeed the only condition. Systems e. g., consisting of spherical, mutually equal molecules, will not be distributed canonically, for they are still subjected to another condition, namely the distance of two centres of molecules can never be less than the diameter. To assume the canonical distribution comes therefore to the same as to neglect the volume of the molecules, but it is not easy to decide whether nothing else is neglected. In fact choosing the distribution of the systems of an ensemble is equivalent to choosing the cases, which we are to consider as "cases of equal probability" in a more direct application of the calculus of probabilities. Both are subject to the chance, that the probability a posteriori will prove to be another than we had assumed a priori.

Yet such like considerations can be useful, in the *known* region of thermodynamics, because they bring its laws very simply and elegantly together under one point of view; in the yet *unknown* region, because they may perhaps suggest formulae, for which comparison with the experiments may decide, whether they are in accordance with the phenomena of nature or not.

Law of conservation of density-in-phase.

In an investigation, whether the considerations of Gibbs are also applicable for electro-magnetic systems, we have in the first place to examine, whether the "law of conservation of density-in-phase" holds also for them. In the beginning we will confine ourselves to systems devoid of material, electrical or magnetical masses.

Now we imagine an ensemble of systems. The different systems are congruent spaces, enclosed by perfectly reflecting walls. We divide each system into n equal cubic elements of space $dx\ dy\ dz$. These elements are so small that the electric and magnetic forces in them may be considered to be constant. The state of each system will be perfectly defined, if in each element of space the components f, g and h of the electric displacement, and the components α, β and γ of the magnetic induction are given. So the state is determined by means of $6\ n$ data; according to the assumption, that electric energy is potential, magnetic energy kinetic, the $3\ n$ components of the electric displacement would represent coordinates, the $3\ n$ components of magnetic conduction generalized momenta, or at least they would be proportional to them.

We mark the elements of space with successive numbers and represent the components of the vectors in the r^{th} element by f_r, g_r, h_r, α_r, β_r and γ_r. Let us select from an ensemble those systems whose data lie between the limits f_1 and $f_1 + df_1$, f_2 and $f_2 + df_2 \ldots$ f_n and $f_n + df_n$ and in the same way for the other components; the number of these systems may be represented by:

$$D\, df_1 \ldots df_n\, dg_1 \ldots dg_n\, dh_1 \ldots dh_n\, d\alpha_1 \ldots d\alpha_n\, d\beta_1 \ldots d\beta_n\, d\gamma_1 \ldots d\gamma_n$$

or

$$D\,[(df_1)]\,[(d\alpha_1)]. \qquad (1)$$

Here the brackets indicate, that also the other components, the parentheses that the same quantities also for the other elements of space are to be taken. We will call $[(df_1)]\,[(d\alpha_1)]$ an element of extension-in-phase, D the density-in-phase, $P = \frac{D}{N}$ the coefficient of probability-in-phase (N representing the total number of systems in the ensemble) and η, defined by the equation $P = e^{\eta}$, the index of probability-in-phase.

Let us consider the same ensemble after a short lapse of time dt, then the number of systems being in a certain phase, will have varied. We may conceive the variation of that number to be composed of $12\,n$ parts, as the systems may enter or leave a certain phase by passing one of $12\,n$ different limits, $[(f_1)]$, $[(f_1 + df_1)]$, $[(\alpha_1)]$ and $[(\alpha_1 + d\alpha_1)]$.

The systems passing the limit f_1 contribute:

$$D \frac{df_1}{dt}\, dt\, df_2 \ldots df_n\, dg_1 \ldots dg_n\, dh_1 \ldots dh_n\, [(d\alpha_1)]. \qquad (2)$$

to the total number with which the quantity $D\,[(df_1)]\,[(d\alpha_1)]$ increases.

The systems passing the limit $f_1 + df_1$ contribute a decrease amounting to:

$$\left\{ D \frac{df_1}{dt} + \frac{\partial}{\partial f_1} \left\{ D \frac{df_1}{dt} \right\} df_1 \right\} dt\, df_2 \ldots dh_n\, [(d\alpha_1)]. \qquad (3)$$

Adding these quantities we get an increase with:

$$- \frac{\partial}{\partial f_1} \left\{ D \frac{df_1}{dt} \right\} dt\, [(df_1)]\, [(d\alpha_1)] \qquad (4)$$

Now we have:

$$\frac{\partial}{\partial f_1} \left\{ D \frac{df_1}{dt} \right\} = \frac{\partial D}{\partial f_1} \frac{df_1}{dt} + D \frac{\partial}{\partial f_1} \frac{df_1}{dt}. \qquad (5)$$

The second term of the second member is zero, for $\frac{df_1}{dt}$ depends only on the rotation of the magnetic induction, and is independent of the value of f_1.

In the same way we find the increase in consequence of the systems passing the other limits, — taking into account that all quantities of the form $\frac{\partial}{\partial a_1}\frac{da_1}{dt}$ are zero. — Taking the sum of all these partial increases and dividing by $[(df_1)]\,[(da_1)]$ we find:

$$\frac{\partial D}{\partial t} = -\left[\left(\frac{\partial D}{\partial f_1}\frac{df_1}{dt}\right)\right] - \left[\left(\frac{\partial D}{\partial a_1}\frac{da_1}{dt}\right)\right] \quad . \; . \; . \; . \; . \; . \; . \qquad (6)$$

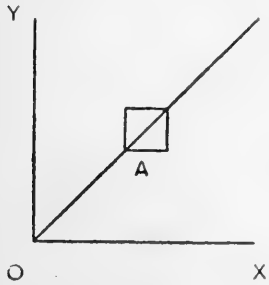
or:

$$\frac{\partial D}{\partial t} + \left[\left(\frac{\partial D}{\partial f_1}\frac{df_1}{dt}\right)\right] + \left[\left(\frac{\partial D}{\partial a_1}\frac{da_1}{dt}\right)\right] = \frac{dD}{dt} = 0. \; . \; . \qquad (7)$$

Here $\frac{\partial D}{\partial t}$ represents the fluction of the density for a phasis whose limits are constant, $\frac{dD}{dt}$ for a phasis whose limits partake of the motion of the systems of the ensemble.

So the density proves to be constant for a phasis, partaking of the motion of the systems, and as, of course, the systems can never pass the limits of an extension-in-phase, when these limits move with the systems, the total number of systems within every extension-in-phase, i. e. $D\,[(df_1)]\,[(da_1)]$ remains constant, and so also $[(df_1)]\,[(da_1)]$.

This proof of the laws of conservation of density-in-phase and of extension-in-phase quite agrees with that one given by Gibbs. In our case, however, we have still to pay attention to one circumstance. In calculating $\frac{\partial D}{\partial t}\,[(df_1)][(da_1)]$, we have assumed, that this number is the sum of the numbers of systems passing the different limits. This comes to the same as to say that no system will pass more than one of the limits during the time dt, or at least, that the number of the systems that pass more than one limit is so small, that it may be neglected. In the proof of Gibbs we may assume, that this is really the case, provided we take dt so small, that $\frac{dq}{dt}\,dt$ is small compared with dq (where q represents one of the generalized coordinates, and dq one of the dimensions of an element of extension-in-phase). For our case however this proof is incomplete. Be r and s two adjacent elements of space, then $[f_r]$ and $[f_s]$, $[a_r]$ and $[a_s]$ are no independent quantities, but they must be approximately equal, as $[f]$ and $[a]$ vary only fluently from point to point.



In order to investigate the consequences of this circumstance we imagine an ensemble of systems with only two coordinates x and y, which are subjected to the condition that x and y must be equal and continue to be so. All systems will then be found on the line OA and will move in the direction of this line, so all systems leaving the element of space drawn in the figure, or entering into it, will pass the two limits dx and dy at the same moment. If the condition is not that x and y must be rigorously equal, but only that their difference must be very small, then all systems will be huddled up very near the line OA and a great part of those that pass the limit dx will also pass the limit dy. It is evident, that this circumstance is caused by the fact, that within the element $dx\,dy$ the density is not homogeneous. If we choose therefore the the dimensions dx and dy so small, that the whole element lies within a region, where the density may be considered as constant, then we may again assume that the number of systems, passing both limits may be neglected, compared with the number of systems passing only one of the two limits.

If we choose therefore $[(df_1)]$ and $[(da_1)]$ small compared with the mean value of $\left[\left(\frac{\partial f_1}{\partial x}\,dx\right)\right]$ and $\left[\left(\frac{\partial a_1}{\partial x}\,dx\right)\right]$, so e. g. having a finite ratio to dx^2, and dt again small compared with the quantities $[(df_1)]$ and $[(da_1)]$, so e. g. having a finite ratio to dx^3, it appears that in fact the number of systems passing more than one of the limits may be neglected. So the proof of the law of conservation of density-in-phase is complete.

The quasi-canonical distribution.

If we wish to distribute the systems of an ensemble over the different phases in such a way, that the distribution does not vary with the time, so that the state of the ensemble is stationary, it is evident that we have to choose for P a function of the coordinates, which is constant in time. GIBBS chooses for this purpose the function $e^{\frac{\psi-\varepsilon}{\theta}}$ where ε represents the energy of a system, and ψ and θ are constant quantities for a given ensemble. He calls this distribution the canonical distribution. This simple law cannot be applied to systems consisting of ether. If we assumed it, the quantities $[f]$ and $[a]$ would vary abruptly from element to element instead of varying fluently, and moreover the distribution would depend on the dimensions of the elements of space, which we have arbitrarily chosen. We must therefore assume another distribution which secures a fluent variation of the electric and magnetic displacements.

To this purpose we will assume a distribution closely resembling those, discussed by GIBBS in his chapter IV as "other distributions having the same properties as the canonical." These distributions have the characteristic property, that the index of probability η is a linear function of one or more functions F_1, F_2 etc. of the coordinates; the functions F_1, F_2 etc. are subjected to the condition that their average value, taken over all systems of the ensemble must be a prescribed quantity. We might form different distributions, all satisfying the conditions. Now we seek the average value of η for all these different distributions; this average value of η will be a minimum for that ensemble where η is a linear function of F_1, F_2 etc. This is proved by GIBBS in his chapter XI. I shall call such a distribution a quasi-canonical distribution. The canonical distribution is nothing else but such a quasi-canonical distribution where there is only one function F_1 and that represents the energy. As the canonical distribution is of little application, e.g. not for systems of molecules with finite diameter, it would perhaps have been preferable to give a broader meaning to the word canonical and to use it in the sense, in which I use quasi-canonical. As GIBBS has however used the word canonical exclusively for ensembles for which $\eta = \frac{\psi - \varepsilon}{\theta}$, I will use the expression quasi-canonical for ensembles for which

$$\eta = \psi - aF_1 - bF_2 - \text{etc.}$$

In the ether we cannot have canonical ensembles, and so we will discuss only quasi-canonical ensembles. We put:

$$\eta = \frac{\psi - \varepsilon}{\theta} - \frac{\varphi + \chi}{k} - \frac{\Omega_1 + \Omega_2}{\sigma_1} - \frac{\omega}{\sigma_2} \quad \ldots\ldots\ldots\ldots \quad (8)$$

where, $d\tau$ representing an element of space:

$$\varphi = \int \left\{ \left(\frac{\partial g}{\partial z} - \frac{\partial h}{\partial y} \right)^2 + \left(\frac{\partial h}{\partial x} - \frac{\partial f}{\partial z} \right)^2 + \left(\frac{\partial f}{\partial y} - \frac{\partial g}{\partial x} \right)^2 \right\} d\tau \quad \ldots \quad (9)$$

$$\chi = \frac{1}{16\pi^2 V^2} \int \left\{ \left(\frac{\partial \beta}{\partial z} - \frac{\partial \gamma}{\partial y} \right)^2 + \left(\frac{\partial \gamma}{\partial x} - \frac{\partial \alpha}{\partial z} \right)^2 + \left(\frac{\partial \alpha}{\partial y} - \frac{\partial \beta}{\partial x} \right)^2 \right\} d\tau \quad (10)$$

$$\Omega_e = \int \left(\frac{\partial f}{\partial x} + \frac{\partial g}{\partial y} + \frac{\partial h}{\partial z} \right)^2 d\tau \quad \ldots\ldots\ldots\ldots \quad (11a)$$

$$\Omega_m = \int \left(\frac{\partial \alpha}{\partial x} + \frac{\partial \beta}{\partial y} + \frac{\partial \gamma}{\partial z} \right)^2 d\tau \quad \ldots\ldots\ldots\ldots \quad (11b)$$

$$\omega = \frac{1}{\lambda} \int (f^2 + g^2 + h^2)\, \lambda\, d\sigma \quad \ldots\ldots\ldots\ldots \quad (12)$$

k, σ_1 and σ_2 are constants, and σ_1 and σ_2 are infinitely small. The term $-\frac{\Omega_1 + \Omega_2}{\sigma_1}$ has been added, that we should have only to deal with systems, consisting of free ether. Systems, containing electric masses are not absolutely excluded, but still their number is very small and may be neglected compared with that of the systems which are devoid of these masses. As $\frac{\partial \alpha}{\partial x} + \frac{\partial \beta}{\partial x} + \frac{\partial \lambda}{\partial y}$ is always zero, systems for which this expression has another value can never occur; yet we may admit them in such a small number, that they have no influence on the results. Finally we cannot take into consideration systems consisting of infinite space, for a finite quantity of energy would spread in it and we could not have a stationary distribution in the ensemble. Therefore it is necessary to enclose the electromagnetic energy within absolutely reflecting walls. But then it is necessary to add a term to η, which expresses, that the walls reflect absolutely, i. e. the quantities $[f]$ are always zero at the walls. The term $-\frac{\omega}{\sigma_2}$ expresses this; λ represents a small line in a direction normal to the surface; we make this line decrease indefinitely; $d\sigma$ represents an element of area.

If this distribution is to be for ether systems, what the canonical distribution is for material systems, then in the first place η must be a constant in time. For the other terms this is immediately evident, so we have only to show it for the term $\frac{\varphi + \chi}{k}$.

The relation, we have to prove may be written:

$$\frac{d\varphi}{dt} + \frac{d\chi}{dt} = 0 \quad \ldots\ldots\ldots \quad (13)$$

We will make use of the relations

$$\frac{d\alpha}{dt} = 4\pi V^2 \left(\frac{\partial g}{\partial z} - \frac{\partial h}{\partial y}\right) \quad \ldots\ldots \quad (14)$$

$$\frac{df}{dt} = -\frac{1}{4\pi}\left(\frac{\partial \beta}{\partial z} - \frac{\partial \gamma}{\partial y}\right) \quad \ldots\ldots \quad (15)$$

and of the following relations, that may be deduced from them:

$$\frac{d^2 f}{dt^2} = V^2 \left(\frac{\partial^2 f}{\partial x^2} + \frac{\partial^2 f}{\partial y^2} + \frac{\partial^2 f}{\partial z^2}\right) \quad \ldots\ldots \quad (16)$$

$$\frac{d^2 \alpha}{dt^2} = V^2 \left(\frac{\partial^2 \alpha}{\partial x^2} + \frac{\partial^2 \alpha}{\partial y^2} + \frac{\partial^2 \alpha}{\partial z^2}\right) \quad \ldots\ldots \quad (17)$$

and also of the corresponding relations for the other components. Now we have:

$$\frac{d\varphi}{dt} = \int \left[\left(\frac{\partial g}{\partial z} - \frac{\partial h}{\partial y}\right)\frac{d}{dt}\left(\frac{\partial g}{\partial z} - \frac{\partial h}{\partial y}\right)\right] d\tau \quad \ldots\ldots \quad (18)$$

Integrating partially we get:

$$\frac{d\varphi}{dt} = \text{a number of surface integrals}$$

$$-\int\left\{\frac{df}{dt}\left(\frac{\partial^2 f}{\partial z^2}+\frac{\partial^2 f}{\partial y^2}-\frac{\partial^2 h}{\partial x\partial z}-\frac{\partial^2 g}{\partial x\partial y}\right)+\frac{dg}{dt}\left(\frac{\partial^2 g}{\partial z^2}+\frac{\partial^2 g}{\partial x^2}-\frac{\partial^2 f}{\partial x\partial y}-\frac{\partial^2 h}{\partial y\partial z}\right)\right.$$
$$\left.+\frac{dh}{dt}\left(\frac{\partial^2 h}{\partial y^2}+\frac{\partial^2 h}{\partial x^2}-\frac{\partial^2 f}{\partial x\partial z}-\frac{\partial^2 g}{\partial y\partial z}\right)\right\}dt\,. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (19)$$

In the coefficient of $\frac{df}{dt}$ in the cubic-integral we have:

$$-\frac{\partial^2 h}{\partial x\partial z}-\frac{\partial^2 g}{\partial x\partial y}=-\frac{\partial}{\partial x}\left(\frac{\partial g}{\partial y}+\frac{\partial h}{\partial z}\right)=\frac{\partial^2 f}{\partial x^2} \quad . \quad . \quad . \quad (20)$$

at least if we put, $\frac{\partial f}{\partial x}+\frac{\partial g}{\partial y}+\frac{\partial h}{\partial z}=0$, so if we neglect the systems in which electric masses occur. So we get for the coefficient of $\frac{df}{dt}$ the expression $\frac{1}{V^2}\frac{\partial^2 f}{\partial t^2}$ and for the cubic integral:

$$-\frac{1}{V^2}\int\left[\frac{df}{dt}\frac{d^2 f}{dt^2}\right]d\tau=-\frac{1}{16\pi^2 V^2}\int\left[\left(\frac{\partial\beta}{\partial z}-\frac{\partial\gamma}{\partial y}\right)\frac{d}{dt}\left(\frac{\partial\beta}{\partial z}-\frac{\partial\gamma}{\partial y}\right)\right]d\tau=-\frac{d\chi}{dt}.$$

As at the absolutely reflecting walls $[f]$ and therefore also $\left[\frac{df}{dt}\right]$ continue to be zero, the surface integrals disappear; so equation (13) is proved.

The quantities φ and χ which are introduced in order that the variation of the electric displacement and the magnetic induction may take place fluently, are defined as the sum of the squares of the components of the rotations of those vectors, if we disregard the coefficient $\frac{1}{16\pi^2 V^2}$ introduced in order that equation (13) may be satisfied. This seems to me the simplest definition for φ and χ. It might, however, appear that we are not yet sure that $\frac{\partial f}{\partial x}$, $\frac{\partial g}{\partial y}$ and $\frac{\partial h}{\partial z}$ get convenient values. In order to show that this is not the case, we will prove the following relations

$$\varphi = \int\left[\left(\frac{\partial f}{\partial x}\right)^2+\left(\frac{\partial f}{\partial y}\right)^2+\left(\frac{\partial f}{\partial z}\right)^2\right]d\tau \quad . \quad . \quad (21)$$

$$\chi = \frac{1}{16\pi^2 V^2}\int\left[\left(\frac{\partial\alpha}{\partial x}\right)^2+\left(\frac{\partial\alpha}{\partial y}\right)^2+\left(\frac{\partial\alpha}{\partial z}\right)^2\right]d\tau \quad . \quad . \quad (22)$$

where again the brackets indicate that we have to take also the corresponding terms in which the other components occur, In order to show this we expand the squares of equation (9) and consider separately the terms:

$$S = -\int \left\{ 2\frac{\partial g}{\partial z}\frac{\partial h}{\partial y} + 2\frac{\partial h}{\partial x}\frac{\partial f}{\partial z} + 2\frac{\partial f}{\partial y}\frac{\partial g}{\partial x} \right\} d\tau \quad . \quad . \quad . \quad (23)$$

For $2\frac{\partial g}{\partial z}\frac{\partial h}{\partial y}$ we write $\frac{\partial g}{\partial z}\frac{\partial h}{\partial y} + \frac{\partial g}{\partial z}\frac{\partial h}{\partial y}$ and integrate the first term partially according to z, the second according to y. The surface integrals vanish again and we get:

$$S = +\int \left\{ g\frac{\partial^2 h}{\partial y \partial z} + h\frac{\partial^2 g}{\partial y \partial z} + h\frac{\partial^2 f}{\partial x \partial z} + f\frac{\partial^2 h}{\partial x \partial z} + f\frac{\partial^2 g}{\partial x \partial y} + g\frac{\partial^2 f}{\partial x \partial y} \right\} d\tau$$

$$S = \int \left\{ f\frac{\partial}{\partial x}\left(\frac{\partial g}{\partial y} + \frac{\partial h}{\partial z}\right) + g\frac{\partial}{\partial y}\left(\frac{\partial h}{\partial z} + \frac{\partial f}{\partial x}\right) + h\left(\frac{\partial f}{\partial x} + \frac{\partial g}{\partial y}\right) \right\} d\tau \; . \quad (24)$$

$$S = -\int \left[f\frac{\partial^2 f}{\partial x^2} \right] d\tau. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (25)$$

By integrating once more partially, where once more the surface integrals vanish, we get:

$$S = \int \left[\left(\frac{\partial f}{\partial x} \right)^2 \right] d\tau$$

so equation (21) is proved. Equation (22) is proved in the same way.

Three constants occur in the exponent η namely ψ, θ and k. ψ is a constant which must be chosen such, that integration of P over all systems of the ensemble yields 1. The two constants θ and k determine therefore the state of the systems. This is connected with the fact, that the nature of the radiation inside a closed surface, as LORENTZ [1]) has shown, depends besides on the temperature, also on the charge of the electrons by which the radiation is emitted. The fact that inside all bodies radiation of the same nature is formed, proves that in all bodies the electrons have the same charge. The constant quantity k must depend on that charge; it will therefore have the same value for spaces enclosed within all bodies as they are found in nature at least if the temperature is the same and its value would for a certain temperature only be different, if we imagined walls with electrons whose charge was different from those actually occurring.

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[1]) LORENTZ. Proceedings. Vol. III, p. 436.

Botany. — *"On the prussic acid in the opening buds of Prunus."*

By Prof. E. Verschaffelt. (Communicated by Prof. Hugo de Vries).

During last winter and the spring of 1902 I made a series of determinations to ascertain the amount of hydrocyanic acid which can be prepared from different organs in species of Prunus. They were untertaken with the view of investigating the changes that occur during the budding, regarding the prussic acid-compounds. In these analyses the titration-method of Liebig was always used in the following manner. The parts of the plants to be examined — mostly 5—15 grs. freshly gathered material, — were heated in 200—300 cm.^{3} of water to 60° C., so as to kill the protoplasm without destroying the emulsin. Though it will directly be shown that this treatment answers the purpose, the heating to 60° was repeated after some hours or the next day, to be certain that no cells were still living. Between both treatments and also during 24 hours after the second heating, the organs remained, immersed in water, in a well corked flask, that the emulsin might have time to split completely the HCN-glucosides. After that, the distillation was performed, the prussic acid being collected in a little flask containing some drops of KOH-solution, and the titration was made after the method described in the treatises, with $^1/_{10}$ normal nitrate of silver. The distillate was always collected in a flask of 100 cm.^{3} capacity; by taking with a pipette a known volume, I was able to repeat the titration two or three times in the same experiment. The quantities of plant-material and water being as above, it appeared without exception that the whole of the prussic acid had been condensed together with the first 100 cm.^{3} of water.

The necessity of allowing the objects to macerate for some time after the killing is clearly shown by the following preliminary experiment.

From 25 leaves, one year old, of *Prunus Laurocerasus* (Bot. G. Amsterdam) gathered 9. 12. 01. the halves of the blades were cut on each side of the middle-nerve. The halves *a* weighed 11,85 grs., the halves *b* 11,35 grs. The first portion was immediately submitted to distillation after having been immersed in the proper quantity of water, and gave 0,0160 grs. HCN. The portion *b* was heated to 60° C., and remained under water till the next day; this time the amount of HCN was 0,0254 gr. As soon however as both portions are treated as *b*, the concordance of the results is very satisfactory:

12. 12. 01. 25 l., *a.*: 0,0223 gr., *b.*: 0,0226 gr. HCN.
13. 12. 01. 25 l., *a.*: 0,0378 gr., *b.*: 0,0387 gr. HCN.
10. 1. 02. 25 l., *a.*: 0,0239 gr., *b.*: 0,0242 gr. HCN.

In the same manner it could be ascertained that it was quite sufficient, after killing at 60°, to macerate during one day only, to obtain a complete splitting of the glucoside; also that the heating in 200—300 cm.^{3} at 60°, at two different times or even once, had left no living portions in the plant-organs.

The species studied were *Prunus Laurocerasus L.* and *Prunus Padus L.* It was chiefly my intention to follow the changes undergone by the prussic acid-compounds during the opening of the leaf-buds. As of both above named species the second is the earliest, and also yielded shoots a long time before the cherry-laurel, when cut branches were placed in the hot house, it was with *P. Padus* that the most complete experiments were made, those with *P. Laurocerasus* rather serving to control the former.

In the very first place, I asked myself the question whether the amount of HCN in resting buds — whatever might be the form of combination — did exhibit changes, when the buds began to grow. To know this, the estimation of the percentage in buds and young shoots issued therefrom is insufficient; one must compare the absolute quantity of prussic acid contained in a given number of buds with the amount in a same number of shoots. As the dimensions of both the buds and the shoots vary considerably, a satisfactory medium-value could only be obtained by the analysis of a great number of these objects, a precaution already made necessary on account of the buds being small.

The amount of HCN contained in resting buds of *P. Padus* will appear with sufficient exactness by the following three estimations:

10. 2. 02. 195 buds (Bot. G. Amsterdam); weight: 4,80 gr.-HCN: 0,0067 gr., i. e. 0,14 %; in 100 buds: 0,0034 gr.

11. 2. 02. 280 buds (B. G. Amsterdam); weight: 6,35 gr.-HCN: 0,0094 gr., i. e. 0,15 %; in 100 buds: 0,0034 gr.

20. 3. 02. 100 buds (B. G. Amsterdam; the buds are about to open, many show a green top); weight: 2,75 gr.-HCN: 0,0040 gr., i. e. 0,15 %; in 100 buds: 0,0040 gr.

In the first two analyses, the buds, as always was the case with the parts examined, in order to avoid losses of hydrocyanic acid, were immersed in water without being cut into fragments, and killed by heat. However, as it might be feared that the bud-scales should hinder the diffusion of glucoside and enzyme, the buds were, in the third experiment, cut in halves, to see whether they should yield more HCN. As no marked difference was to be noticed, there surely was no prussic acid that in the first two instances had remained unestimated.

It was presently the turn of the opening buds to be studied. On the 2th of February cut branches of *P. Padus*, dipping in water, were placed on a well lighted spot in the hot house, the temperature being circa 20° C. After some weeks, a great number of buds had opened, and yielded shoots, which, though short, were nevertheless well furnished with leaves.

5. 3. 02. 75 shoots taken; weight: 5,20 gr.-HCN: 0.0079 gr., i. e. 0,15 °/₀; in 100 shoots: 0,0105 gr.

Cut branches placed in hot house 26. 2. 02.

14. 3. 02. 60 shoots; weight: 8,70 gr.-HCN: 0,0108 gr.; i. e. 0,12 °/₀; in 100 shoots: 0,0180 gr.

When one considers the weight of the shoots examined, it will be seen that in the second experiment they were more fully developed than in the first. It is clear that, as the shoots go on growing, a steadily increasing absolute amount of HCN-compounds gathers therein, so much so that even at a very early stage they contain three to four times the quantity found in the resting buds. As, on the other hand, the percentage of prussic acid depends on a number of circumstances, chiefly on the proportion of water in the shoots, a factor which itself is so very liable to modification, the changes undergone by this relative amount of HCN are much less interesting. It will however be noticed that, notwithstanding the fact that the weight of the young shoots exceeds many times that of the buds, the percentage of prussic acid is but feebly or not diminished.

I should wish to recall here that *Edm.* and *Em. Tuma* [1]), estimating the HCN in young leaf-buds of *P. Padus,* while these were opening in April, found no higher proportion than 0,05 °/₀. This undoubtedly is due to the fact that the authors, distilling off after having added some sulfuric acid, did not obtain a complete splitting up of the glucosides.

It will now be asked, whether the prussic acid which appears in the growing shoots is formed in the same, or perhaps transferred to them from the branches. As the green unfolding leaves will very probably begin to assimilate, it seems credible enough that the hydrocyanic acid should be made by a process of "photosynthesis". Whether

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[1]) *Zeitschr. Allgem. Oesterr. Apoth. Ver.* 1892, p. 330.

this is the case or not will easily be ascertained by analysing shoots developed in the dark.

Branches of P. Padus, placed in the hot house 10. 2. 02., covered by a blackened box. After some weeks, numerous etiolated shoots had been developed.

5. 3. 02. 50 short shoots taken; weight: 5,40 gr.-HCN: 0,0061 gr., i. e. 0,11 %; in 100 shoots: 0,0122 gr.

Branches put in the dark 24. 2. 02.

17. 3. 02. 30 well grown, etiolated shoots, for the most part ½ — 1 dM. in length; weight: 7,90 gr.-HCN: 0,0054 gr; i. e. 0,07 %; in 100 shoots: 0.0180 gr.

There can be no doubt, from the results given above, that shoots grown in the dark also contain a much larger quantity of HCN-compounds than the resting buds, and that these substances cannot have been built up by an assimilatory process, under the action of sunlight.

Results of quite the same kind were obtained in studying *Prunus Laurocerasus.*

Resting buds.-28. 12. 01. 115 buds, mostly axillar (from the growers of medicinal plants Groeneveld and Lindhout, at Noordwijk); weight: 1,65 gr.-HCN: 0,0040 gr.; i. e. 0,24 %; in 100 buds: 0,0035 gr.

Shoots developed in the light (also mostly from axillar buds).-24. 4. 02. 50 shoots, still short, cut from the shrubs growing in the Botan. G. Amsterdam; the pale green leaves are not quite unfolded; weight: 9,30 gr.-HCN: 0,0278 gr., i. e. 0,30 %; in 100 shoots: 0,0556 gr.

27. 4. 02. 50 shoots, younger than the former, or newly opened buds; weight: 4,90 gr.-HCN: 0,0138 gr.; i. e. 0,28%; in 100 shoots: 0,0276 gr. [1])

Etiolated shoots. — Branches of *P. Laurocerasus* (B. G. Amsterdam) placed in the hot house, under blackened cylinders 23. 4. 02.

10. 5. 02. 5 shoots taken; weight: 2,25 gr.-HCN: 0,0047 gr.; i. e. 0,21%; in 100 shoots: 0,0940 gr.

Branches in the dark 25. 4. 02. 4. 5. 02. 10 very short shoots; weight: 1.65 gr.-HCN: 0,0037 gr., i. e. 0,22%; in 100 shoots 0,0370 gr.

Branches in the dark 27. 4. 02. 12. 5. 02. 11 shoots; weight: 4,70 gr.-HCN: 0,0083 gr.; i. e. 0,18%; in 100 shoots: 0,0755 gr. [2])

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[1]) A. J. van de Ven. (*Cyaanwaterstofzuur bij de Prunaceae.* Dissertation Amsterdam. 1898; also Archives Néerlandaises, 2e Série, tome II, 1899 (reports (p. 34 resp. p. 391) for young shoots 0,19-0,23%.

[2]) Van de Ven (l. c. p. 37 resp. p. 393) applying the test of Greshoff—Treub, was not able to detect prussic acid in etiolated shoots of *P. Laurocerasus.* This affords a new proof that microchemical reactions, as soon as the substances are not very abundant, necessarily require analytical confirmation. Mostly so when the test yields negative results.

Referring to what has been said with relation to *P. Padus*, the above given results require no further discussion. That in both species the percentage of HCN appears to be smaller in the etiolated shoots than in the green ones, has no very great importance. Etiolated shoots indeed are known to contain much more water, the evaporation being less active under the opaque bell-jar.

After it has thus been shown that buds opening in the dark also increase, as they grow, their amount of HCN, there still remain two ways of accounting for this augmentation. Perhaps the prussic acid — in whatever form it may be present — is made in the growing shoots out of other substances; it could however be drawn from other parts of the plants; that is to say the branches in *P. Padus*, possibly also the leaves in the evergreen *P. Laurocerasus*. I regret not to have succeeded in establishing with certainty which of the two explanations is the right one. All I can say for the present is that the HCN gathering in the shoots is not derived from the internodes, which bear the buds examined. However, the possibility of the acid being supplied by more distant parts cannot at the present time be said to be excluded completely.

In this part of the research, I again chiefly made use of *P. Padus*, as this species, bearing no leaves in winter, was especially favourable. The point to be ascertained was whether the increase of HCN in the opening buds should be accompanied by changes in the adjacent internodes.

In the first place the amount of HCN was determined in the internodes below resting buds. As the length and thickness of these organs are exceedingly variable, it once more was necessary to analyse a not too small portion of plant-material.

10. 2. 02. 100 internodes (Bot. G. Amsterdam); weight : 11,75 gr.-HCN : 0,0108 gr., i. e. 0,09°/₀ ; in 100 internodes : 0,0108 gr.

7. 3. 02. 250 internodes (B. G.); weight : 18,95.-HCN : 0,0246 gr.; i. e. 0,13°/₀ ; in 100 internodes : 0,0098 gr.

With these amounts will be compared those observed in the internodes below etiolated shoots.

Branches (B. G. Amsterdam) placed in hot house 24. 2. 02., and covered by opaque bell-jars.

17. 3. 02. 30 internodes are taken from below long etiolated shoots; weight : 3,85 gr.-HCN 0,0057 gr.; i. e. 0,15°/₀ ; in 100 internodes : 0,0190 gr.

Already this first experiment does not prove in favour of the view, that the HCN-compounds should be drawn from the adjacent internodes. That this really is not the case will clearly be shown by the further analyses, in which were examined, on the one hand resting buds, on the other etiolated shoots, both with the corresponding internodes.

Resting buds — 18. 2. 02. 80 buds *P. Padus* (Bot. G.), and internodes bearing them; weight: 8,80 gr.-HCN: 0,0121 gr.; i. e. $0,14\,^0/_0$; in 100: 0,0151 gr.

18. 2. 02. 125 buds and internodes; weight: 9,90 gr.-HCN: 0,0159 gr.; i. e. $0,16\,^0/_0$; in 100: 0,0127 gr.

21. 3. 02. 100 buds and internodes (the buds beginning to open at the top for the greater part); weight: 8,35 gr.-HCN: 0,0092 gr.; i. e. $0,11\,^0/_0$; in 100: 0,0092 gr.

29. 3. 02. 127 buds and internodes (cut on other shrubs as the foregoing; buds about to open); weight: 13,30 gr.-HCN: 0,0125 gr.; i. e. $0,09\,^0/_0$; in 100: 0,0098 gr.

Young shoots. — Branches placed in the dark 24. 2. 02.

17. 3. 02. 30 shoots and internodes; weight: 11,75 gr. HCN: 0,0111 gr., i.e. $0,09\,^0/_0$; in 100: 0,0370 gr.

Branches in the dark 24. 2. 02.; 25. 3. 02. 25 shoots and internodes; weight: 5,05 gr.-HCN: 0,0051 gr.; i.e. $0,10\,^0/_0$; in 100: 0,0204 gr.

The considerable increase in the quantity of prussic acid: two to three times the original amount, shows clearly that it has not been augmented in the shoots at the cost of the internodes immediately belonging to the buds. I can even go farther, and suggest that neither it can have been supplied by the more distant internodes, one year old. In the analyses of shoots with the adjacent internodes, as well as in the experiment with internodes only, the material was taken from twigs developed the summer before, which in the experiment had yielded shoots at different heights. Therefore, if the more basal internodes had furnished the HCN-material for the shoots nearer the top, then the estimations would have shown it, since in that case so great an increase as was noticed would have been impossible. If consequently during the growth of the young shoots prussic acid might be drawn from the branches, it could be only from the older parts.

I should have liked very much to establish with certainty whether the shoots form themselves the hydrocyanic acid they contain. For that purpose I several times analysed branches of *P. Padus* as well as of *P. Laurocerasus*, so as to determine the amount of HCN present in the *entire* branches, before and after the opening of the buds. These estimations however did not yield satisfactory results, because, when the branches used were small, the buds in the dark only gave short shoots, containing too small a quantity of HCN, and the difference between the two portions compared lay within the range of individual variation. If on the other side one will use larger branches, it is exceedingly difficult to choose two portions which can be compared; the limits of error of the experiment presently widen, and consequently the desired end is not reached. The experiments on branches longitudinally cut in two, which were undertaken with *P. Laurocerasus*, one moiety being immediately analysed, the other one, bearing the buds, being put in the dark till it had given off etiolated shoots, failed for the same reason. In consequence this question must remain unanswered for the present; perhaps experiments to be made next spring with rooted cuttings will meet with more success.

I will now endeavour to show that the cherry-laurel behaves in so far quite like *P. Padus*, that the parts situated immediately below the growing shoots retain their percentage of HCN nearly completely unchanged. Here the experiment becomes in a certain degree complicated, but also on the other hand is made more interesting, by the presence of the leaves. Therefore I must begin to tell something respecting the amount of HCN in these organs.

They have been analysed several times for pharmaceutical purposes. I only will recall here that FLÜCKIGER [1]) gave as the average of estimations, protacted during ten years, on cherry-laurels growing on the banks of the lake of Thune, 0,12°/₀ of the weight of fresh leaves. Folia Laurocerasi, bought in December and January from GROENEVELD and LINDHOUT, yielded 0,14—0,16°/₀, while the shrubs grown in the Botanical Garden at Amsterdam were found to contain in their leaves an amount ranging from 0,12 till 0,21°/₀, according to the individual analysed. Those were at least the quantities found in the course of the season December—May. The last named high figure is regularly yielded by the leaves of a certain shrub, that consequently could if wished be made the starting point of a selection to obtain a race containing much prussic acid.

It also may be of importance to acquire an idea of the absolute quantity of hydrocyanic acid contained in one leaf. Of course, owing to the variable dimensions of these organs, this quantity also varies considerably. I found 0,0015 — 0,0036 gr. HCN, the maximum-value in large leaves supplied by GROENEVELD and LINDHOUT, with a percentage of 0,15°/₀.

Before studying the modifications in the amount of HCN in the

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[1]) Pharmakognosie des Pflanzerreichs. 3e Aufl. 1891 p. 766.

leaves, brought about by the opening of the buds, also in the dark, one should know the changes caused by the occlusion of the light, independently of the formation of shoots. I properly ought to have done the same with the twigs of *P. Padus,* but nobody will, I trust, expect that these organs, with their peridermal coating, should show energetical processes of assimilatory kind.

The experiments with *P. Laurocerasus* took place not only with cut leaves, but also with branches bearing leaves. To examine whether cut leaves should change in the dark their amount of HCN, the halves of the freshly plucked organs were cut off along the middle-nerve and killed immediately. The other halves, with the middle-nerves still adhering to them, were brought in the hot house, and placed, under blackened bell-jars, in a glass, the petioli dipping in water. At the end of the experiment, the middle nerves were cut off, and the remaining halves of the blades analysed.

It appears that by staying even a fairly large number of days in the dark, the leaves undergo no modification whatever as regards the amount of HCN, at least not in winter [1]).

25 leaves (Noordwyk). 13. 12. 01.

Halves *a* analysed immediately: HCN: 0,0135.

Halves *b*, after staying in the dark till 29. 12. 01., HCN: 0,0142 gr.

25 leaves (Noordwyk).

Halves *a*: 13. 12. 01., 0,0357 gr. HCN.

Halves *b*: 9. 1. 02., 0,0351 gr. HCN.

It follows that even after about one month no change whatever is to be noticed. Recently F. F. Blackman and G. L. C. Matthaei [2]) have shown that the leaves of the cherry-laurel remain fresh and living in the dark even after fifty days. On the other side, the results given above quite agree with those obtained by A. J. van de Ven [3]), using microchemical methods.

However, after a longer stay in the dark, or even, in certain cases, at a temperature of 20° C., after a shorter stay, pathological changes become noticeable in the leaves. Yellow spots, originating along the middle-nerve and the more important side-nerves, cover by and by the surface of the leaf till it becomes uniformly yellow. However, these organs don't die at once; they remain fresh many days, but the analysis shows that they lose rapidly their hydrocyanic acid.

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[1]) J. Colard (Journal de Pharmacie de Liège, 2e année, 1895 p. 1) states that leaves of cherry-laurel, when the entire shrubs remained in the dark from May till August, yielded a percentage of HCN, somewhat inferior to the percentage in plants exposed to the light.

[2]) *Annals of Botany*, XV. 1901, p. 553.

[3]) Dissertation Amsterdam. 1898, p. 35. *Archives Néerlandaises*, l. c. p. 392.

25 leaves (Noordwyk).

Halves *a:* 23. 12. 01., 0,0165 gr. HCN.

Halves *b:* 7. 1. 02., (beginning to show yellow streaks along the nerves): 0,0142 gr. HCN.

20 leaves (Bot. G. Amsterdam).

a: 27. 4. 02. . . . . 0,0162 gr. HCN.
b: 9. 5. 02. (yellow patches) 0,0113 gr. HCN.

25 leaves (Noordwyk).

a: 27. 12. 01. . . . 0,0283 gr. HCN.
b: 20. 1. 02. (yellow) 0,0089 gr. HCN.

25 leaves (Bot. G. Amsterdam),

a: 17. 12. 01. . . . 0,0283 gr. HCN.
b: 20. 1. 02. (yellow) 0,0067 gr. HCN.

Just the same processes can be observed, when cut branches bearing leaves are placed under opaque cylinders. The leaves can remain fresh and green many weeks, and keep their amount of HCN unaltered. The halves *a* of the blades were analysed immediately; the halves *b* remained, adhering to the middle-nerve, on the branches till the end of the experiment.

25 leaves, from branches placed in the dark 5. 12. 01.

a: 5. 12. 01. 0,0270 gr. HCN.
b: 22. 12. 01. 0,0283 gr. HCN.

25 leaves, from the same branches (5. 12. 01 in the dark).

31. 12. 01.; halves cut off; the other ones remain on the branches.

a: 0,0243 gr. HCN.

b: 16. 1. 02.; remaining halves yellow; it appears that in this stage they fall off, or sit but loosely on the branches: 0,0196 gr. HCN.

Branches placed in the dark 17. 12. 01.;

1. 1. 02.; 10 yellow leaves, about to be dropped; weight: 17,65 gr.-HCN: 0,0094 gr.; i. e. 0,05 %.

From the same branches I took the same day 25 fresh green leaves, and cut off the halves; weight: 13,15 gr.-HCN: 0,0229 gr., i. e. 0,17 %.

Halves *b*; 14. 1. 02 for the greatest part yellow, and falling off — HCN: 0,0155 gr.

This experiment therefore is also of importance, because it shows how the diminution in the amount of HCN goes clearly together with the discoloration and dropping of the leaves, and does not directly depend upon the length of the stay in the dark. In fact, when I placed separated branches in the hot house, but exposed them to the light, there always were a certain number of leaves that became yellow; and in those the amount of HCN could also be shown to have diminished considerably.

Branches in hot house 26. 12. 01. Leaves yellow and falling off 22. 1. 02.; weight: 20,10 gr.-HCN: 0,0089 gr.; i. e. 0,04 °/₀.

Moreover, the same is the case with certain leaves directly taken from the shrubs grown in the Botan. G.

27. 4. 02.; 15 yellowish leaves are picked; weight: 24,95 gr.-HCN: 0,0158 gr.; i. e. 0,06 °/₀; in one leave: 0,0011 gr.

The figures for fresh leaves, mentioned formerly, show that but a small part of the HCN normally present had been retained here.

As the hydrocyanic acid was also observed to disappear from the cut leaves, when they became yellow, it seems very probable that this substance — or its compounds — are not transferred from the leaves to the branches, but must have undergone a chemical transformation.

The budding however, at least in the first periods that I examined, has no influence whatever on the quantity of prussic acid in the leaves and twigs. For instance, 30. 4. 02 were gathered, on the cherry-laurels of the Bot. G. Amsterdam, 10 leaves, one year old, each being inserted below a well grown young shoot; weight: 11,60 gr.-HCN: 0,0251 gr.; i. e. 0,22 °/₀; in one leaf: 0,0025 gr. These figures are of quite the same order as were yielded in December by the same shrub. 30. 4. 02 also were cut, below opening buds, twigs one year old; I chose intentionally twigs which though they bore numerous, and fairly big shoots, had no more leaves, these being cut or having fallen off at an earlier period, before the budding; weight: 8,25 gr.-HCN: 0,0086 gr., i. e. 0,10 °/₀. I have found however, in twigs one year old, taken from the different shrubs in the Bot. G., during winter, a percentage of HCN ranging from 0,06 till 0,11 °/₀. It is clear that there was no diminution after the opening of the buds.

Neither was this the case after the budding in the dark. Branches having been placed in the hot house, under darkened boxes, 29. 4. 02, leaves were cut 4. 5. 02, below etiolated shoots. The percentage: 0,14 °/₀, was the same as leaves from the same shrub had yielded before.

Finally, it could be shown in *P. Padus* that, though the young branches issued from the winter buds are already considerably developed, and bear numerous leaves of fair size, the amount of HCN-compounds in the internodes below is still the same as before the budding.

This was observed 25. 4. 02, when 130 internodes of *P. Padus*, from the year before, were taken below long shoots, well furnished with leaves; weight: 10,90 gr.-HCN: 0,0140 gr.; i. e. 0,13 %; in 100 internodes: 0,0108 gr.

Resuming, I am brought to the conclusion that in both species of *Prunus* examined (*P. Padus* and *P. Laurocerasus*), when the buds open, there appears in the shoots growing from them a steadily increasing absolute quantity of HCN-compounds, whereas the percentage changes little in the period examined. In this same period at least, and at any rate for a great part, these substances appear independently of the light. Neither is this prussic acid drawn from the internodes directly bearing the buds, and developed the year before. Whether it is supplied by more distant organs, or is formed in the growing twigs out of other substances, this remains to be shown.

It is also still a point of research in what form the prussic acid is contained in the growing parts. That it is necessary to macerate the killed organs before the total amount of hydrocyanic acid can be distilled off, speaks in favour of the presence of a compound that can be split up by an enzyme. Moreover, as the liquid distilled from etiolated as well as from green shoots of *P. Padus* and *Laurocerasus*, has an intense smell of benzaldehyde, it is very probable that these organs also contain glucosides of the amygdalin-type.

Physics. — *"Observations on the magnetic rotation of the plane of polarisation in the interior of an absorption band"*. By Prof. P. Zeeman.

1. The difficulties of a complete theory of emission are partly avoided in a treatment beginning with the absorption, and this may have been the reason why Voigt [1]) has followed this procedure, though it must be granted that in his method an explanation of the mechanism of the phenomenon as in Lorentz's theory cannot be given [2]). In Voigt's theory the separation of a spectral line by the action of a magnetic field is found as the separation of an absorption line.

Some particulars in this separation were anticipated by this theory [3]) and confirmed by experiment [4]).

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[1]) Voigt. Wied. Ann. **67**, p. 345, 1899.

[2]) For a comparison of the advantages of the theories of Lorentz and of Voigt, see Lorentz. Rapports, congrès, Paris T. III. p. 16, 33, 1900. en Phys. Zeitschr. **1** p. 39, 1899. cf. also Planck. Sitz.ber. Ak. Berlin, p. 470, 1902.

[3]) Voigt. Drude's Ann. **1**, p. 376, 1900.

[4]) Zeeman. Versl. Akad. Amsterdam. Dec. 1899. Archiv. Néerl. (2), **5**, p. 237.

The long since known phenomenon of the rotation of the plane of polarisation and the magnetic separation of the spectral lines were closely connected [1]).

One result however of VOIGT's [2]) theory relating to the rotation of the plane of polarisation in the interior of an absorption band seemed to be in contradiction with the results of CORBINO [3]) or at least were not confirmed by the experiments of SCHMAUSS [4]) The theory of VOIGT requires a negative [5]) rotation of the plane of polarisation in the interior of an absorption band, CORBINO however only succeeded in observing a very small positive rotation.

It would be very remarkable however, if there existed a disagreement between theory and observation in this special field so closely connected with other well understood phenomena.

I have been experimenting already some time on this subject. In executing these experiments I have been aided in an excellent manner by Mr. HALLO.

I have succeeded in observing a negative rotation in the interior of an absorption band, the results of my observations being in perfect *qualitative* agreement with VOIGT's theory.

2. The method used in the following observations on the rotation in sodium vapour is principally the same as that which has been used by VOIGT [6]) in his demonstration of the double refraction of sodium vapour placed in a magnetic field. Already HUSSEL [7]) used it in a determination of the naturel rotation of the plane of polarisation in quartz, and also CORBINO in his first experiments on sodium.

By means of a system of quartz prisms (as has been used by FRESNEL in his experiment on the division of a plane-polarised ray into two circularly polarised rays) a number of horizontal interference fringes are formed in a spectrum. The light traverses the prism in the direction of the axis and the edges are horizontal and perpendicular to the slit of the spectroscope. The prism system (length 50 mm.) was placed in my experiments as near as possible before the slit of spectral apparatus and a small Nicol, used as analysator, behind the slit. The polarising Nicol was placed, of course, before the electro-

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[1]) cf. also LARMOR. Aether and Matter, p. 203.

[2]) VOIGT. Ann. der Physik. (4), **6**, p. 784, 1901.

[3]) CORBINO. Atti R. Acc. dei Lincei. Vol. 10 p. 137, 1901, Nuovo cimento Febbraio 1902.

[4]) SCHMAUSS. Ann. d. Phys. **2** p. 280, 1900.

[5]) The magnetic rotation in the vicinity of the band is positive in sodium vapour.

[6]) VOIGT. Wied. Ann. **67**, p. 360, 1899.

[7]) HUSSEL. Wied Ann. Bd. **43**, p. 498, 1891.

magnet (of the Ruhmkorff type). The spectroscope was a Rowland's grating, for which I am indebted to the kindness of the Directors of the Dutch Society of Sciences at Harlem; it has a radius of 6.5 M., 10.000 lines to the inch and a divided surface of nearly 14 cm.

The grating was mounted for parallel light in the manner indicated by Runge and Paschen [1]). The source of light was in most cases the electric arc, in some the sun.

Using this arrangement of the experiment we can deduce immediately from the deformation of the interference fringes in the neighbourhood of the absorption bands, when the sodium vapour is under the action of the magnetic field, the value of the rotation of the plane of polarisation for different wave lengths. Fig. 1 of the Plate gives an idea of the aspect of the fringes in absence of the field in the neighbourhood of the sodium lines, rather much sodium being present in the flame between the poles. The observations were made in the second order.

3. In the experiments first to be described, the distance between the perforated poles was about 4 m.m. and the intensity of the field about 15.000 c. g. s. units. In this field was placed a gas flame fed with oxygen and a small quantity of sodium introduced in it by means of a glass rod. After removal of the polarisator and of the Fresnel prism the two doublets, in which the sodiumlines are separated, in the inverse magnetic spectral effect were observed. Between the components of the doublet were seen the very narrow reversed sodiumlines due to the arc light itself.

The polarisator and the prism were now introduced in their proper places. The field of view was then crossed by the above mentioned (2) dark, nearly horizontal interference fringes.

I now wished to ascertain the deformation of the fringes by increasing continuously the quantity of sodium vapour, the field remaining constant. This method must be preferred for obvious reasons to the other which might have been followed also, viz: the examination of a flame with constant percentage of sodium under varying magnetic intensities.

The following observations refer to D_1:

If the quantity of sodium in the magnetic field was only extremely small, the interference fringe exhibited at the place of the reversed sodium line a protuberance — let us say *downward* — the lines of the doublet being somewhat stronger just above the interference fringe. In fig. 1 this behaviour is represented schematically.

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[1]) Kayser. Handbuch. Bd. I, p. 482.

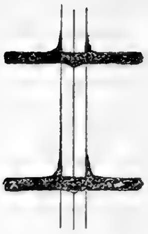

Fig. 1.

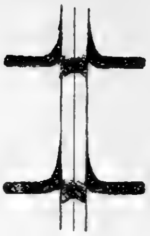

Fig. 2.

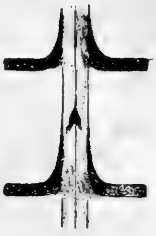

Fig. 3.

Increasing now the quantity of sodium (always remaining very small however, absolutely) the interference fringes moved upward along the components of the doublet, whereas the part of the fringe between the components seemed no longer connected to the exterior fringes and accepted the shape figured schematically in fig. 2.

Increasing still further the density of the vapour the interior part of the fringe slid downward with increasing velocity and then resembled an arrow with point directed upward, the parts more removed from the medium line fading away and disappearing (cf, the schematic fig. 3). At last the arrow entirely disappeared by the increase of the density of the vapour. It then became impossible to distinguish the fringes or any trace of structure in the field between the components. Rather much light was transmitted. The entire width of the components of the doublet was now about of the same order as the distance of their central lines.

A further increase of the quantity of sodium obscured the central part more and more (see further (8)).

The exterior fringes moved continuously upward while the density was being increased.

In a field of about 20000 units the downward displacement could be followed over a distance of more than the double of the distance between two fringes, corresponding to a *negative* rotation of above 2 × 180°, say 400°. The distance between the poles was 4 mM.

Some more accurate data will be given on another occasion.

In the case of D_2 the phenomena were in the main of the same character.

For D_2 it was however characteristic that the stage of the nearly or entirely vanishing of the interior fringes was reached with smaller field, whereas also the shape of the interior fringe differed from the one observed in the case of D_1. Hence there exists also in this case a difference between D_1 and D_2, a difference already known to exist in the phenomena of reversal, of the separation by a magnetic field and of the rotation of the plane of polarisation in the vicinity of the absorption band.

4. It appeared possible to keep stationary each of the stages described in (3) during a considerable time. Excellent photographs could be secured with plates which were sensitised for yellow light with erythrosine silver. Instead of the gasflame fed with oxygen it was easier, in the case of greater distances between the poles, to use a Bunsen burner wherein common salt was introduced.

5. If the density of the vapour was maintained as constant as possible and if it and the fieldintensity corresponded to the circumstances represented in fig. 3 (3) then an *increase* of the field gave a motion of the arrow (fig. 3) (3) upwards, corresponding to a *decrease* of the negative rotation and reciprocally. It was possible to observe by eye observation very clearly this decrease when the field was changed e. g. from 18000 to 25000. If the circumstances were more in accordance with fig. 2 (3) then the same change of field produced a change only just perceptible of the negative rotation but in the same sense as mentioned in the case of fig. 3.

An enlarged reproduction of one of the photographs is shown in fig. 2 of the plate. The distance between the poles in this experiment was 6,3 mM., the field intensity about 14000 [1]). The negative rotation in the case of D_1 is somewhat less than 90°. In the case of D_2 yet only some traces of the interior fringes can be seen (3). The negative rotation is about 180°. In the photograph are seen also the reversed very narrow D_1-line and the broader D_2-line, which are due to the arc itself and have nothing to do with our subject.

6. The observations (3, 4, 5) agree qualitatively in an excellent manner with the conclusions from VOIGT's theory. According to it, the negative rotation must be of the same order of magnitude as the positive one. This last was known from MACALUSO's and CORBINO's experiments to be very great. The enormous value and the sign of the negative rotation given in (3) may thus be regarded as a beautiful confirmation of the theory.

As much is this the case with the direction (5) of the change of the negative rotation with increasing field. In order to see this we must know the value of the quantity occurring in the theory $P = \frac{cR}{\vartheta}$ ($R =$ fieldintensity, c and ϑ parameters of the absorptionband), for which the comparison must take place. It was possible to assign a value to P by comparison of the phenomenon with VOIGT's figure 1 [2]).

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[1]) The intensities of the field were measured by means of a bismuth spiral in the centre of the field. Probably the values given are somewhat too high. Measurements of the magnetic change of the spectral lines give lower values.

[2]) Annalen der Physik. **6** p. 789. 1901.

This figure gives $n\chi_0$ (χ_0 angle of rotation, n a mean value of the index of refraction) as function of a certain variable Δ, whereas our phenomenon is a representation of χ_0 as a function of λ. Reducing the abscis of the mentioned fig. 1 to $^1/_{20}$ or $^1/_{25}$ we obtain diagrams resembling in the main features fig. 2 of the Plate. To the greater observed negative rotation (3) correspond values of P, which can be estimated at 5 or 8. The smallest easily observed rotations in the used strong field are probably in the vicinity of the critical value $P = 1.73$.

7. The slope of the exterior interference fringes is greater towards the side of the greater wavelengths than towards the violet, at least so far as the rotation due to one band does not influence visibly the rotation due to the other. At the same distances, if not very small, of each of the two D lines the rotation at the side of the violet is greatest. The interior fringes also show a slight asymmetry, so e. g. the point of the arrow in fig. 3 (3) ought to be asymmetrical. The part at the side of the violet is predominating.

It is clear that these phenomena depend upon an asymmetry of the dispersion curve.

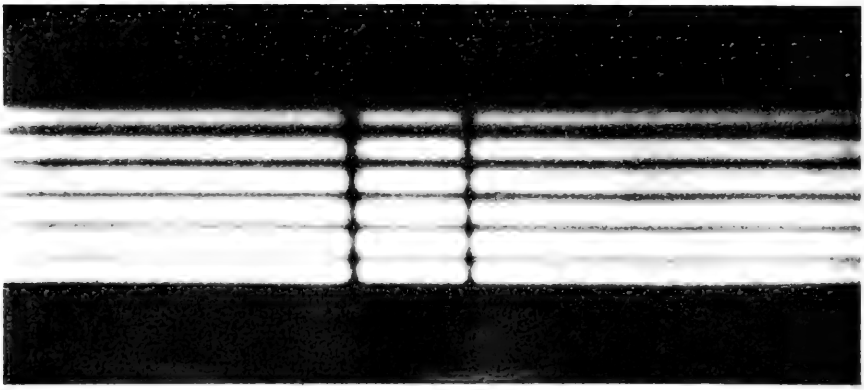
8. With very dense sodium vapour, hence under circumstances which are beyond the last stage of (3), I observed phenomena very probably identical with those observed by Corbino. In my first experiments with those dense vapours I thought it absolutely necessary for securing sufficient intensity to widen the slit beyond the width used in the already given experiments. I now see however that this is unnecessary.

Using these very dense vapours one sees in the absorption band a horizontal part of an interference fringe, which seems to have undergone a very small displacement *upwards* by the action of the field. These horizontal parts are more ill-defined and broader and the whole phenomenon in the bands is darker than under the circumstances described in (3), (4), (5).

Figs. 3 and 4 of the Plate will give a clearer impression of the change in the phenomenon than a long description.

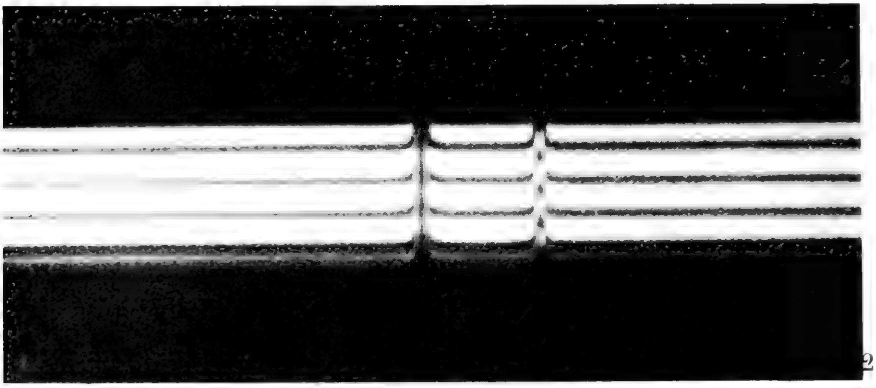
Fig. 3 was obtained with a field of 4500 units and much sodium. I have made some measurements, according to a method not to be given here, concerning the displacement of the central (in horizontal and vertical direction) part of the interference fringe, and I have found a displacement, which would correspond to a *positive* rotation of about 8° with both D-lines. Fig. 4 was taken with a field of 10700 and much sodium. The exterior interference fringes are very clear and much deformed; the rotation in the parts adjacent to the absorp-

P. ZEEMAN. Magnetic Rotation in the Interior of an Absorption Band



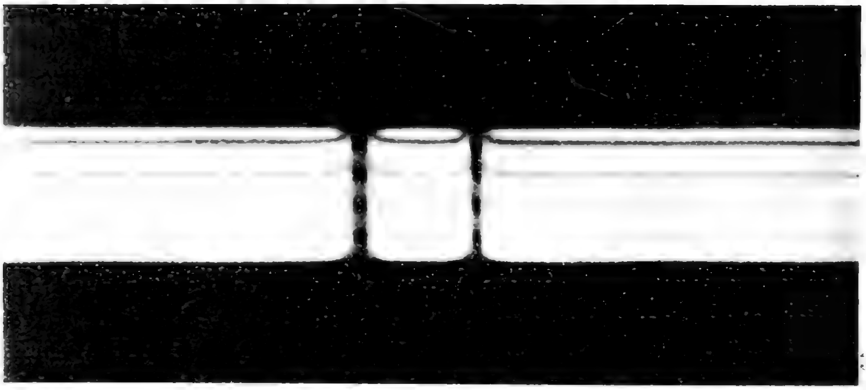
1.

D_2 D_1



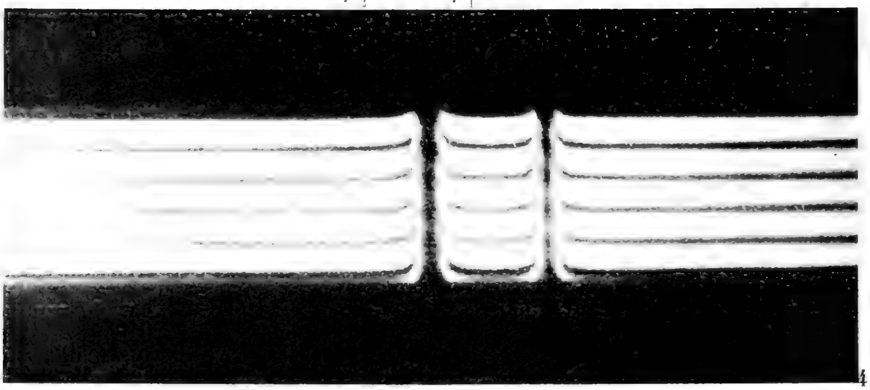
2.

D_2 D_1



3.

D_2 D_1



4.

D_2 D_1

tion band surpass 180°. The interior interference fringes are very indistinct. Their appearance would suggest that in the case of D_1 in Fig. 4 the stage has been scarcely surpassed, reached for D_2 in fig. 2.

This however cannot be the case because there was too much sodium in the flame. A comparison with fig. 2 will show that the lines are much broader in fig. 4. Measurements taken on other negatives gave me for fields of 11000, displacements of about $^1/_{16}$ of the distance between two fringes, corresponding to a positive rotation of 11°. Hence the displacements in these cases are precisely of the same order of magnitude as in CORBINO's experiments. The paleness of the boarders of the band is easily accounted for by the remark that there the intensity one of the circularly polarised rays largely exceeds the other.

I do not believe that these facts are in contradiction with theory. It is true that it requires for very high values of P a value zero for $(n\chi_0)_1$. If we must take as the locus of the fringe the mean vertical height, then really the rotation would be positive. It seems possible that with those broad fringes the case is different. It is also possible that the circumstances, assumed in the theory are not wholly realised in the experiments with dense vapours. I am making some new experiments about this subject and therefore shall not discuss further the different possibilities.

EXPLANATION OF THE PLATE.

The Plate gives about sixfold enlargements of the photographs.

Fig. 1. Interference fringes and absorption lines in absence of the field and rather much sodium. (2)

Fig. 2. Same lines. Field intensity about 14000, little sodium. (3) (5)

Fig. 3. Same lines. Field intensity about 4500, much sodium. (8)

Fig. 4. Same lines. Field intensity about 10700, much sodium. (8)

Anatomy. — "*A new Method for demonstrating cartilaginous Mikroskeletons.*" By Prof. J. W. VAN WIJHE.

It is a well-known quality of cartilage that it firmly retains certain anilinstains. Taking advantage of this quality, I have for some years endeavoured to find a stain, which will remain permanent in the cartilage, after it will have been entirely extracted out of the other tissues. If the object is made transparent in canada balsam, the cartilaginous skeleton will then be seen as if it were prepared. I was more or less successful with most of the so-called basal anilin-pigments, best of all however with methylene-blue, and so I was induced to use this latter stain exclusively.

The coloring of the cartilage was attempted with full-grown objects, as well as with embryos, but as the coloring-method is chiefly useful when applied to small objects, with which the ordinary preparation-method proves deficient, it will chiefly be applied to embryos.

Whenever we wanted to examine the cartilaginous skeleton of an embryo, we were, up to the present time, obliged to make series of sections and to construct an enlarged model after these sections, all of which took up a good deal of time. As a rule it would have taken much too long to model a whole skeleton; therefore in most cases only a part was constructed, for instance the head-skeleton or the pelvis.

Working on this plan a single object requires many months of labor, and besides at the end you have not the object itself, but an imitation.

Following the coloring-method, on the contrary, a great number of entire skeletons are obtained in a short time with little trouble, not clumsy imitations, but the objects themselves with all parts in their natural connection and the contours of the whole embryo and of different organs besides, for notwithstanding the transparency of the organs the outlines of many are still clearly recognizable. Although the cartilage is colored intensely blue, it remains transparent: so for instance the spinal column glimmers through the shoulder-blade.

The method is as follows:

The embryo is fixed in the usual way in 5°/$_0$ sublimate-solution, or 10°/$_0$ formol, or in ZENKER's liquid and is preserved in alcohol. No doubt it may be fixed in many other ways; I even obtained useful results with old preparations of alcohol from the collection. I mostly fix the embryos in 5°/$_0$ sublimate-solution, to which is added $^1/_{10}$ volumen formol, shortly before using.

The object may now be brought immediately from the alcohol into the pigment-solution, but it has seemed advisable to me to extract previously for a day or two with alcohol, which contains some ($^1/_4$ °/$_0$) hydro-chloric acid. The acid alcohol must be renewed if it has turned yellow the next day, which often happens when iodine has been used in extracting the sublimate. The iodine is fatal for the coloring, as it forms with methylene-blue an almost insoluble precipitate and with neutral alcohol the iodine cannot be quite removed. This is proved when seemingly white objects, preserved for a year and more in alcohol which has remained colorless, being brought into acid alcohol, cause this liquid to turn yellow the next day. The yellow color disappears after the addition of a few drops of sublimate-solution.

From the acid alcohol the object is placed for a day at least, rather for a week, into an alcoholic solution of methylene-blue, to which 1% hydro-chloric acid has been added. It is sufficient when $^1/_4$ gram of methylene-blue is dissolved in 100 cc. alcohol of about 70%. If more coloring-matter is taken, a sediment remains on the bottom of the bottle. After the addition of the hydro-chloric acid, blue crystalline needles separate themselves from the liquid. For this reason it is desirable that this addition should be made not at the moment of using, but some time before.

The object when taken from the pigment, should not show any sediment. If it does, it has not been extracted long enough with acid alcohol. Although it is not lost yet, it may cost months before the sediment is removed. The intensely blue-colored object is treated in the usual manner in the above mentioned acid alcohol, which is renewed several times on the first day and once daily afterwards. The renewal is continued until the alcohol shows no blue tinge the next day. The time required for this is, of course, dependent on the size of the embryo. This time can be shortened by taking alternately alcohol of about 70% and a stronger one and hanging the object one day in the stronger alcohol, whereas the next day it is allowed to settle on the bottom of the bottle; this is not necessary however. In about a week the stain has been removed from all the tissues, except from the fundamental substance of the cartilage. It is not necessary anxiously to observe the day when the alcohol shows no more coloring; objects kept for a year and longer in the colorless acid alcohol, showed the cartilage still distinctly blue.

The object is now dehydrated in absolute alcohol, in the usual way, and rendered transparent in xylol. To avoid wrinkles, it is not put immediately from the alcohol into xylol, but first in a mixture of two parts of absolute alcohol with one part of xylol, then in a mixture of one part of absolute alcohol with two parts of xylol and only after that in xylol only. Larger-sized embryos are cut in halves or in different pieces with the razor. After that the objects are put first in a thin, afterwards in a thick solution of canada-balsam in xylol and finally in a solution, which in ordinary temperature is solid, but liquid at 60°. In this solution they remain in the thermostat at 60° during a couple of hours and are then enclosed in glass-cells under a covering-glass.

The glass-cells in trade are usually too low, higher ones can easily be obtained by fixing stripes of window-pane with canada-balsam on an object-glass.

My experience has not been long enough to enable me to assure that the objects will not fade in the long run, I can only say, that even my oldest preparations, which have been enclosed in canada-balsam for a couple of years, have not faded visibly. I have taken care however to dissolve in xylol the solid, neutral canada-balsam of Grübler's myself because the commercial solution often contains turpentine.

The staining method here described has been successful with the cartilaginous skeleton of representatives of all classes of vertebrate animals, as for instance with Amphioxus, with embryos of sharks and rays, of salmons and roaches, of frogs and lizards, of birds, of mice, rabbits and man.

With regard to man, it is of importance that the coloring can still be successful with embryos in a far proceeded state of dissociation and which otherwise one would be inclined to throw away.

Magnified slightly, the preparations are particularly suitable for demonstration. I here demonstrate the skeleton of a human embryo of about five weeks old and draw your attention to the rudiment of the shoulder-blade. It is still exclusively adjacent to the neck, on a level with the 5th, 6th and 7th cervical vertebrae, with the point still above the first rib. Eleven ribs show the blue color of the cartilage, the undermost, the twelfth, not yet.

In this second embryo, which is somewhat older, the shoulder-blade has left the 5th cervical vertebra and lies on a level with the 6th and 7th cervical- and the 1st and 2d thoracic vertebrae; it reaches with its point as far as the third rib. Not only all the twelve ribs are visible on the twelve thoracic vertebrae, the rudiment of a rib on the last cervical vertebra is seen besides, which rudiment fuses with this vertebra later on, as is well-known.

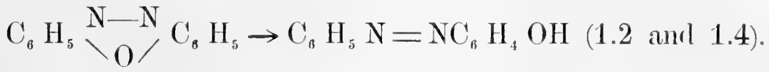
In this third embryo, which I received in perfect condition and which after fixation was 25 mm. long in its natural curve, it may be seen that the shoulder-blade has again gone down a little. At the neck it does not reach higher than the level of the last cervical vertebra and reaches with the point as far as the 4th rib. Further the rudiment of the pelvis may here be noticed, on the level of the fourth lumbar — and the first sacrum-vertebrae and on the head the cartilage of the occiput, the ear case, the cartilage of Meckel and the rudiment of the incus.

Other preparations show the paired rudiment of the rabbit's and the chicken's sternum.

Also for macroscopic museum-preparations this is a suitable method; I could show you, for instance, the cartilaginous skeleton of sharkembryos more than 2 dm. long, preserved in xylol. These preparations were exceedingly beautiful at first and the non-cartilaginous tissues transparent, as clear as crystal; later on however they lost the transparency for the greater part and became opalescent. The cause of this change is unknown to me. Such macroscopic preparations ought therefore also to be enclosed in canada-balsam or dammar-resin.

Chemistry. — "*Intramolecular rearrangement of atoms in azoxybenzene and its derivatives.*" By Dr. H. M. Knipscheer. (Communicated by Prof. Lobry de Bruyn.)

Wallach and Belli [1]) noticed a long time ago that azoxybenzene is converted into its isomer *p*-azoxybenzene by gently heating it with sulphuric acid, or by means of fuming sulphuric acid at the ordinary temperature. Bamberger found that in this process there is also formed half a percent of *o*-oxyazobenzene a substance discovered by him some time ago when acting on nitrosobenzene with aqueous caustic soda at 100°. The reaction noticed by Wallach and Belli must be represented as follows:



$$C_6H_5\underset{\diagdown O \diagup}{N-N}C_6H_5 \rightarrow C_6H_5N{=}NC_6H_4OH \text{ (1.2 and 1.4).}$$

Sulphuric acid was up to the present the only reagent capable of causing the said intramolecular rearrangement of atoms. Wacker [2]), however, when stating in his paper on *α*-azoxynaphtalene that this substance turns red by exposure to direct sunlight, also remarks that azoxybenzene is likewise sensitive to sunlight, but he only mentions that it turns deep yellow without having investigated the nature of the change.

Various derivatives of azoxybenzene also appeared to be liable to the same intramolecular rearrangement of atoms, but again sulphuric acid is mentioned as the only reagent capable of causing the change. The result of those investigations showed that some of the substitution products, namely the meta-derivatives, are almost quantitatively converted into the isomeric phenols, while the ortho- and para-derivatives are only affected to a small extent or not at all.

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[1]) Ber. **13.** 525 (1880).

[2]) Ber. **33.** 3192 (1900).

[3]) Ber. **33.** 1939 (1900).

[4]) Ann. **317.** 313 (1901).

Schultz scarcely obtained any dichloro-oxyazobenzene when treating *p*-*p*-dichloro-azoxybenzene with fuming sulphuric acid, but *p*-*p*-dichloro-azobenzene was formed; *m*-*m*-dichloro-azoxybenzene however yielded *m*-*m*-dichloro-oxyazobenzene in large quantity.

Klinger and Pitschke[6]) succeeded in almost entirely converting *m*-*m*-dinitro-azoxybenzene into *m*-*m*-dinitro-oxyazobenzene by heating the same with sulphuric acid at 140°. By heating *o*-*o*-azoxytoluene with sulphuric acid at 100°—120° they could only obtain *o*-*o*-azotoluene accompanied by acids such as *o*-tolylazobenzoic acid.

Limpricht[1]) converted azoxytoluidine into oxyazotoluidine in an analogous manner, whilst Elbs and Schwarz[2]) succeeded in converting *p*-*p*-diamino-*o*-*o*-azoxytoluene into *p*-*p*-diamino-*o*-*o*-oxyazotoluene by heating it with sulphuric acid at 100°—105°.

My object now was to ascertain whether the above described intramolecular rearrangement might be realised by other means than by the use of sulphuric acid. It was ascertained that the intramolecular rearrangement of atoms in azoxybenzene is also possible by raising the temperature to at least 200° and by the influence of direct sunlight. In the first case a mixture is formed of *p*- with much *o*-oxyazobenzene; in the second case only *o*-oxyazobenzene is obtained. None of these changes is reversible. Also those derivatives of azoxybenzene which undergo intramolecular rearrangement by the action of H_2SO_4 are converted by the said agencies, but the action is slower and the amount is smaller than that obtained from azoxybenzene. The investigation of these derivatives has not yet been quite concluded.

Acetic anhydride is without effect on azoxybenzene at the boiling temperature; on heating however at 200° the change already takes place in a notable degree, much better than by merely heating the substance itself, while an acetate is either not formed at all, or only in very small quantity. *P*-oxyazobenzene is not formed at 200° but only the *o*-isomer. Solutions of azoxybenzene derivatives in acetic anhydride do not however suffer any intramolecular change at 200°,

Addition of $ZnCl_2$ or P_2O_5 to acetic anhydride does not enable it to cause the change at the boiling point; heating with the so-called Beckmann's mixture is also without avail. By heating a solution of azoxybenzene in this mixture at 150° and 180° it appears that azoxybenzene which, when prepared in the ordinary way is a yellow substance, is perfectly white when in a pure condition. The ordinary

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[5]) Ber. **17**, 464 (1884).

[6]) Ber. **18**, 2552 (1885).

[1]) Ber. **18**, 1405 (1885).

[2]) Journ. f. pr. chem. **171**. 567 (1901).

product therefore contains a yellow impurity, which cannot be removed by recrystallisation.

The intramolecular change was attempted in vain by means of the following reagents:

Acetyl chloride, butyryl chloride, benzoyl chloride, phosphorus pentachloride, phosphorus oxychloride, phosphoric acid, aluminium chloride, aqueous caustic soda, copper oxide, zinc oxide and zinc carbonate. Of these reagents the following deserve to be specially mentioned on account of their action on azoxybenzene:

Acetyl chloride: formation of *p*-*p*-dichloro-azobenzene and *p*-chloro-acetanilide; benzoyl chloride: formation of azobenzene; phosphorus pentachloride: formation of azobenzene with evolution of chlorine; aluminium chloride: formation of *p*-chloro-azobenzene.

Mathematics. — "*On the connection of the planes of position of the angles formed by two spaces S_n passing through a point and incident spacial systems.*" By Prof. P. H. SCHOUTE.

1. If in a space S_{2n} with $2n$ dimensions two spaces S_n are given arbitrarily, these have in general only a single point O in common and they form in this point with each other n angles differing in general respectively. These angles are situated in n definite planes through O and the line at infinite distance of such a *plane of position* has a point in common with the two given spaces $S_n^{(1)}$, $S_n^{(2)}$ as well as with the spaces $S_n'^{(1)}$, $S_n'^{(2)}$ drawn perpendicular to the just named spaces through any arbitrary point, say O, not at infinite distance. In this way the two planes of position of two planes ε_1, ε_2 taken arbitrarily in S_4 are determined by the common transversals of four lines situated in a three-dimensional space, viz. of the lines g_1, g_2 of ε_1, ε_2 in the space S_3 at infinite distance in S_4 and the lines g_1', g_2', normally conjugate in this S_3 to g_1, g_2.

2. Let us consider the particular case when the n angles formed by $S_n^{(1)}$, $S_n^{(2)}$ are alike; as an introduction we take in S_4 again two planes ε_1, ε_2 forming with each other in their point of intersection O two equal angles. It is known that in that case the four above mentioned lines g_1, g_2, g_1', g_2' are generators of an hyperboloid; so they admit of not only two but of an infinite number of common transversals, to which answer likewise an infinite number of planes of position. If the system of those transversals t is indicated by (t), the

system of the lines g intersecting all the lines (t) by (g), there exists between the two incident systems of lines (g), (t) at infinite distance this reciprocal connection that the plane passing through an arbitrarily chosen point O at finite distance and an arbitrary line of one of the two systems is a plane of position for the pair of the planes connecting the point O with two arbitrary lines of the other system. From the manner in which the quadratic scroll (t) is formed out of g_1, g_2 g_1', g_2' namely ensues that the surface H^2 of order two, bearer of the two systems (g), (t), agrees with itself in the polar system at infinity in S_4 of which the imaginary sphere B^2_∞ common to all hyperspheres is at the same time the locus of the points lying in their polar planes and the envelope of the planes passing through their poles; for to each line t intersecting g_1, g_2, g_1', g'_2 regarded as locus of points agrees in that correspondence a line t' lying with g_1', g_2', g_1, g_2 in a plane regarded as axis of a pencil of planes, etc.

If we make the lines g, g' of (g) normally conjugate to each other to correspond to each other, then between the lines of (g) a quadratic involution is formed; the double rays g_i, g_j of this involution must lie on B^2_∞, being normally conjugate to themselves. Likewise does B^2_∞ contain the double rays t_k, t_l of the involution formed in quite the same way between the lines t, t' normally conjugate to each other. So H^2_∞ and B^2_∞ intersect each other in the sides of a skew quadrilateral whose pairs of opposite sides are the double rays (g_i, g_j) and (t_k, t_l) of the pairs of rays (g, g') and (t, t') of (g) and (t) normally conjugate to each other.

If (g, g') are two normally conjugate rays g and (t, t') likewise two normally conjugate rays t and if we take the planes Og, Og' and Ot, Ot' as coordinate planes OX_1X_2, OX_3X_4 and OX_2X_3, OX_4X_1, then the surface H^2_∞ must be characterised with respect to this rectangular system of coordinates by the equation $x_1x_3 = x_2x_4$ between the infinite coordinates. For the quadratic surface $x_1x_3 + px_2x_4 = 0$, brought through the lines at infinite distance of the four mentioned coordinate planes, corresponds to itself in the polar system with the sphere $x_1^2 + x_2^2 + x_3^2 + x_4^2 = 0$ at infinite distance as surface of incidence only when the absolute value of p is equal to unity. For the normally conjugate line of $x_1 = \lambda x_3$, $\lambda x_2 + px_4 = 0$ is $\lambda x_1 + x_3 = 0$, $px_2 = \lambda x_4$ and this new line lies only for $p^2 = 1$ with the original one on $x_1 x_3 + px_2 x_4 = 0$. So by reversing if need be the sign of one of the coordinates we can always bring the equation of H^2_∞ into the form $x_1 x_3 = x_2 x_4$.

3. Before passing on to the general case we shall consider the

case, when in S_6 two three-dimensional spaces $S_3^{(1)}$, $S_3^{(2)}$ are given arbitrarily. The line g_∞ at infinite distance of the plane of position of one of the angles formed by those spaces in their point of intersection O is then a common transversal of the planes at infinite distance $\varepsilon_\infty^{(1)}$, $\varepsilon_\infty^{(2)}$ of $S_3^{(1)}$, $S_3^{(2)}$ and the planes $\varepsilon_\infty'^{(1)}$, $\varepsilon_\infty'^{(2)}$ normally conjugate to these. As the common transversals g_∞ of the three planes $\varepsilon_\infty^{(1)}$, $\varepsilon_\infty^{(2)}$, $\varepsilon_\infty'^{(1)}$ form a "variety" V_3^3 of order three of three dimensions and this curved space is intersected in three points by $\varepsilon_\infty'^{(2)}$, the spaces $S_3^{(1)}$, $S_3^{(2)}$ make in O three angles with each other. This variety V_3^3 is not only (compare i. a. the first part of my "Mehrdimensionale Geometrie", vol. XXXV of the Sammlung SCHUBERT", N°. 102, 103) the locus of a twofold infinite series of transversals g_∞, but at the same time the locus of a simple infinite series of planes ε_∞, each of which determines with $\varepsilon_\infty^{(1)}$, $\varepsilon_\infty^{(2)}$, $\varepsilon_\infty'^{(1)}$ on the lines g_∞ quadruples of points with a definite anharmonic ratio, i. e. V_3^3 is the bearer of two incident systems which we represent according to the nature and the multiplicity of the elements by $(g_\infty)_2$ and $(\varepsilon_\infty)_1$. Beside the general case, where $\varepsilon_\infty'^{(2)}$ has in common with V_3^3 three points not situated on a right line, the particularity may arise that $\varepsilon_\infty'^{(2)}$ has a line in common with one of the planes ε_∞ of $(\varepsilon_\infty)_1$ or coincides with one of those planes; to this answer the particularities that two of three generally different angles of position or all three of them become equal to each other. In the last case of the three equal angles of position, to which we restrict ourselves here, there is between the two systems of incidence this connection, that the plane passing through an arbitrarily chosen point O at finite distance and an arbitrary line g_∞ of $(g_\infty)_2$ is a plane of position for the pair of spaces connecting O with each of two arbitrarily chosen planes ε_∞ of $(\varepsilon_\infty)_1$. If namely we make on each of the lines g_∞ of $(g_\infty)_2$ those points to correspond to each other which are conjugate to each other in the involution determined by the pairs of points of intersection of that line with the planes $\varepsilon_\infty^{(1)}$, $\varepsilon_\infty'^{(1)}$ and $\varepsilon_\infty^{(2)}$, $\varepsilon_\infty'^{(2)}$, then between the planes ε_∞ of $(\varepsilon_\infty)_1$ is formed a quadratic involution, from which ensues that the plane ε_∞' normally conjugate to the plane ε_∞ of the variety V_3^3 lies likewise in V_3^3, etc.

The two double planes ε_i, ε_j of the involution $(\varepsilon_\infty, \varepsilon_\infty')$ form part of the imaginary hypersphere B_4^2 with four dimensions at infinite distance common to all hyperspheres B_5^2 with five dimensions of S_6. So the section V_2^6 of V_3^3 and B_4^2 consists of these two planes and a V_2^4 which must now necessarily be the locus of the transversals g_∞ of $(g_\infty)_2$ lying entirely on B_4^2. Whilst as is known the lines g_∞ resting on any arbitrary right line of ε_∞ form a surface of order two, the locus of the lines g_∞ resting on the conic of section of ε_∞ and B_4^2 is a V_2^4.

4. If finally in S_{2n} two spaces S_n are taken arbitrarily, these form with each other, as was mentioned above, in their point of intersection O in general n angles differing from each other and the line at infinite distance of the plane of position of each of those angles in the space at infinite distance S_{2n-1} of S_{2n} intersects again four spaces S_{n-1}, the spaces at infinite distance $S^{(1)}_{n-1}$, $S^{(2)}_{n-1}$ of the two given spaces $S^{(1)}_n$, $S'^{(2)}_n$ and the spaces $S'^{(1)}_{n-1}$, $S'^{(2)}_{n-1}$ normally conjugate to these. If now the special case presents itself that each right line cutting three of the four spaces $S^{(1)}_{n-1}$, $S^{(2)}_{n-1}$, $S'^{(1)}_{n-1}$, $S'^{(2)}_{n-1}$ also cuts the fourth, the n angles of position are mutually alike and the locus of the n-fold infinite system $(g_\infty)_n$ of the lines g_∞ at infinite distance of the planes of position is a variety V^n_n of order n with n dimensions, appearing likewise as the locus of a simple infinite number of spaces S_{n-1}, i.e. in the form of $(S_{n-1})_1$, namely of the spaces S_{n-1}, determining with $S^{(1)}_{n-1}$, $S^{(2)}_{n-1}$, $S'^{(1)}_{n-1}$ and now also with $S'^{(2)}_{n-1}$ on the lines g_∞ of $(g_\infty)_n$ mutually projective series of points. In that case a plane connecting an arbitrary point O at finite distance with a line g_∞ of $(g_\infty)_n$ is always a plane of position of each two of the spaces S_n connecting O with spaces S_{n-1} of $(S_{n-1})_1$.

As is immediately evident, in this special case the section V^{2n}_{n-2} of V^n_n with the hypersphere S^2_{n-1} with $2n-2$ dimensions common to all hyperspheres B^2_{2n-1} of S_{2n} breaks up into the two double spaces $S^{(i)}_{n-1}$, $S^{(j)}_{n-1}$ of the involution of the spaces S_{n-1}, S'_{n-1} of $(S_{n-1})_1$ normally conjugate to each other and into a $V^{2(n-1)}_{n-1}$, locus of the lines g_∞ of $(g_\infty)_n$, lying entirely on B^2_{2n-1}.

Physiology. — "*The principle of entropy in physiology.*" By Dr. J. W. LANGELAAN. 3rd part. (Communicated by Prof. T. PLACE).

All investigations made with the intention of testing the law of FECHNER at the experiment, have proved, that this law is only satisfied within a small interval and within that interval only by approximation.

In order to find out the causes of these deviations, I have tried to deduce the law of FECHNER (considered as a physiological law) from a general physical principle. It has appeared from this deduction that this formula rests on very special premises, and that the circumstances assumed in these premises, are never realized in nature.

In a series of experiments I have tried to fulfil as accurately as possible the conditions required by this law according to its deduction. To this purpose the spinal cord of a frog [1]) was cut between the cranium and first vertebra; then the whole frog, with exception of the hind leg which was used for the experiment, was wrapped up in wads and fastened to a glass rod. The leg hung down in a wide vessel which could contain about 600 ccm. of fluid. In the sole of the foot a hook was put and a horsehair was attached to this hook, which passed outside through a very small opening in the bottom of the vessel. This horsehair was fixed to the arm of a length-recorder.

The small opening through which the hair passed was filled up with vaseline; this prevented almost perfectly the fluid to drip out, while the friction experienced by the horsehair was very slight. By suspending a weight to the length-recorder the leg was charged with 15 grams. Then the vessel was filled with 350 ccm. of water, and the leg immersed till the knee. To the stand bearing the glass and the frog, a clamp was fixed bearing a burette. This burette contained a solution of oxalic acid in distilled water. By opening the tap this solution flowed into the water in which the leg hung. A bent stirrer always kept in slow motion (but which did not touch the leg), caused the acid to be thoroughly mixed with the fluid. Then so much acid was slowly added to the liquid till the leg began to contract. The vertical motion of the leg, three times magnified, was registered on a slowly rotating cylindre by the length-recorder. In order to prevent too large excursions, the length-recorder struck against a piece of cork, so that the contraction in the beginning took place isotonically, at the end isometrically.

After the leg had returned to rest, we waited about 5 minutes and

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[1]) Small male specimens of Rana esculenta proved to be the most suitable for the experiment.

then again so much acid was added, till a new group of reflex-contractions appeared. In these experiments the acid in the burette contained 40 grams of oxalic acid per liter solution. As a measure of the stimulus in physical units the concentration of the solution, in which the leg was immersed, was chosen. The concentration is defined as the proportion between the quantities of oxalic acid and water, while as the unity of weight the molecular weight was chosen (126 for oxalic acid, 18 for water).

The result of the experiments was given in a table in the following way. The first column gives the concentration of the solution in the vessel, just at the moment the leg begins to show a group of reflex-contractions. The second column contains the increment, which the concentration in the vessel must undergo to produce again a set of reflex-contractions. The third column gives the relation between this quantity and the absolute value of the concentration at the moment that the reflex-contractions appear. This column contains therefore the quotient of WEBER.

Let us now consider in how far this experiment satisfies the conditions put by the formula. The researches of ECKHARD, KOSCHEWNIKOFF, C. MEYER and SHERRINGTON have proved, that the same spinal segments which innervate the skin of the hind leg, supply also the muscles of the leg with nerves. If we have cut the spinal cord at the upper end and have therefore annulled the influence of the higher centra, we have in the hind leg a segmental primary reflex-apparatus. The receptive organs of this reflex-apparatus lay in the skin, while the muscle forms the transformer. Adopting the simple law of distribution, I record only the mechanical effect. In this respect the experiment fulfils the required conditions.

The interpretation of the mechanical effect is very difficult as the new state of equilibrium is not reached at once, but only after oscillating round this new state. It is therefore hard to say what part of the total effect must be considered as the quantity ΔE of the formula. Fig. I is the reproduction of a typical tracing. After the reflex-apparatus is in perfect rest, the tap of the burette is opened at the moment indicated in the curve by a couple of vertical small lines on the base line and oxalic acid is slowly added under continuous stirring. At the moment that the first contraction appears, the tap of the burette is closed and no more acid is added. At this moment the increase of concentration amounted to 3.2×10^{-5} the initial concentration being 15.9×10^{-5}. The curve represents the mechanical effect, following upon this increase of the concentration of the acid in the vessel. This effect consists of a group of great contractions, followed by some smaller ones of decreasing size. If we should be at first inclined to consider this group of large contractions as the mechanical effect corresponding to the quantity ΔE of the formula, this conception offers many difficulties when the mechanical effect assumes a form as is represented by the curve which is reproduced by fig. II. In consequence of a small increase of concentration we do not see a definite effect appear, not even partly defined, but the reflex-apparatus comes in rythmical contraction. Where in the first case the resistances in the chemical system are such that the oscillations rapidly die away, and the new state is reached after a few oscillations, these resistances in the second case are so small, that once the equilibrium disturbed, the system remains oscillating round its new state of equilibrium. This oscillation documents itself as a rythmical mechanical effect. If the rate of decay of these oscillations is very small, these rythmical

TABLE I. (Fig. V).

No 4. (12. 9. 01.)

Conc.	Δ Conc.	$\frac{\Delta \text{ Conc.}}{\text{Conc.}}$
0.0×10^{-5}		
	10.4×10^{-5}	
10.4		
	2.8	0.218
12.9		
	3.4	0.209
16.3		
	4.0	0.196
20.3		
	4.1	0.167
24.4		
	4.3	0.150
28.7		
	4.9	0.147
33.6		
	4.8	0.123
38.4		
	10.7	0.218
49.1		
	20.8	0.298
69.9		
	10.7	0.133
80.6		

Section of the medulla 10 A.M.
beginning of the experiment 11.15 A.M.
Temp. 13.5 C.

TABLE II. (Fig. VI.)

No 35. (25. 12. 01.)

Conc.	Δ Conc.	$\frac{\Delta \text{ Conc.}}{\text{Conc.}}$
0.0×10^{-5}		
	26.6×10^{-5}	
26.6		
	5.0	0.158
31.6		
	2.9	0.086?
34.5		
	3.2	0.085
37.7		
	2.3	0.058
40.0		
	2.0	0.047
42.0		
	1.6	0.037
43.6		
	2.7	0.059
46.3		
	3.5	0.069
49.8		
	5.4	0.098
55.2		
	10.8	0.164
66.0		
	19.3	0.226
85.3		

Section of the medulla 10.35 A.M.
beginning of the experiment 12.40 P.M
Temp. 13 C.

contractions can last for several hours and often with great regularity [1]). Under these circumstances, however, ΔE is no more a determined quantity and the experiment cannot fulfil the condition of the formula, that ΔE be a constant quantity in the successive determinations. If we only use those experiments, in which the resistances are pretty considerable, and the new state of equilibrium is reached after a few oscillations, ΔE fulfils the condition, that it represents a small quantity in successive determinations. The experiment does not allow another more definite conception of this quantity.

By the addition of acid from the burette to the liquid in which the leg is immerged, the level of the liquid rises, and the stimulated surface increases. So the experiment does not fulfil the condition of the formula in this respect either.

TABLE III.

No 21. (7. 12. 01.)

Conc.	Δ Conc.	$\frac{\Delta \text{ Conc.}}{\text{Conc}}$
0.0×10^{-5}		
	3.6×10^{-5}	
3.6		
	1.7	0.327
5.3		
	1.4	0.203
6.7		
	2.1	0.236
8.8		
	3.6	0.292
12.4		
	6.3	0.339
18.7		
	10.5	0.359
29.2		
	12.4	0.297
41.6		
	8.7	0.173
50.3		
	26.0	0.271
76.3		

Section of the medulla 10.15 A.M.
beginning of the experiment 12.56 P.M.
Temp. 15 C.

TABLE IV. (Fig VII.)

No. 14. (21. 9. 01.)

Conc.	Δ Conc.	$\frac{\Delta \text{ Conc.}}{\text{Conc.}}$
0.0×10^{-5}		
	15.9×10^{-5}	
15.9		
	3.2	0.168
19.1		
	4.5	0.192
23.6		
	7.3	0.235
30.9		
	8.0	0.207
38.9		
	4.3	0.098
43.2		
	3.8	0.082
47.0		
	19.9	0.297
66.9		
	27.6	0.292
94.5		
	16.8	0.151
111.3		
	15.3	0.121
126.6		

Section of the medulla 10 P.M. 20.9.
beginning of the exper. 12.1 P.M. 21.9
Temp. 16.5 C.

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[1]) It seems to me that the heart is in this condition, and it would be worth while to repeat many experiments from the physiology of the heart on this rythmically acting reflex-apparatus.

Similar experiments as described by me, were performed by **Winkler** and **Van Wayenburg** some years before. The method followed by them, which slightly deviated from mine, enabled them to extend the experiment only over a small interval of variation of concentration. They concluded for this small interval, that the reflex-apparatus of the frog follows the law of **Fechner**[1]). In the experiments communicated by them slight deviations from this law proved to occur and it was with the purpose of learning something about these deviations, that I repeated these experiments extended over a greater interval. Table I, II, III and IV represent four of these experiments. If we take R as the value of the stimulus in physical measure (i. e. the concentration of the solution of the acid in which the leg is immerged) and if we take ΔR as the value of the increment of this stimulus which is required to call forth a change in the system, the quotient $\frac{\Delta R}{R}$ is not constant, but in general a function of R.

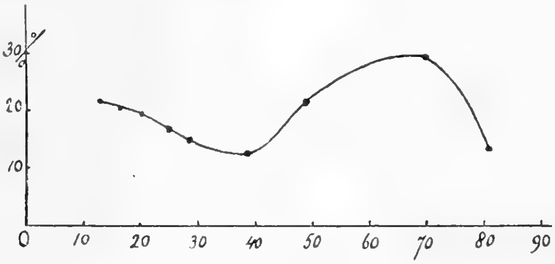

Fig. V (table I, exper. 4).

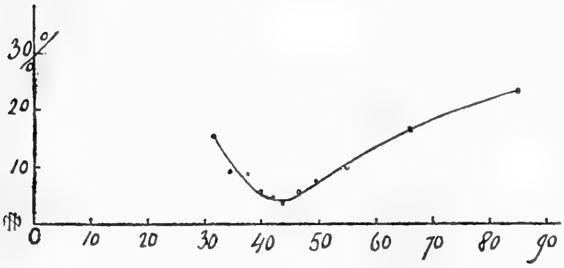

Fig. VI (table II, exper. 35).

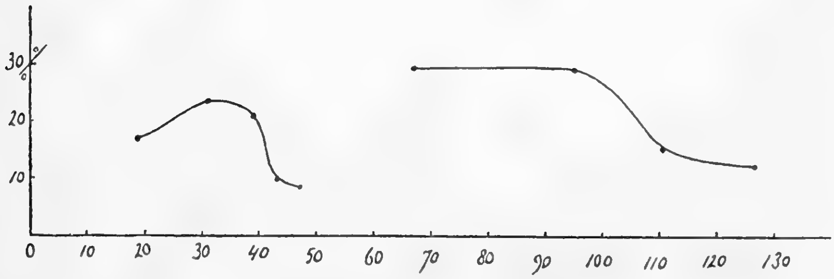

Fig. VII (table IV, exper. 14).

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[1]) **Van Wayenburg**, Dissertation 1897. pag. 117.

Fig. V, VI, and VII are the graphical representation of Table I, II and IV. In this graphical representation I have considered the amount of water as constant (10^5 unities of weight) and put as abscissae the number of solved unities of weight of the acid. The relative increases of the concentration, in percents, have been chosen as ordinates. The points, representing successive determinations, are connected by a curve. The graphical representation of the result of the experiment by a continuous curve is only an approximation, remaining in the same course of thoughts as that, which has led us to represent the phenomenon analytically by a continuous function.

If the law of FECHNER was satisfied, the line representing graphically the quotient $\frac{\Delta R}{R}$ as function of R, would be a straight one. But instead the experiment furnishes a curved line. In order to elucidate the form of this curve further, fig. V is given, which is the graphical representation of an experiment, where the first descending branch is determined by as large a number of observations as is possible. Fig. VI shows a reduction in the extent of the first descending branch and this enables us to determine the ascending branch by a greater number of observations. In the experiment represented by fig. VII this reduction of the first descending branch is so considerable, that it no more appears in the experiment; this makes it possible to determine the top of the ascending branch and the descending branch following on it. The whole course of the second descending branch cannot be given, as always a discontinuity occurs at a point which seems to be near a second minimum. After this discontinuity a new period sets in, and as far as it is possible to follow this new period, it appears to be considerably greater, whereas the oscillation which the value of the quotient $\frac{\Delta R}{R}$ shows in this period, seems to be relatively smaller. For a skin-muscle reflex-apparatus the quotient $\frac{\Delta R}{R}$ must therefore be considered as a periodic function of R. If we inquire what is the signification of this discontinuity, it seems that only those variables, which are the representation of the independently variable components of the chemical system, can be able to show discontinuities. This brings about a change in the nature of the system and this must be attended by a discontinuous variation of the quantity R, which occurs in formula I of the second communication. The experiment communicated by MASSART [1]) seems

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[1]) Bull. Acad. royale de Belgique 3me Série, T. 16, 1888, pag. 590.

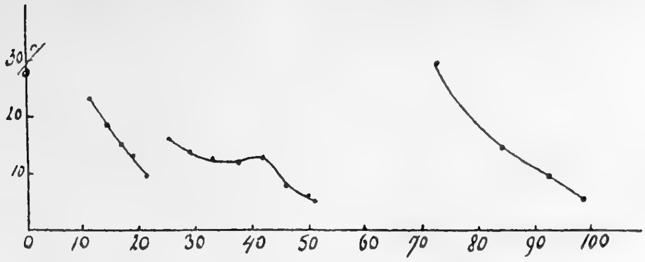

Fig. VIII (table V, exper. 25).

TABLE V. (Fig. VIII.)

No. 25. (11. 12. 01.)

Conc.	Δ Conc.	Δ Conc. / Conc.
0.0×10^{-5}		
	8.8×10^{-5}	
8.8		
	2.7	0.232
11.5		
	2.7	0.187
14.2		
	2.6	0.156
16.8		
	2.4	0.129
19.2		
	2.0	0.093
21.2		
	4.0	0.160
25.2		
	4.0	0.136
29.2		
	4.1	0.123
33.3		
	4.5	0.120
37.8		
	4.3	0.123
42.1		
	3.8	0.079
45.9		
	3.0	0.061
48.9		
	2.5	0.050
51.4		
	21.0	0.289
72.4		
	11.8	0.141
84.2		
	9.1	0.097
93.3		
	5.0	0.051
98.3		

Section of the medulla 8.30 A.M.
beginning of the experiment 12.5 P.M.
Temp. 13 C.

to show the same phenomenon. Another phenomenon, which sometimes occurred in my experiments, was the dividing of a period into several parts. Fig. VIII (table V) is the graphical representation of such an experiment.

As far as my experiments go, this small discontinuity can appear at every moment in a given period, followed by the outset of a new period.

If we compare these results obtained by the primary reflex-apparatus with those of experimental psychology, they appear to concord in many points. As appears from the critical summary of FOUCAULT [1]) also there a variable quantity showing a minimum is found for the quotient $\frac{\Delta R}{R}$ in most cases. The shape of the curve representing the quotient $\frac{\Delta R}{R}$ as function of R, makes us suppose, that the experimental psychology has seen only part of a large period. By the dividing of a period into several parts, the quotient $\frac{\Delta R}{R}$ seems to show multiple minima and this occurs also in some experiments of the experimental psychology. Hence there is agreement in these respects between the results of the psychological and the physiological experiment.

With regard to the mechanical effect I have pointed out, that this is greatly dependent on the rate of decay of the oscillations of the system. The rapidity of this decay is determined by the passive resistances in the chemical system. If these passive resistances are slight, a small increase of R will be sufficient to call forth a change in the system. Therefore the value of the quotient $\frac{\Delta R}{R}$, which is a measure of the value of these passive resistances, will determine the rapidity of the decay of these oscillations.

In correspondence with this the experiment shows that the height and the number of the elevations in every successive determination increases with decrease of the value of the quotient $\frac{\Delta R}{R}$. Fig. III (table II) observation 2, 3, 4, 5 shows this clearly. At the 5th observation the resistances are so slight, that the system continues to oscillate for several seconds. Observation 8 and 10 show this same phenomenon at a higher value of R, in the same series of observations. If we compare, however, observation 8 with observation 5, in which two observations the value of the quotient $\frac{\Delta R}{R}$ is almost the same, and

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[1]) M. FOUCAULT. La psychophysique, 1901.

also observation 10 with observations 3 and 4, it appears, that in the second place the rate of decay is dependent on the absolute value of R. Supported by these and more similar observations we may say that the rapidity of the decay of the oscillations increases with increasing value of R and with increasing value of the quotient $\frac{\Delta R}{R}$.

In this we have to keep in view, that the first observation always occupies a special place; for this observation ΔR is always very large, and though the method followed does not enable us to determine the quotient $\frac{\Delta R}{R}$ for this observation, this quotient is probably also very great. Notwithstanding this we always see that the rate of decay is very slight and from this we should have to conclude, that the influence of the absolute value of R on the rapidity of this decay is preponderant in the beginning.

The same experiments which I have described for the frog whose spinal cord is cut through, can also be performed with perfectly intact frogs. For this it is necessary to wrap up the whole animal carefully in wads with exception of the hind leg which is used for the experiment. If we take care to avoid tactile and auditory stimuli, the frog remains quiet during the experiment also under these circumstances [1]). In this case the result of the experiment is the same as that of the preceding one.

Fig. IX (table VI) is the graphical representation of an experiment,

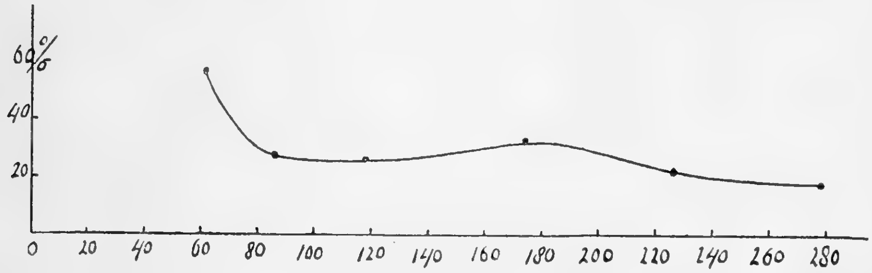

Fig. IX (Table VI, exper. 46).

If the first period is small, it is possible to see also here a part of a second period appear (Fig. X, table VII). This second period seems also greater than the first, while the oscillation, which the value of the quotient $\frac{\Delta R}{R}$ shows in this period, seems relatively to be smaller.

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[1]) In these experiments the solution of acid in the burette contained 80 grams of oxalic acid per liter solution.

TABLE VI. (Fig. IX.)

No. 46. (18. 1. 02.)

Conc.	Δ Conc.	Δ Conc. / Conc.
0.0×10^{-5}		
	26.9×10^{-5}	
26.9		
	34.6	0.562
61.5		
	24.1	0.282
85.6		
	32.1	0.273
117.7		
	55.9	0.322
173.6		
	52.3	0.231
225.9		
	52.2	0.187
278.1		

Medulla intact. Beginning of the experiment 11.46 A.M Temp. 13.5 C.

TABLE VII. (Fig. X.)

No 50. (26. 1. 02.)

Conc.	Δ Conc.	Δ Conc. / Conc.
0.0×10^{-5}		
	29.3×10^{-5}	
29.3		
	44.9	0.605
74.2		
	22.6	0.234
96.8		
	39.0	0.546
135.8		
	35.2	0.206
171.0		
	24.4	0.125
195.4		
	53.0	0.213
248.4		
	71.6	0.224
320.0		
	55.4	0.148
375.4		
	38.5	0.093
413.9		

Medulla intact. Beginning of the experiment 3.0 P.M. Temp. 11.5 C.

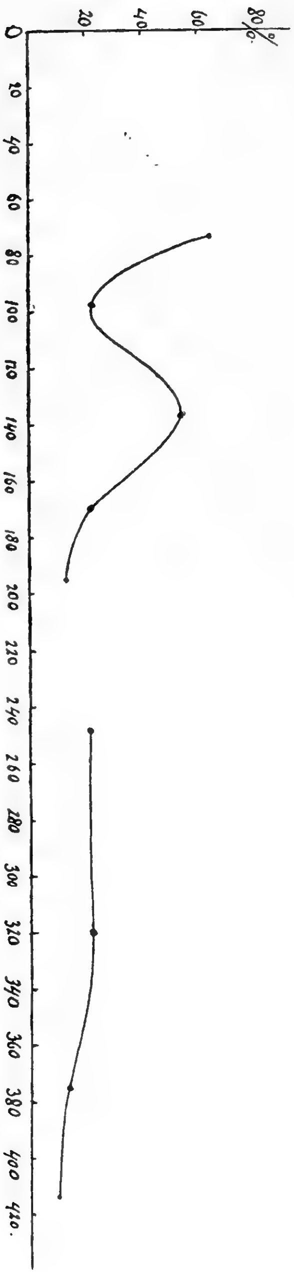

Fig. X (table VII exper. 50).

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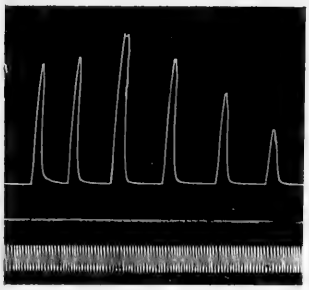


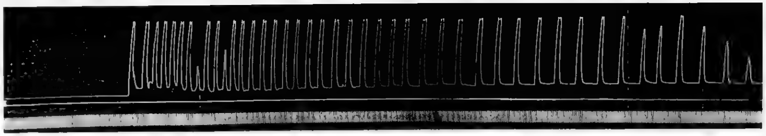
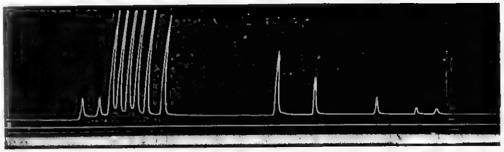


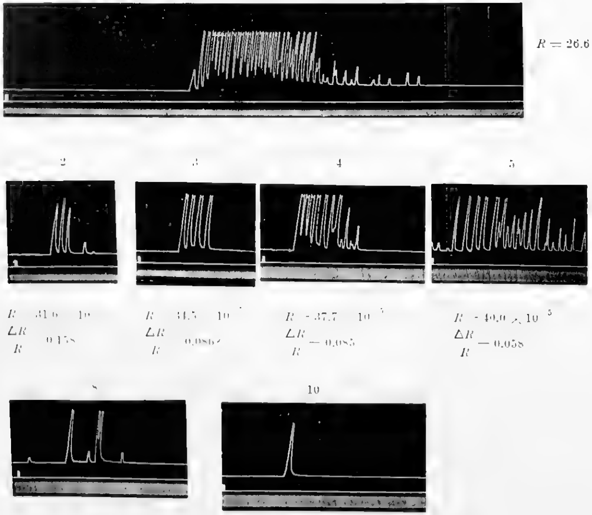
Fig. II. (Exp. N°. 24.) Tuningfork 2 vibrations per second



$\frac{\Delta R}{R} = 0.168$

$R = 19.1 \cdot 10^{-5}$

Fig. I. (Exp. N°. 14.) Tuningfork 2 vibrations per second



1

$R = 26.6 \cdot 10^{-5}$

2

$R = 31.6 \cdot 10^{-5}$
$\frac{\Delta R}{R} = 0.158$

3

$R = 34.5 \cdot 10^{-5}$
$\frac{\Delta R}{R} = 0.0867$

4

$R = 37.7 \cdot 10^{-5}$
$\frac{\Delta R}{R} = 0.085$

5

$R = 40.0 \times 10^{-5}$
$\frac{\Delta R}{R} = 0.058$

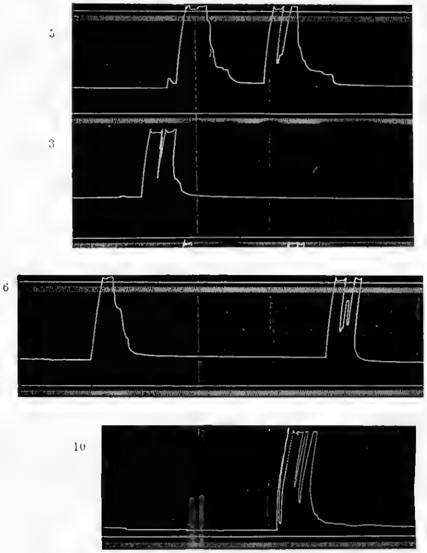
8

$R = 46.3 \times 10^{-5}$
$\frac{\Delta R}{R} = 0.059$

10

$R = 55.2 \times 10^{-5}$
$\frac{\Delta R}{R} = 0.098$

Fig. III. (Exp. N°. 35.) Tuningfork 2 vibrations per second



5

$R = 171 \cdot 10^{-5}$
$\frac{\Delta R}{R} = 0.206$

3

$R = 96.8 \cdot 10^{-5}$
$\frac{\Delta R}{R} = 0.234$

6

$R = 195.4 \cdot 10^{-5}$
$\frac{\Delta R}{R} = 0.125$

10

$R = 413.9 \cdot 10^{-5}$
$\frac{\Delta R}{R} = 0.093$

Fig. IV. (Exp. N°. 50.) Tuningfork 2 vibrations per second

The number of my experiments in which a second period appears, is, however, not great. Therefore we may say also in this case, that the quotient $\frac{\Delta R}{R}$ is probably to be considered as a periodical function of R. The value of the quotient $\frac{\Delta R}{R}$, however, is in these experiments considerably greater than in the preceding experiments, while in concordance with this the rapidity of the decay of the oscillations of the system is also greater.

Figure IV (table VII) which is the reproduction of four observations from the same series, shows this clearly ; the new state of equilibrium is reached after a few oscillations. If we compare observation 3, 5 and 6, the system proves to be a periodical one, at the third observation ; at observation 5 and 6 the rapidity of the decay decreases with decreasing value of the quotient $\frac{\Delta R}{R}$. At the tenth observation, where the quotient $\frac{\Delta R}{R}$ shows a very low value, the rapidity of the decay is very small notwithstanding the high value of R. If we summarize these differences briefly, we conclude that in consequence of the high section of the spinal cord, the passive resistances in the chemical system of the skin-muscle reflex-apparatus considerably decrease. On account of clinical observation chiefly regarding the plantar-reflex, it seems to me, that we have to deal here with a very general phenomenon occurring always where there is a wasting of systems. In this case the rapidity of the decay of the oscillations of the system is very small in consequence of the decrease of the passive resistances in the chemical system. It is obvious that a good motor function can only exist, when the rapidity of the decay is so great, that the system is almost aperiodic. The motor disturbances, which occur in multiple sclérosis, in locomotor ataxy and many other diseases of the nervous system seems to be partly due to the decreasing resistances in the chemical system of the reflex arc.

If the system is perfectly aperiodic, then the quantity ΔE is a perfectly determined quantity. This condition must also be fulfilled by the systems, to which the experimental psychology extends its experiments; if this condition is not satisfied, then the effect is a not determined quantity as in the physiological experiment.

Astronomy. — "*On the yearly periodicity of the rates of the Standard-clock of the observatory at Leiden,* Hohwü Nr 17." First part. By Dr. E. F. van de Sande Bakhuyzen.

I. *Introduction.*

1. When the observatory at Leiden was founded in 1861, it was fitted with a clock made by Mr. A. Hohwü of Amsterdam, and by him designated as Nr 17. Accurate investigations of Kaiser [1] soon showed the great regularity of its rate, in which point it was superior to all clocks about which an investigation had so far been published. Since that time it has continually been used as the standard-clock of the observatory and at the present moment its rate is still eminently satisfactory.

The clock was originally mounted in the transit-room of the observatory on a brick pier which rests on the foundations of the meridian-circle. The stability of the mounting thus left nothing to be desired. On the other hand the temperature at this place was rather variable, showing very clearly a daily period; moreover entirely irregular changes of temperature were often caused by the opening and closing of the shutters.

From 1861 the clock has been going regularly until 1874, without being touched during this time except for the purpose of winding once a week. On the 17th of June of the latter year however it stopped spontaneously, after having shown for about a month a particular irregularity.

As the intention existed already to make considerable changes as well in the transit-room as in the meridian-circle, it was thought best to defer a thorough cleaning and overhauling of the clock till the time of these alterations. Accordingly the clock was then only provisorily cleaned, and was set going again after a few days.

The intended alterations were made in the second half of 1876 and the beginning of 1877, and in June of that year everything was again in working order, and also the clock Hohwü 17 was mounted again.

Though Prof. H. G. van de Sande Bakhuyzen did consider the possibility of removing it to a better position, out of the transit-room,

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[1] F. Kaiser, Onderzoekingen omtrent den gang van het hoofduurwerk der sterrenwacht te Leiden, de pendule Hohwü N0. 17. *Versl. en Meded. K. Akad. Amsterdam D. XVII, 1865.*

F. Kaiser, Untersuchungen über den Gang der Hauptuhr der Sternwarte in Leiden, Hohwü N0. 17. *Astr. Nachr.* N0. 1502.

this gave rise to too many difficulties at the time, and it was only tried to diminish the variations of temperature by making a second wooden case round the clock. [1]

In the meantime the chronographic method had been generally adopted at the observatory for the meridian observations. Now it had been shown repeatedly that the introduction of an electrical contact in a clock diminishes the regularity of its rate, and on the other hand we had found that the comparison of two clocks could be effected with extreme accuracy by means of signals given by hand [2]. Accordingly the clock HOHWÜ was not connected with the chronograph, but the clock by KNOBLICH was used for this purpose.

On the 26th of November 1877 the clock was stopped for a short time in order more completely to adjust its beats; since that date however it has been going uninterruptedly until August 1898. At that time the clock was again dismounted at the occasion offered by alterations in the transit-room, and cleaned and overhauled by Mr. HOHWÜ,

In December 1898 the clock was remounted, and this time the former plan of removing it from the transit-room was carried out, and it was fixed to the pier of the 10 inch refractor. In order better to secure a constant temperature, Prof. H. G. VAN DE SANDE BAKHUYZEN resolved to have a niche cut out from this pier in the large hall of the observatory, and to place the clock in this niche.

The clock HOHWÜ N° 17 has now been in its new place for over three years. It is still enclosed in two wooden cases, and the niche itself is closed by a glass door. We may remark already at this place that by this arrangement the aim of excluding rapid variations of temperature has been attained in a very perfect manner.

2. In 1887 Mr. WILTERDINK investigated for a special purpose the rate of the clock HOHWÜ 17 during the period 1886 January to 1887 July. It then appeared that after reduction for temperature and barometer the mean rates for the summer- and the winter-half-years were in very satisfactory agreement, while on the other

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[1] At the same time a small mirror was attached to the pendulum-bob, to permit more accurate determinations of the amplitude of oscillation. See: H. G. VAN DE SANDE BAKHUYZEN, *Verslag van den staat der sterrenwacht te Leiden* 1876—1877, page 12.

[2] From series of signals given by the two observers WILTERDINK and E. F. VAN DE SANDE BAKHUYZEN immediately after each other, on a great number of days, the Mean Error of the result of a series of about 24 signals, (including the variation of the constant error during an interval of about a month) is found to be ± $0^s.0077$.

hand a very marked systematic difference existed between the means for the half-years January—June and July—December.

Mr. **Wilterdink** found

		Obs.—Comp.
1886	January—June	+ $0^{s}.045$
	July—December	— 0 .03
1887	January—June	+ 0 .035.

Consequently, when in 1890 I undertook the definitive discussion of the time-determinations and clock-rates for the period 1877—1882, it appeared desirable to me to investigate whether a similar phenomenon would again show itself. I then found that the years 1878—1882 (before May 1878 the rate was not yet sufficiently regular) were in this respect entirely similar to 1886—87, and, investigating the phenomenon more closely, I moreover found that the rates, after correction for temperature, still showed a yearly periodicity which accordingly had its maxima in the months of equal temperatures April and October and the amplitude of which was about $0^{s}.10$.

I then continued my investigation (the results of which were briefly published in the "*Verslag van den staat der sterrenwacht te Leiden* 1889—1890," pages 14—15) in the same direction and included on the one side the years 1882—90, using provisional results of the time-determinations, and on the other side the years 1862—1864, using the results of **Kaiser**'s investigation in *Astr. Nachr.* 1502. For these two periods I also found the same unexplained inequality.

After 1890 this investigation was abandoned for the time being, and it was only taken up again last year. In the mean time the clock had been removed to its new position, and it now appeared that, notwithstanding the fact that the changes of temperature had become much more gradual, still the yearly periodicity of the rate showed itself in the same way as before, and its deviation from the yearly periodicity of the temperature was certainly not less evident [1]).

It became thus evident that there was no question of accidental circumstances, which could be altered by cleaning the clock, nor of such conditions as depend on the special nature of the changes of temperature to which the clock is subjected, but that the cause of the phenomenon must lie deeper.

It therefore appeared desirable to subject the way in which it showed itself in the three periods (*viz:* before and after the cleaning

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[1]) See also „Verslag van den staat der sterrenwacht te Leiden 1898—1900 pages 12—13.

of 1877, and after the cleaning and removal of 1898) to a new investigation which had to embrace the whole of these periods. The results of this investigation are given in the present paper.

I have confined myself to such results as could be derived from the mean daily rates during periods of about a month. Thus it was not necessary that the time-determinations on which the investigation is based were discussed with the utmost accuracy. In this way I investigated successively the three periods, 1877—1898, 1862—1874 and 1899—1902. The results for these three periods will be communicated in this order. Then the observed amplitudes of the period 1877—1898 will be investigated, so far as their yearly periodicity is concerned, and finally the several results will be compared with each other.

As a consequence of the restriction of the investigation to the monthly means, the question is considered from one point of view only. In the mean time however Mr. **Weeder** has definitively discussed all the time-determinations from 1882—1898, and has undertaken investigations about the rates of the clock during shorter periods. It is to be expected that, when these investigations will be completed, the comparison of his results with mine will also throw more light on the phenomenon which is here treated.

Very recently, while my investigation was already nearly completed, I had occasion more closely to study the computations which **Kaiser** made about the clock **Hohwü** 17 during the last years of his life, and which are preserved in manuscript at the observatory. I then found that as early as 1870 his attention had been drawn to this particular yearly inequality as to a remarkable phenomenon. Among the papers I found a summary of monthly means of rates, corrected for barometer and temperature, from which mean results had been formed by combining the corresponding months of the years 1862—1870. These means show clearly a periodicity having its maxima in May and October, and a total amplitude of $0^{s}.09$. Further I found means for the half-years February—July and August—January for each of the years 1863 to 1870. The differences between the two half-years vary between $+ 0.^{s}026$ and $+ 0.^{s}048$ and **Kaiser** adds the remark that the only difference between the two half-years is that in one of them the temperature is, in the mean, rising, while in the other it is falling.

II. *The period* 1877—1898.

3. The clock-rates which were taken as the basis of the investigation were, for the period 1877—March 1882, derived from the

definitive discussion of the time-determinations during that period. For the following years they were taken from the provisional results which had been computed immediately after the observations, Mr. Weeder's results being not yet completed last year. I only applied small corrections in a few cases for the personal differences between the observers, which have become better known since the provisional computations were made. I always used time-determinations as near as possible to the beginning of each month.

The mean temperatures and barometerreadings required for the investigation were derived in the following way.

The temperature was read on two thermometers suspended in the clock-case, one at the level of the upper part of the pendulum rod the other at the level of the pendulum bob. These thermometers were read five times a day viz. at 8 a.m., noon, 4 p.m., 8 p.m. and midnight. The scales were Reaumur's and were divided into full degrees.

We will first investigate the relation between the results given by the two thermometers. The readings of the years 1878, 1879, 1884 and 1885 were discussed for this purpose. In the following table the monthly means of the differences between the two thermometers are given for each of these four years, after application of the index-corrections. The differences are taken in the sense upper thermometer-lower thermometer. The last column gives the means of the four years.

	1878	1879	1884	1885	Mean
January	+ 0.16	+ 0.12	+ 0.19	+ 0.16	+ 0.16
February ...	+ 0.18	+ 0.16	+ 0.19	+ 0.21	+ 0.18
March	+ 0.20	+ 0.21	+ 0.22	+ 0.20	+ 0.21
April	+ 0.33	+ 0.25	+ 0.24	+ 0.27	+ 0.27
May	+ 0.28	+ 0.29	+ 0.27	+ 0.24	+ 0.27
June........	+ 0.29	+ 0.26	+ 0.26	+ 0.29	+ 0.28
July.... ...	+ 0.26	+ 0.24	+ 0.25	+ 0.28	+ 0.26
August	+ 0.22	+ 0.22	+ 0.27	+ 0.25	+ 0.24
September ..	+ 0.21	+ 0.20	+ 0.22	+ 0.22	+ 0.21
October.....	+ 0.18	+ 0.19	+ 0.20	+ 0.19	+ 0.19
November...	+ 0.16	+ 0.18	+ 0.20	+ 0.18	+ 0.18
December...	+ 0.13	+ 0.18	+ 0.18	+ 0.17	+ 0.16

There appears to be a constant difference of about + 0°.2 between the two temperatures. There also seems to be a small yearly inequality. We will return later on to these small differences between the separate months, and investigate the influence which they can have had on the rate of the clock, *if they are real.*

For the rest of the investigation the readings of the upper thermometer were used exclusively. I first formed daily means [1]) — the day being reckoned from midnight to midnight — and then means for the periods of about one month. The index-correction, which may be taken constant and equal to — 0°.6 for the whole period, was not applied.

Until May 1886 the heights of the barometer were read and reduced in exactly the same way as the temperatures. The readings were made on a mercurial barometer which was suspended in the transit-room from the same pier which also carried the clock. After that time a barograph of RICHARD was used, which was placed on the top of this same pier. Its corrections were determined by comparison with the mercurial barometer [2]). The daily means were then derived by integration by means of a planimeter of AMSLER.

During the period in question three different cistern barometers were used; in consequence of cleaning and refilling we must however distinguish 7 periods. The corrections for these 7 periods were determined by intercomparisons, by comparisons with simultaneous readings of the barometer of the Meteorological Institute at Utrecht, and finally by comparisons with a "Cistern-syphon" barometer by FUESS, which in 1890 was provided for the observatory, to be used as a Standard barometer. Since however before 1890 no correction had been applied and the neglected corrections amounted to approximately + 0.3 mm. during the whole period, the readings after 1890 were reduced to: Normal barometer — 0.3 mm.

The barometer-readings were not reduced to 0°. This reduction was omitted on purpose, though the errors introduced thereby are by no means negligible (at 760^{mm} the effect of 1° RÉAUM. is 0.15^{mm}). The influence of these errors on the rate of the clock is however nearly completely compensated by the fact that also the influence of the temperature on the rate, which is thus found, differs from the true one. It is here supposed that the temperatures of the barometer has always been equal to that of the pendulum, which condition is

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[1]) The mean was taken of the readings at 12^{h}, 20^{h}, 4^{h}, 12^{h}, giving half weight to the extreme values.

[2]) A constant correction was taken for each weekly barograph sheet derived from one or two readings of the mercurial barometer daily.

nearly fulfilled in the present case [1]). The only thing that is thus neglected is the difference between the influence of the same temperature on high and on low barometer-readings, which is extremely small.

4. The observed rates were first reduced to 760^{mm} and $+10°$ R. by means of previously determined values of the coefficients b and c in the formula:

$$\text{Daily Rate} = a + b\,(h - 760) + c\,(t - 10°)$$

$$b = +0^s.0140$$
$$c = -0\ .0268$$

The value of b was derived from a rigorous discussion of the period 1877—1882, in which only rates observed under high and low barometric pressure during the same month were compared. This value must be very near to the truth. In all investigations, not only about Hohwü 17, but also about other clocks with similar, or even with different forms of pendulum, barometer-coefficients have always been found of nearly the same amount, and it is not probable that its value would vary with the time for one and the same clock.

The value $b = +0^s.0140$ has therefore been considered definitive, and I have not attempted to improve it.

The following table gives, for each month from 1877 December to 1898 July, the mean observed daily rate, the mean height of the barometer and the mean temperature, and, in the column headed „Red^d. D. R. I.", the daily rates reduced to 760^{mm} and $+10°$ R by the formula given above. The meaning of the two last columns can only be explained later.

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[1]) See also the particulars given in connection with the investigation of the period 1862—1874.

	Obs^{d} D. R.	Bar.	Temp.	Red^{d} D. R. I	Red^{d} D. R. II	O.—C.
1877 Dec.	$+\,0\overset{s}{.}144$	760.7	+ 4.4	$-\,0\overset{s}{.}016$		
1878 Jan.	0.241	66.8	3.9	— 0.016		
Febr.	0.191	67.7	6.1	— 0.020		
March	0.163	59.4	4.9	+ 0.034		
April	0.148	59.5	8.6	0.118		
May	0.106	58.9	11.2	0.152		
June	0.135	62.0	13.7	0.206		
July	0.100	63.4	14.7	0.179		
Aug.	0.038	58.3	14.6	0.184		
Sept.	0.103	62.5	13.0	0.149		
Oct.	0.043	56.9	9.6	0.077		
Nov.	0.062	53.9	5.4	0.025	$+\,0\overset{s}{.}112$	+ 8
Dec.	0.151	54.4	2.5	0.030	097	— 13
1879 Jan.	0.344	61.6	1.6	0.097	144	+ 28
Febr.	0.145	50.9	2.8	0.079	106	— 16
March	0.326	62.2	4.1	0.137	149	+ 21
April	0.151	53.6	6.3	0.144	146	+ 12
May	0.241	62.6	8.3	0.161	161	+ 20
June	0.084	59.5	12.8	0.165	163	+ 16
July	0.024	58.1	13.1	0.133	145	— 8
Aug.	0.039	61.3	14.0	0.127	158	— 1
Sept.	0.061	62.6	12.3	0.088	153	— 12
Oct.	0.139	65.2	9.1	0.042	141	— 30
Nov.	0.301	64.7	+ 4.6	0.092	181	+ 4
Dec.	0.598	69.3	— 0.3	[0.191]		
1880 Jan.	0.529	71.5	+ 1.7	[0.145]	179	— 10
Febr.	0.203	56.6	4.5	0.102	126	— 70
March	0.321	65.6	6.2	0.141	148	— 54
April	0.214	60.8	8.4	0.158	156	— 52
May	0.245	64.1	9.8	0.183	180	— 34
June	0.078	60.2	12.8	0.149	147	— 73
July	0.070	61.0	14.1	0.167	177	— 48

	Obs^d D. R.	Bar.	Temp.	Red^d D. R. I	Red^d D. R. II	O.—C.
1880 Aug.	$+\overset{s}{0}.111$	763.3	+ 15.4	$+\overset{s}{0}.208$	$+\overset{s}{0}.236$	+ 6
Sept.	0.080	62.0	13.8	0.152	214	— 21
Oct.	0.171	60.0	9.1	0.147	246	+ 7
Nov.	0.314	61.2	5.7	0.183	269	+ 27
Dec.	0.279	58.7	5.9	0.189	249	+ 6
1881 Jan.	0.471	58.7	0.4	[0.233]	244	0
Febr.	0.333	58.2	3.1	0.174	201	— 43
March	0.375	59.2	5.1	0.255	265	+ 21
April	0.361	61.1	6.8	0.258	259	+ 16
May	0.306	65.5	10.4	0.239	229	— 13
June	0.226	62.6	12.3	0.250	238	— 2
July	0.180	63.7	15.0	0.264	252	+ 15
Aug.	0.073	58.0	13.4	0.191	209	— 26
Sept.	0.128	62.2	12.0	0.152	208	— 24
Oct.	0.217	61.8	7.4	0.124	231	+ 2
Nov.	0.272	63.0	7.3	0.158	245	+ 19
Dec.	0.322	62.7	4.6	0.140	215	— 8
1882 Jan.	0.479	71.0	4.2	0.170	225	+ 5
Febr.	0.499	71.0	3.5	0.171	213	— 4
March	0.352	64.5	7.0	0.208	219	+ 5
April	0.189	57.7	8.1	0.171	171	— 40
May	0.250	64.6	11.3	0.221	206	— 1
June	0.135	60.7	12.5	0.192	179	— 25
July	0.113	60.9	13.9	0.205	199	— 2
Aug.	0.086	59.7	13.6	0.187	204	+ 7
Sept.	0.105	59.8	12.0	0.162	218	+ 24
Oct.	0.087	59.1	9.3	0.081	178	— 13
Nov.	0.113	54.1	6.1	0.091	185	— 2
Dec.	0.156	54.0	4.3	0.087	164	— 20
1883 Jan.	0.309	60.9	3.5	0.122	181	0
Febr.	0.361	66.4	5.2	0.142	175	— 3
March	0.349	59.8	3.3	0.172	202	+ 27

	$\mathrm{Obs^d}$ D. R.	Bar.	Temp.	$\mathrm{Red^d}$ D. R. I	$\mathrm{Red^d}$ D. R. II	O.—C.
1883 April	$+\,0\overset{s}{.}301$	761.4	+ 7.7	$+\,0\overset{s}{.}223$	$+\,0\overset{s}{.}225$	+ 53
May	0.203	62.4	11.0	0.196	183	+ 15
June	0.134	62.6	13.0	0.178	163	— 2
July	0.053	59.2	13.9	0.169	163	+ 1
Aug.	0.107	63.8	13.9	0.159	174	+ 16
Sept.	0.020	59.5	12.7	0.099	151	— 4
Oct.	0.050	60.0	9.8	0.045	139	— 13
Nov.	0.078	59.0	7.3	0.020	107	— 41
Dec.	0.254	64.2	4.9	0.058	132	— 13
1884 Jan.	0.212	63.1	5.9	0.058	105	— 37
Febr.	0.242	62.1	5.0	0.078	112	— 28
March	0.221	61.0	6.6	0.116	129	— 9
April	0.182	57.3	7.5	0.153	156	+ 18
May	0.205	64.0	11.2	0.181	172	+ 32
June	0.150	63.9	12.1	0.151	147	+ 3
July	0.052	62.7	15.6	0.164	164	+ 15
Aug.	0.087	64.3	15.7	0.179	199	+ 44
Sept.	0.078	63.6	13.8	0.130	187	+ 27
Oct.	0.104	62.4	10.1	0.073	169	+ 4
Nov.	0.323	65.9	5.7	0.125	214	+ 44
Dec.	0.272	59.0	4.4	0.136	203	+ 28
1885 Jan.	0.403	58.8	1.4	[0.190]	212	+ 32
Febr.	0.262	57.2	5.6	0.183	208	+ 23
March	0.399	63.6	4.8	0.210	224	+ 34
April	0.201	56.5	8.7	0.215	212	+ 17
May	0.148	58.1	9.2	0.154	153	— 47
June	0.151	63.6	13.2	0.187	194	— 11
July	0.191	67.7	14.5	0.204	225	+ 15
Aug.	0.117	61.9	12.9	0.168	210	— 4
Sept.	0.097	60.3	11.7	0.138	211	— 8
Oct.	0.031	54.2	8.8	0.080	180	— 43
Nov.	0.305	60.5	4.8	0.159	239	+ 11

	Obs^d D. R.	Bar.	Temp.	Red^d D. R. I	Red^d D. R. II	O.—C.
1885 Dec.	$+\,0\overset{s}{.}422$	765.1	+ 4.3	$+\,0\overset{s}{.}197$	$+\,0\overset{s}{.}251$	+ 19
1886 Jan.	0.313	51.6	2.3	0.225	257	+ 21
Febr.	0.505	63.4	1.5	0.229	244	+ 5
March	0.451	63.6	5.0	0.267	269	+ 26
April	0.353	61.7	7.4	0.259	256	+ 10
May	0.250	61.3	11.4	0.269	268	+ 18
June	0.207	61.6	12.2	0.244	251	— 2
July	0.123	61.4	14.4	0.221	242	— 14
Aug.	0.123	63.0	14.4	0.199	241	— 19
Sept.	0.126	64.1	14.1	0.178	251	— 12
Oct.	0.117	59.1	9.9	0.127	227	— 39
Nov.	0.197	59.0	7.3	0.139	219	— 50
Dec.	0.236	52.1	3.7	[0.178]	215	— 57
1887 Jan.	0.492	63.3	1.4	[0.215]	247	— 27
Febr.	0.595	70.4	2.9	0.259	287	+ 11
March	0.437	62.1	3.8	0.241	257	— 21
April	0.394	62.2	6.6	0.272	281	+ 1
May	0.257	61.3	9.7	0.230	239	— 43
June	0.296	69.0	13.1	0.253	269	— 15
July	0.200	64.4	15.0	0.272	300	+ 14
Aug.	0.195	62.4	14.0	0.268	310	+ 22
Sept.	0.181	61.7	12.3	0.219	273	— 16
Oct.	0.307	61.4	8.0	0.233	294	+ 5
Nov.	0.304	56.4	5.5	0.233	294	+ 4
Dec.	0.384	55.9	3.5	0.268	322	+ 32
1888 Jan.	0.583	67.6	2.3	[0.271]	305	+ 15
Febr.	0.530	59.3	1.3	[0.307]	292	+ 2
March	0.325	50.9	3.3	0.273	289	— 1
April	0.391	59.2	6.6	0.311	320	+ 30
May	0.384	64.9	10.2	0.320	329	+ 39
June	0.188	60.0	13.4	0.279	295	+ 5
July	0.115	57.8	13.0	0.226	254	— 36

	Obs^d D. R.	Bar.	Temp.	Red^d D. R. I	Red^d D. R. II	O. - C.
1888 Aug.	$+0^{s}.188$	763.6	+ 13.1	$+0^{s}.221$	$+0^{s}.263$	— 27
Sept.	0.257	66.2	11.9	0.221	275	— 15
Oct.	0.304	62.6	8.2	0.220	281	— 9
Nov.	0.333	59.4	5.9	0.231	292	+ 2
Dec.	0.415	63.0	4.7	0.231	285	— 5
1889 Jan.	0.544	66.5	2.6	0.255	297	+ 7
Febr.	0.420	57.3	3.1	[0.273]	296	+ 6
March	0.437	60.6	4.4	0.279	295	+ 5
April	0.270	56.0	7.6	0.262	271	— 19
May	0.204	59.7	13.0	0.289	298	+ 8
June	0.216	64.1	15.0	0.292	308	+ 18
July	0.150	60.3	14.0	0.252	280	— 10
Aug.	0.133	59.3	13.6	0.239	281	— 9
Sept.	0.232	63.1	12.2	0.247	301	+ 11
Oct.	0.181	55.7	8.8	0.210	271	— 19
Nov.	0.408	66.9	6.4	0.215	276	— 14
Dec.	0.518	66.1	2.9	0.242	296	+ 6
1890 Jan.	0.420	60.9	4.3	0.254	296	+ 6
Febr.	0.589	67.4	2.6	0.287	315	+ 25
March	0.324	57.1	6.1	0.260	276	— 14
April	0.282	55.5	7.2	0.270	279	— 10
May	0.226	58.4	11.4	0.285	294	+ 5
June	0.282	63.6	12.4	0.295	311	+ 23
July	0.199	60.0	13.7	0.299	327	+ 40
Aug.	0.180	61.3	13.5	0.256	298	+ 13
Sept.	0.264	66.8	13.1	0.251	305	+ 22
Oct.	0.283	63.4	9.6	0.225	286	+ 5
Nov.	0.245	57.8	+ 7.1	0.198	259	— 19
Dec.	0.677	63.3	— 0.8	[0.340]		
1891 Jan.	0.711	64.8	— 0.2	[0.368]		
Febr.	0.620	73.2	+ 3.3	0.256	284	+ 15
March	0.320	56.8	4.7	0.223	239	— 28

	Obs^d D. R.	Bar.	Temp.	Red^d D. R. I	Red^d D. R. II	O.—C.
1891 April	$+\,0\overset{s}{.}360$	760.8	+ 5.8	$+\,0\overset{s}{.}236$	$+\,0\overset{s}{.}245$	− 20
May	0.183	57.0	9.6	0.215	224	− 40
June	0.184	63.1	13.1	0.223	239	− 24
July	0.158	62.2	14.3	0.242	270	+ 7
Aug.	0.111	58.0	13.3	0.227	269	+ 7
Sept.	0.125	63.7	13.4	0.164	218	− 44
Oct.	0.136	57.4	10.9	0.198	259	− 3
Nov.	0.356	61.3	5.6	0.220	281	+ 19
Dec.	0.424	62.2	4.2	[0.238]	262	0
1892 Jan.	0.382	57.3	2.6	[0.221]	237	− 25
Febr.	0.326	56.6	3.6	0.202	230	− 32
March	0.466	63.0	3.3	[0.244]	255	− 7
April	0.375	61.3	7.3	0.285	294	+ 32
May	0.296	62.4	9.9	0.261	266	+ 4
June	0.220	62.8	12.7	0.253	254	− 8
July	0.172	63.6	13.7	0.221	231	− 31
Aug.	0.153	62.6	14.6	0.239	259	− 3
Sept.	0.169	62.7	13.0	0.212	250	− 12
Oct.	0.148	55.3	9.2	0.192	251	− 11
Nov.	0.263	62.3	7.7	0.169	234	− 28
Dec.	0.382	61.5	4.2	[0.206]	259	− 3
1893 Jan.	0.568	63.1	0.6	[0.272]		
Febr.	0.313	56.2	4.3	0.214	258	− 4
March	0.391	64.7	6.1	0.221	247	− 15
April	0.428	67.1	9.2	0.307	314	+ 52
May	0.275	64.2	11.7	0.263	261	− 1
June	0.250	63.7	13.5	0.292	290	+ 28
July	0.153	60.7	14.9	0.274	279	+ 17
Aug.	0.168	64.9	15.5	0.248	265	+ 3
Sept.	0.184	59.5	12.6	0.260	300	+ 38
Oct.	0.213	60.1	10.6	0.227	281	+ 19
Nov.	0.333	60.9	5.7	0.204	276	+ 14

	Obs^{d} D. R.	Bar.	Temp.	Red^{d} D. R. I	Red^{d} D. R. II	O.—C.
1893 Dec.	+ 0^{s}.390	762.2	+ 5.0	+ 0^{s}.224	+ 0^{s}.292	+ 30
1894 Jan.	0.459	61.3	2.5	[0.239]	278	+ 16
Febr.	0.431	62.1	4.2	[0.247]	274	+ 12
March	0.348	61.7	6.2	0.223	248	— 14
April	0.263	60.5	9.9	0.253	258	— 4
May	0.293	60.2	10.5	0.302	296	+ 34
June	0.252	62.6	12.0	0.269	258	— 4
July	0.139	60.9	15.0	0.260	237	— 25
Aug.	0.136	61.2	13.8	0.220	221	— 41
Sept.	0.246	64.7	11.9	0.232	260	— 2
Oct.	0.221	60.9	9.3	0.190	246	— 16
Nov.	0.297	63.4	7.5	0.182	253	— 9
Dec.	0.310	60.0	4.7	0.168	254	— 7
1895 Jan.	0.320	54.3	1.8	[0.181]	268	+ 8
Febr.	0.562	61.3	0.0	[0.275]	227	— 32
March	0.247	56.2	4.6	0.156	205	— 53
April	0.250	60.8	8.6	0.201	211	— 45
May	0.296	64.0	11.4	0.270	260	+ 6
June	0.273	64.6	13.6	0.306	282	+ 31
July	0.141	60.2	14.6	0.261	241	— 8
Aug.	0.133	61.1	14.6	0.241	235	— 11
Sept.	0.238	67.4	14.2	0.248	257	+ 14
Oct.	0.190	58.4	9.7	0.203	256	+ 16
Nov.	0.291	61.1	6.9	0.191	267	+ 29
Dec.	0.273	55.3	4.2	0.183	273	+ 38
1896 Jan.	0.458	68.9	3.3	0.155	241	+ 9
Febr.	0.481	72.4	4.2	0.152	216	— 14
March	0.279	58.5	5.9	0.190	229	+ 2
April	0.359	64.3	7.6	0.234	252	+ 28
May	0.356	66.2	10.0	0.269	267	+ 46
June	0.171	62.7	14.2	0.248	219	+ 1
July	0.166	64.1	14.9	0.239	217	+ 2

	Obs^d D. R.	Bar.	Temp.	Red^d D. R. I	Red^d D. R. II	O.—C.
1896 Aug.	$+ 0^s.156$	762 7	+ 14.0	$+ 0^s.226$	$+ 0^s.225$	+ 12
Sept.	0.089	57.8	13.2	0.206	224	+ 14
Oct.	0.148	57.2	9.5	0.173	228	+ 21
Nov.	0 289	62.1	5.7	0.145	230	+ 25
Dec.	0.248	58.8	3.1	0.081	180	— 23
1897 Jan.	0.300	58.4	2.1	0 111	206	+ 04
Febr.	0.312	63.3	4.5	0.119	188	— 14
March	0.161	55.2	6.4	0.130	184	— 17
April	0.224	60.7	8.1	0.163	203	+ 2
May	0.191	61.4	10.9	0.195	212	+ 11
June	0.170	63.8	13.8	0.218	212	+ 11
July	0.129	63.6	14.8	0.206	192	— 9
Aug.	0.034	59.1	14.7	0.172	158	— 43
Sept.	0.174	64.1	12.0	0.170	178	— 23
Oct.	0.329	67.5	9.2	0.203	234	+ 33
Nov.	0.388	66.6	6.1	0.191	247	+ 46
Dec.	0.340	62.3	4.1	0.148	220	+ 19
1898 Jan.	0.367	70.0	5.5	0.106	167	— 34
Febr.	0.216	58.1	4.9	0.106	172	— 29
March	0.248	58.6	5.0	0.133	198	— 3
April	0.221	60.5	8.8	0.182	216	+ 15
May	0.185	58.3	10.1	0.211	235	+ 34
June	0.174	63.5	13.1	0.207	206	+ 5
July	0.181	64.8	13.4	0.205	202	+ 1

The table shows clearly that during the first months following the starting of the clock the rate has been varying rather considerably, as probably will be the case with all clocks. It will be seen at the same time that only after about 10 years the greatest regularity was attained. In the last years however the rate again began to get slightly less regular, which is shown especially in the mean rates during short periods, and when the clock was taken to pieces in 1898 it appeared that this ought not to have been deferred so long. It was found that the pivots were more or less affected, and on the suspension-spring there was a small stain of rust, which had fortunately not eaten into the metal.

Further rather large deviations are shown by the reduced rates, whenever the temperature was below 0°. This is clearly shown by the monthly means for 1890 December and 1891 January, during which months the temperature was almost constantly below zero. It might be thought that this points to the existence of a term depending on the square of the deviation of the temperature from its mean value. Such a term might be explained by an influence of the temperature on the elasticity of the suspension-spring. [1]

It appeared however, as will more amply be shown below, that the monthly means show little evidence of the influence of a quadratic term, so long as the temperature remains above zero. It would seem that the temperature-coefficient changes more or less abruptly near 0°, its value for lower temperatures being much larger.

I have therefore excluded all periods during which the temperature was below 0° (or rather below — 0.°6 R.) Four months, *viz*: 1879 Dec., '90 Dec., 91 Jan. and 93 Jan. must consequently be excluded entirely. In 16 other months the temperature was below zero on 104 days. For these months new means were formed, excluding those days. [2] The following table gives the altered reduced mean daily rates, together with the corresponding mean temperatures.

	Temp.	Red^{d} D. R. I		Temp.	Red^{d} D. R. I
1880 January .	+ 2.1	+ 0^{s}.133	1891 December	+ 5.4	+ 0^{s}.208
1881 January .	+ 2.3	.199	1892 January .	+ 3.1	.195
1885 January .	+ 2.5	.161	» March . .	+ 3.9	.239
1886 December	+ 4.2	.161	» December	+ 4.6	.190
1887 January .	+ 1.5	.205	1894 January .	+ 3.2	.216
1888 January .	+ 2.9	263	» February	+ 4.9	.232
» February	+ 2.7	.264	1895 January .	+ 2.3	.174
1889 February	+ 3.4	.268	» February	+ 2.2	.146

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[1] Investigations by Dr. P. J. Kaiser about the clock Hohwü 27, belonging to the Bureau of Verification of the Nautical instruments belonging to the Dutch navy, have shown that the nature of the suspension-spring has a considerable influence on the value of the temperature-coefficient.

[2] Since there were not always time-determinations exactly at the beginning and the end of each cold period, some more days had to be excluded.

These means have further been used instead of the original values.

5. The reduced daily rates I, as given in the tables above, formed the basis of the further investigation. The first 5 months have been excluded from the beginning.

To begin with, it is possible without much computation, simply by combining the reduced rates into groups, to show that they must still contain a term of yearly period which cannot be explained by a *direct* influence of the temperature.

This is done as follows. The monthly means of the rates and of the temperatures were arranged in groups of one year each, the year beginning with May and ending with the following April. Then the means were taken of the rates for each year, and the differences between the monthly means and their yearly mean were formed. Thus I derived for each year a series of 12 differences: monthly means of rate — yearly mean, and also a series of 12 corresponding temperatures. In each of these series the mean was then taken of the first and the last value, of the second and the last but one, and so on. Finally also similar results were derived substituting for the temperatures the differences between the actual temperature of the month and that of the preceding month (△ Temp).

Then the same process was repeated with the only difference that the yearly groups commenced with February and ended with January.

The aim of this process will become clear when the results are considered. For brevity's sake I confine myself here to the five years 1884 to 1888. The differences: monthly means of rate — yearly mean are given separately for each year, and also for the mean of the five years. For the temperatures and the △ Temp. only the means are given. The differences of the rates are expressed in thousandth parts of a second as unit.

It is evident at first sight that in the first arrangement all the series of rates show a very marked progression, while the temperatures are nearly the same. In the second arrangement the reverse is true. On the other hand the variation of the rate is roughly parallel to that of the △ Temp. Hence the rates contain a term which does not depend on the actual temperature, but of which the maxima coincide with those of the yearly *change* of temperature, or, in other words, the yearly periodicity in the rate of the clock does not coincide with that of the temperature, and from the values just quoted we easily derive that the first lags about half a month behind the latter.

6. Before a closer investigation of the phenomenon is possible, it

	1884	1885	1886	1887	1888	84—88	Temp. 84—88	Δ Temp. 84—88
May, April.........	+39	+18	+60	+14	+42	+35	+ 8.9	+ 3.0
June, March	+22	+38	+32	+ 6	+27	+25	+ 8.5	+ 2.0
July, February.....	+14	+28	+30	+11	— 5	+16	+ 8.8	+ 1.3
August, January ...	+11	+ 8	— 8	+ 8	—16	+ 1	+ 8.2	— 1.3
September, December	—26	—22	—40	—14	—26	—26	+ 8.5	— 1.5
October, November..	—60	—70	—77	—24	—24	—51	+ 7.4	— 3.5
February, January	—18	+27	+ 9	+10	+ 3	+ 6	+ 3.0	— 0.8
March, December...	—11	+27	+ 6	+ 4	— 2	+ 5	+ 4.5	— 0.2
April, November...	+ 2	+10	— 9	+ 2	+20	+ 5	+ 6.6	— 0.2
May, October	—10	—60	—10	—20	+16	—17	+ 9.6	— 0.4
June, September ...	+ 4	—14	+ 3	—15	— 4	— 5	+12.8	+ 0.6
July, August	+34	+ 9	+ 2	+19	—30	+ 7	+14.2	+ 0.6

must first be ascertained whether the adopted temperature-coefficient represents the observations for the whole period.[1])

For this purpose each year was treated separately. The years beginning with February were used, since in that case the temperature-coefficient is found nearly independent of the changes in the rate which are proportional to the time.

Gradual variations with the time are namely clearly marked, and over long periods they are not even proportional to the time. This is seen from the following summary of the yearly means in which I have taken the years beginning with May in order to be able to include 1878.

1878	$+\,0^{s}.122$	1883	$+\,0^{s}.111$	1888	$+\,0^{s}.252$	1893	$+\,0^{s}.243$
1879	.120	1884	.159	1889	.254	1894	.208
1880	.189	1885	.189	1890	.247	1895	.220
1881	.186	1886	.210	1891	.218	1896	.176
1882	.157	1887	.257	1892	.222	1897	.169

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[1]) In the investigation of this section and also in that of § 7, it was inadvertently omitted to apply corrections amounting to $0^{s}.005$ to six rates of the years '88 and '89. The influence of this omission is negligible. For the four months, in which the rates were rejected on account of the low temperatures, interpolated values were used.

Two methods have been applied to derive the temperature-coefficients. In the first method I used the deviations of the monthly means from the yearly means, while in the second the deviations of these same monthly means from approximate values of the term a, i.e. the non-periodic part of the rate, were used. These values were derived from a curve which represents as nearly as possible the yearly means for years beginning with May, with August, with November and with February [1]).

These two methods gave the following series of corrections, headed I and II respectively, which must be applied to the value $-0.^s0268$ of the temperature-coefficient. They are expressed in units of one tenthousandth part of a second.

	I	II		I	II
1879	+ 15	+ 23	1889	+ 9	+ 12
1880	+ 8	+ 19	1890	+ 32	+ 21
1881	+ 47	+ 41	1891	— 11	— 5
1882	+ 70	+ 68	1892	+ 25	+ 28
1883	+ 48	+ 47	1893	+ 52	+ 46
1884	+ 29	+ 31	1894	+ 65	+ 64
1885	— 25	— 17	1895	+ 98	+ 96
1886	— 2	— 3	1896	+ 102	+ 96
1887	— 2	— 5	1897	+ 64	+ 67
1888	— 12	— 11			

The two methods thus give practically the same results. Although this agreement is of course not a measure of the real accuracy of the corrections found, it is nevertheless evident that the temperature-coefficient has not been constant during the whole period, but that the adopted value requires a positive correction as well in the first as in the last years, the latter being the most marked.

If the whole period is divided into three parts, we get the following mean results, according to the second computation (those of the first method are nearly the same):

$$\begin{array}{lr} 1879\text{—}1884 \quad \Delta c = & +38 \\ 1885\text{—}1892 \qquad\qquad & +\ \ 2 \\ 1893\text{—}1897 \qquad\qquad & +74 \end{array}$$

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[1]) In first approximation it was assumed that e.g. the mean for the year from '78 May to '79 April gave the value of a for '78 Nov. 1. Afterwards these values were in some cases slightly altered.

Throughout the preceding investigation it was assumed that the influence of the temperature is proportional to its first power. It is important to investigate the results which will be found, if we represent the influence of the temperature by the formula:

$$c_1\,(t-t_0)+c_2\,(t-t_0)^2.$$

For this purpose I used the deviations of the monthly means from the values of a derived from the curve. These deviations were represented by the formula

$$\Delta a+\Delta c_1\,(t-t_0)+c_2\,(t-t_0)^2.$$

I did not investigate the separate years, but I derived mean results for the three periods mentioned above; t_0 is then in each case the mean temperature of the period, and differs but little from + 8.7 (= + 8.1 Réaumur).

In this way I found the following values of Δc_1 and c_2, both expressed in tenthousandth parts of a second:

	Δc_1	c_2
1879—1884	+ 30	+ 3.9
1885—1892	— 5	+ 3.9
1893—1897	+ 75	— 7.9

The values of Δc_1 nearly agree with those previously found for Δc. Those of c_2 are small and of different sign, and their reality is doubtful. The rates for temperatures below zero would require positive and much larger values of c_2. In order to represent e. g. the two results for the months 1890 Dec. and 1891 Jan. it would be necessary to assume $c_2 = + 15$.

I think therefore to have acted correctly by excluding the rates corresponding to temperatures below 0°. For the other temperatures we may certainly provisionally adopt a linear formula for the influence of the temperature.

As to the coefficient c of this formula, I do not think that it could be represented as a function of the time which would have any real meaning. Probably, however, it will be better to assume it constant during shorter periods only, e. g. thus:

	Δc	c
1879—80	+ 21	— 247
1881—83	+ 52	— 216
1884	+ 31	— 237
1885—91	— 1	— 269
1892—93	+ 37	— 231
1894—97	+ 81	— 187

Finally I will show how these coefficients would be altered (see before) if the barometer-readings had been reduced to one temperature, in other words, what are the values of the *true temperature-coefficients.* For 760 m.m. the reduction for 1° Réaumur amounts to 0,152 m.m., of which the effect on the rate is $0^s.0021$. Consequently the *true* temperature-coefficient is found by applying a correction of $+ 0^s.0021$ to the *apparent* value.

7. We shall now apply to the reduced mean rates the reductions due to the corrections found for the temperature-coefficient. The adopted corrections are of this coefficient:

1878 May—1884 April $\Delta c = + 39$
1884 May—1893 April 0
1893 May—1898 July $+ 75$

Though probably the values mentioned at the end of § 6 are preferable, it did not seem necessary to repeat the computations with these altered values.

After this the deviations of the corrected monthly means from the values of a [1]) derived from the curve were formed and these means were arranged in yearly groups, each year beginning with May. [2]) For brevity's sake I do not give the results for the separate years, but only the means for four groups of years, viz: 1879—1882, 1883—1886, 1887—1891 and 1892—1896. If the deviations of the monthly means from the yearly means are used, the mean results for those four groups are not appreciably altered. All values are given in units of one thousandth part of a second.

It will be seen that the results of the first and the second groups agree very well inter se, and also those of the third and the fourth groups, I have therefore finally formed the means for the periods 1879—1886 and 1887—1896. The principal difference between these two periods seems to be that the low minimum in October which is shown in the first, has disappeared in the last. In the years, 1892—1896, however, the whole periodicity begins to be less marked, and in 1897 it is no longer shown by the monthly means. The monthly means of 1878 (i. e. '78 May—'79 April) are in good agreement with the results for the period 1879—1886.

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[1]) Since this curve is relative to the temperature + 10°, while the mean yearly temperature is + 8°.7 its first and last part had to be slightly altered, to account for the altered values of the temperature-coefficient.

[2]) The curve for a can only be drawn from '78 Nov. to '98 Jan., therefore the present investigation can only include the period '79 May—'97 April.

	79—82	83—86	87—91	92—96	1879 — 1886	1887 — 1896
May......	+ 37	+ 38	+ 22	+ 40	+ 38	+ 31
June	+ 14	+ 24	+ 23	+ 27	+ 19	+ 25
July.... .	+ 12	+ 22	+ 13	— 4	+ 17	+ 5
August ...	— 3	+ 7	— 4	— 16	+ 2	— 10
September.	— 38	— 32	— 27	— 9	— 35	— 18
October...	— 64	— 85	— 29	— 23	— 74	— 26
November.	— 22	— 54	— 26	— 21	— 38	— 24
December.	— 22	— 26	— 13	— 16	— 24	— 14
January ..	+ 12	— 5	— 7	— 6	+ 4	— 6
February .	— 1	+ 19	+ 11	— 9	+ 9	+ 1
March	+ 40	+ 34	+ 11	— 8	+ 37	+ 1
April	+ 39	+ 46	+ 30	+ 24	+ 42	+ 27

During the period 1887—1896 the periodicity can be very satisfactorily represented by a simple sinusoide. We find:

$$\Delta r = + 254 \cos 2\pi \frac{T - May\ 5}{365}$$

where the amplitude has been expressed in tenthousandth parts of a second [1]).

For the first period such a representation is impossible, and even when a term containing the double angle is introduced, the representation is not entirely sufficient. In that case we find:

$$\Delta r = + 455 \cos 2\pi \frac{T - Apr.\ 24}{365} - 95 \cos 4\pi \frac{T - Apr.\ 23}{365}.$$

An entirely satisfactory representation can only be obtained by an empirical curve.

This curve, together with the points which indicate the observations to be represented, is here reproduced in fig. 1. The sinusoide of the second period is given in fig. 2 [2]).

Moreover the following table gives for the first period the differences

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[1]) From the period 1887—1891 alone we find

$$\Delta r = + 274 \cos 2\pi \frac{T - May\ 1}{365}.$$

[2]) These figures will be published together with the second part of this paper.

Obs.—Comp I and Obs.—Comp. II, where Computation I means the representation by the formula, while Comp. II refers to the curve. For the second period the differences Obs.—Comp. are also given. Everything is expressed in thousandths of a second.

	79 — 86		87—96		79 — 86		87—96
	O.—C. I	O.—C.II	O.—C.		O.—C. I	O.—C.II	O.—C.
May	+ 2	+ 2	+ 6	November .	+ 12	+ 7	+ 1
June	— 12	— 9	+ 5	December..	+ 3	— 5	+ 6
July........	0	+ 3	— 4	January ...	+ 3	+ 1	+ 3
August.....	+ 11	+ 9	— 6	February ..	— 14	— 11	— 3
September..	+ 2	+ 3	— 2	March	+ 4	+ 4	— 15
October.....	— 20	— 6	— 2	April	+ 6	+ 4	+ 3

Finally attention must be drawn to the fact that a term with the argument $4\pi T$ might be explained by the direct influence of the temperature, if a quadratic term is assumed therein. In fact the yearly variation of temperature can be approximately represented by:

$$t - t_m = + 5.^\circ 5 \, sin \, 2\pi \frac{T - May\ 1}{365}$$

which would introduce into the rate a term:

$$\Delta r = - 15 \, c_2 \, cos \, 4\pi \frac{T - May\ 1}{365}$$

which agrees nearly with the second term in the above formula for the period 1879—1886, if we take $c_2 = + 6$. The probability of this explanation is however lessened by the fact that a similar term does not exist after 1886.

8, The results which have so far been derived have finally been used to free the monthly means from all periodic terms and then to represent them by a simple curve.

For this purpose

1st the reduced rates I were reduced to the mean temperature + 8°.7.

2nd the corrections, which become necessary if the temperature-coefficients given at the end of § 6 are adopted, were applied.

3rd corrections were applied for the supplementary periodic term in the following way, viz. for 1878 to 1886 according to the curve for 1887 to 1896 by the formula, while for 1897 and 1898 the correction was adopted = 0.

The reduced rates found in this manner are contained in the general table of the rates given above, under the heading „Redd D. R. II".

The drawing of a curve was *to a large extent* arbitrary. I have tried to make it as simple as possible. It is reproduced in Fig. 3 [1]). The residuals O.—C. (Obs. — Curve) are given in the last column of the general table.

For the years 1879—1896 the mean error of a monthly mean derived from these residuals is

$$M. E. = \pm\ 0^s.0237$$

If the supplementary term had not been applied it would have been

$$M. E. = \pm\ 0^s.0364$$

The difference is considerable.

(June, 25 1902).

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[1]) The curves derived from the yearly means, which were previously used, agree with this one in the principal points, but were more complicate.

KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN
TE AMSTERDAM.

PROCEEDINGS OF THE MEETING

of Saturday June 28, 1902.

(Translated from: Verslag van de gewone vergadering der Wis- en Natuurkundige Afdeeling van Zaterdag 28 Juni 1902, Dl. XI).

CONTENTS.

The following papers were read:

Geology. — "*The Geological Structure of the Hondsrug in Drenthe and the Origin of that Ridge.*" By Prof. Eug. Dubois. (Communicated by Prof. K. Martin.)

(Communicated in the meeting of May 31, 1902).

North-west of Eksloo, on the Hondsrug in Drenthe, remarkable sections of the soil are now to be seen in about fifty pits, dug last winter on behalf of the projected *Noord-Ooster Lokaal-Spoorweg.*

The greatest part of these pits are found on the Noorder Veld of Eksloo, at a distance of about $1^1/_2$ K.M. from this village and at a mutual distance of 50 M., a few at 100 M. mutual distance, in the directions from north-east to south-west and north-west to south-east; some, nearer to the village, on the Hooge Veld. Seven others are on the Buiner Veld, at about $1^1/_2$ K.M. farther N.N.W. from the principal group, succeeding each other at intervals of 100 M. in the direction from south-east to north-west. The pits are square, the edges measuring about 3 M., and though many are not quite as deep now as they have been, owing to their being partly filled again by blown-in sand, the vertical sides of the greater number are still uncovered to a depth of 3 or even $3^1/_2$ M.

Excepted two of them, situated most to the north-eastern border of the Hondsrug, we observe in all a similar section. In the upper part a relatively thin bed of sand, being near the surface of a dark greyish or nearly black colour, owing to much humus contained in it, but for the rest of a light yellowish or brownish grey, this bed showing hardly any traces of stratification and containing irregularly scattered stones of very different size, among which granites and coloured quartzites are predominant [1]. The sand is intimately mixed in some places with a noticeable quantity of brown clay. It is the well-known *boulder-sand* of the Hondsrug. Under it, to the bottom of the pits, rather coarse, loose, white quartz-sand, which is clearly stratified and in which are to be seen, locally, irregular small banks and strings of well rounded, water-worn pebbles, principally of white vein-quartz and next to it of light-grey quartzites and Lydian Stone, the largest of which pebbles have for the greater part only a dimension of 15, some however of 25 mM. The grains of this sand seen through the magnifying-glass prove to be also well rounded and almost all clear as glass. This description of the underground is completely applicable to the "*Preglacial or Rhine-Diluvium*".

Whilst near the bottom of the pits the stratification of this pleistocene alluvium of the Rhine is often nearly undisturbed and pretty well horizontal or sloping in undetermined directions, it is upwards always fantastically folded and wrinkled, contorted, a feature becoming very prominent on account of thin or sometimes thicker veins of sand of a yellow or brown colour, evidently derived from the

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[1] In most cases we find only smaller stones, the bigger ones having already been dug up, which appears from the unevenness of the surface, caused by the irregular reposition of the swards. There where this is not the case, large stones and boulders are still to be found.

upper bed, alternating with the white head mass. In short, the consequences of the pressure and the moving of the land-ice with its bottom-moraine material over the loose underground are beautifully illustrated here.

Of the most part of the pits on the Noorder Veld of Eksloo, viz. of those numbered from VII to XLV, I have measured the thickness of the boulder-sand bed. These dimensions are given (in Meters) in the following small table. Some pits could not be measured on account of the indistinctness of the lower limit of the bed. From those on the Hooge Veld the thickness of the boulder-sand is not more than

NW.

		XLV	XLIV	XLIII	
		0.8—1.0	0.9—1.0	0.35—0.6	
XLII	XLI	XL	XXXIX	XXXVIII	
0.8—1.0	0.8—1.0	0.6—0.9	0.7—1.25	0.4	
XXXIII	XXXIV	XXXV	XXXVI	XXXVII	
0.7—0.8	0.6—0.7	0.6—0.8	—	0.4-0.5	
XXXII	XXXI	XXX	XXIX	XXVIII	
—	0.6—0.7	0.6—0.7	—	0.4—0.5	
XXIII	XXIV	XXV	XXVI	XXVII	
0.7—0.8	0.6—0.8	0.4—0.9	—	±0.3	
XXII	XXI	XX	XIX	XVIII	XVII
0.7	0.3—0.5	±0.4	±0.3	±0.25	0.8 ±1.0 cl
XII	XIII	XIV	XV	XVI	
0.6—0.7	0.3	0.3—0.5	0.3—0.5	0.3	
XI	X	IX	VIII		VII
0.3	0.5—0.6	0.7—0.9	0.3		0.3

SE.

about 0,25 M. On the Buiner Veld (XLVIII to LIV) it varies from 0.2 to 0.8 M., attaining in a single case, locally, 1.5 M. At a distance of 200 M. north-west of XLIII there is on the Noorder Veld, near the Tippen, a pit numbered XLVI, with 0.4 M. of boulder-sand, and, 100 M. N.N.W. of the latter, another pit, numbered XLVII, showing a very irregular thickness of this upper bed, it locally giving way in the stratified white Rhine-sand. Moreover the latter contains, unto a depth of 2 M., boulders of granite and other rocks of Scandinavian origin.

From this table, that refers to an area long 400 M. in the same direction as the Hondsrug extends (from north-west to south-east) and broad 250 M., at right angle on it, and from the other given data, it appears that the thickness of the boulder-sand bed is very slight, attaining seldom 1 M., further that it varies greatly at small distances (often in the selfsame pit). The fact that the difference in height of the position of these pits is much larger than those differences in thickness, proves that the upper or boulder-sand bed follows the undulations of the preglacial nucleus of the Hondsrug and is rather regularly laid down upon it.

Some details may still be mentioned. In pit XII the brownish boulder-sand, having an average thickness of 0.6 to 0.7 M., penetrates wedgelike in the white sand unto 1.25 M. beneath the surface, whilst the strata of that underground are rent asunder unto about 2 M. lower than this wedge. This brings to the mind straining forces having worked laterally to the Hondsrug, such as would have arisen from an uplifting of the sand masses now constituting the nucleus of that ridge. In pit XXXIV two boulders from 0,2 to 0.3 M. in dimension are sunk totally below the general inferior limit of the boulder-sand bed in the pit. In pit XXXIX and XLI the sand, of a darker brown colour, is partly containing enough clay, that it becomes plastic, and also by alluviating it is proven that no small quantity of clay is present there.

But besides such particularities there are to be observed phenomena of greater importance. This is the case with N°. XLVII, showing fluvio-glacial mixing of the bottom-moraine with the sand of the underground, and with the two pits N°. XLI and XVII. In pit XLI there is in the south-western side a boulder of quartzite, almost square, about measuring 0.35 M. in every dimension. It is fixed at the bottom of the boulder-sand bed, having there a thickness of 0.7 M., and depressing, pocketlike, the strata, there rather undisturbed, of the white quartz-sand, unto 0.4 M. below its inferior extremity. Its basis is a plane ascending in the direction from north-west to south-east; but this basis belongs properly to a sheet of the boulder, about 4 c.M. thick, extorted according to a lamination plane parallel with that sloping basis, and the large upper piece has been pushed on, sliding upward $1^1/_2$ c.M. *in the direction from north-west to south-east.* The boulder with its extorted sheet are immovably fastened in the upper boulder-sand bed, which here contains rather much clay and is tolerably hard. In the opposite side there is a somewhat larger boulder of granite, polished and scratched. The contortions in the white sand of the underground are particularly fine in this pit. Apparently no boulders were extracted here, as is shown also by the appearance of the surface.

Pit XVII, which (with XLVII) is nearest to the eastern border of the Hondsrug, at a distance of about 150 M. from the first house along the Beekslanden, shows, as already has been said, a section different from those in the other pits. Above, again the common yellowish grey boulder-sand, 0.8 M. thick, in its lower half without boulders, under this, however, ± 1 M. of reddish brown, hard boulder-clay, containing much small stone fragments and some boulders.

This hard, red boulder-clay is well known in the underground of some of the Velds of Eksloo, where, locally, it occurs, at small distances from the eastern border of the Hondsrug, as far at least as Weerdinghe.

Quite identical reddish brown boulder-clay, under 0.7 to 0.9 M. of block-sand, is visible in a clay digging at the west of the Hondsrug, along the Langhiets Kamp near Odoorn. Going from there in the direction of Valthe it soon disappears from the underground, so that the boulder-sand bed is resting immediately upon the loose Rhine-sand. In a sand digging $2^1/_2$ M. deep, at a distance of about 1 K.M. N. N. E. from Valthe, the boulder-sand is 0.4 M thick. The white sand below it contains well rounded pebbles of white quartz and also of lydite. Halfway Odoorn and the side-branch of the Oranje Kanaal the boulder clay begins at a hunderd Meter westward from the road to Emmen. There, as well as nearer to the road, where the boulder-sand rests immediately on Rhine-sand, this boulder-sand is 0.7 M. thick; but already before the side-canal the boulder-clay reaches the road which remains on it as far as Emmen. Following the high road from Odoorn in north-western direction to Ees we find the boulder-clay in a clay digging, a little farther than the churchyard, under 1 M. boulder-sand. In a well sunk still somewhat farther off, in a meadow to the right of the road, about 3 M. of this boulder-clay was met with, which contained, next to other rock species, especially flint nodules; under the clay again coarse white loose sand with small well rounded pebbles of white quartz. At a distance of 4 K.M. from Odoorn, where the way from Eksloo to Brammershoop crosses the high road, boulder-clay is seen again, under 0.7 M. of boulder-sand; here it is partially of a yellowish brown spotted with greenish grey colour, a difference in connection with the not flowing off of the water in the soil. In sinking a well, this clay proved to have a thickness of $2^1/_2$ M. Farther north it is found at least as far as Ees.

At $2^1/_2$ K.M. south-west of Odoorn, in the Peat-moss of Odoorn, that is in the midst of the Peat-moss of Schoonoord according to Lorié, the boulder-clay is wanting under the ± 1 M. thick bed of boulder-sand, which came to light after the opening of the peat-moss for digging fuel. In its place a bed of light bluish grey clay, 0.3 to 0.4 M. thick, is found. This was observed at a pit dug on purpose and is the case with the whole Peat-moss of Odoorn, as has been observed when digging ditches. This plastic clay, containing no palpable sand, is entirely different from the boulder-clay. It is hardly to be doubted that we have to regard it as lake-clay, the same as the wellknown preglacial Pot-clay from the underground of Drenthe, Groninghen and Friesland, which gave rise to peat-mosses in such cases where it was shaped in the form of basins.

Thus the considered part of the Hondsrug, about the half of the Hondsrug in Drenthe and almost a third of the whole of that ridge which is extended from north-west to south-east, between Groninghen and Emmen, and is elevated only on an average 5 M. above the surrounding region, is constituted by preglacial Rhine-sand, superficially covered, in the same manner as the adjoining ground, by a bed of boulder-sand not 1 M. thick.

That the boulder-sand cannot owe its origin to washing out of the boulder-clay may be admitted for the following reasons:

1st The hard boulder-clay offers great resistence to eroding agencies. This appears amongst others from its forming steep and more or less projecting parts at the coast of the Roode Klif, the Mirdummer Klif and the Voorst, and even isles, at Urk and Wieringhen.

2nd Though undoubtedly the quantity of boulders in the boulder-sand has from the beginning been very variable, it is however a fact, that in the neighbourhood of the villages most boulders have already been dug out and that they were formerly very numerous almost everywhere. At some places one stone was lying next to the other in the sand. An average condition is to be met with at some parts of the Noorder Veld of Eksloo. Now to the north of pit XLV on a surface of 1500 M^2. and to a depth of 0.5 M. there had been freshly dug out 40 M^3. of stones, from the size of a child's fist up to

1 M. in length. Estimating the air spaces between the stones heaped up at $^1/_4$, we find about $^1/_{25}$ of the volume of the boulder-sand bed to have consisted in stones. Between pit XV and XVI a similar estimate, from a surface of 484 M^2., leads to $^1/_{24}$ for that proportion. What an enormous thickness of boulder-clay, which in this region is particularly poor in stones, must have been washed out to leave all these stones!

3rd The boulder-sand contains very little flint, the boulder-clay very much, everywhere. Flint is the kind of rock most frequently occurring in the clay (Odoorn, Zwinderen, Nieuw-Amsterdam, Mirdummer-Klif, Nicolaasga, Steenwijkerwold, Wieringhen etc.).

4th Even the deepest and evidently *not* washed out parts of the boulder-sand, which rest immediately on the Rhine-sand, are as a rule poor in clay.

5th Boulder-clay and boulder-sand are found jointly or the latter alone without this being expressed in the form of the surface.

That the Hondsrug cannot be a terminal moraine, as has been supposed by some geologists, follows sufficiently from the description of its structure as given above.

It neither can owe its origin to an upward folding or pressing of the underground, perpendicular to the direction of the motion of the pleistocene land-ice; for how then to account for the deposition of boulder-clay parallel to the Hondsrug ridge?

The distribution of the boulder-clay in our north-eastern provinces is so, that there can hardly be any doubt that from the beginning it has been very unequal and the boulder-clay has been laid down parallel with the actual Hondsrug ridge.

Can it perhaps by its weight have pressed upward the Rhine-sand, when the soil was still totally drenched with melting-water? This apparently has not been possible. The specific weight of a well compressed sample of that Rhine-sand from the Hondsrug, quite drenched with water, is 2.05. If now that of the boulder-clay had even attained the high value of 2.5, it would require a bed of boulder-clay of a thickness of 20 M. to cause an uplifting of 5 M., as is the average height of the Hondsrug above the surrounding region. In reality the thickness is most probably only $^1/_7$ of that supposed value.

Other causes must have been in action to bring about this elevation of the Hondsrug, but causes which nevertheless were not inconsistent with the deposition of the boulder-clay parallel to that ridge. These causes may be found in what CHAMBERLIN, RUSSELL, SALISBURY, VON DRYGALSKI and already NANSEN have taught us regarding the structure and motion of the inland-ice in Greenland. According to the earlier ideas the bottom-moraine was pushed forward under the ice, from the centrum of dispersion of the latter; to day we know that stones, sand and mud are transported included strata-like in the inferior parts of the ice mass, by the gradually melting of which the bottom-moraine is formed. Further it is known, that the motion of the inferior strata of an inland-ice mass becomes the slighter the more these are laden with stones and mud. Evidently this load was less above the strip of land which actually constitutes the eastern, most elevated portion of the Hondsrug than at the west of this portion, where the ice in its downmost parts must have been thickly laden with clay. Above this strip we may suppose to have existed a relatively more rapid motion of the inland-ice in comparison with above the extensive western clay banks, the result of which difference would have been a lower level of the ice in the first and a higher in the latter parts. Thus, actually, in Greenland a considerable diminishing of the motion and a swelling of the ice is seen there where in its undermost strata it is strongly laden with debris of rock, and lowering of the surface where this motion is not hindered, on account ot the lowest ice-strata being relatively pure. Thence considerable pressure on the underground where those clay banks are now to be found in the Hondsrug and a minimum of pressure near the eastern border; there then the loose Rhine-sand, drenched with water was as a whole mass uplifted.

The situation of the elevated ridge of preglacial sand side by side with the long and broad western strip of boulder-clay makes us also suppose that the direction in which the ice moved was not, as is still generally admitted, from north-east to south-west or from north to south, but the same as the extension of the Hondsrug, from north-west to south-east. Now with this supposition perfectly agrees the at first sight paradoxical direction of motion as derived from the shifted boulder of quartzite.

But how then can we account for the fact that the boulder-clay was laid down principally in a long and broad strip along the western part, whilst the boulder-sand above it is uniformly thick with that in the eastern part on the Hondsrug where clay is generally absent under it? This question too is not difficult to solve with our actual knowledge of the phenomena of the motion of an inland-ice mass. The material of the boulder-sand bed may have been transported as a continuous bed by higher ice-strata, at the same time as disjuncted strips and patches of clay were included in the lower ice-strata, or the sand with its boulders may have been transported at a somewhat later time. Small variations in the direction or in the velocity of the motion of the ice can easily have divided the boulderclay in strips and patches.

Thus all the observed geological phenomena can be viewed in the light of known actual phenomena, which appears to be impossible if we start from the opinions embraced up till now on the nature of the Hondsrug.

Now that it is known that the direction of ice streams which ended in North-Germany has often been considerably modified by the form of the basin of the Baltic and also by the meeting with other ice streams, it is less surprising, that, notwithstanding the predominating or exclusive occurrence of Swedish, at least Scandinavian rock species in the bottom-moraine of our north-eastern provinces, these can nevertheless have arrived there in north-west—south-eastern direction. Suchlike factors, as supposed to have modified the direction of the North-German ice streams, may have been the cause of the deviations of an ice stream, which, coming from Sweden, first took a south-western direction over Denmark, till it arrived in the North-Sea. We do not know how far the ice which came down from southern Scotland and northern England did progress south-eastward in the North-Sea; it might be possible, at least, that as a very powerful stream it has met there with the ice stream coming from Sweden and has pushed this back south-eastward in the direction of Friesland, Groninghen and Drenthe.

Very likely as a result of this motion of the ice over our north-eastern provinces the Hondsrug and some parallel less extended elevations have then arisen, in such a way as indicated above. Farther west of the Hondsrug, however, probably a real folding, under the pushing ice, of strata impermeable for water, should they consist in Potclay or in the boulder-clay itself, raised, perpendicular to that direction, a number of north-east—south-western ridges, leaving between them valleys now occupied by rivulets. Indeed an elevation by folding is more readily to be admitted for compact soils than for the loose sand which constitutes the nucleus of the Hondsrug.

Geology. — "*The Geological Structure of the Hondsrug in Drenthe and the Origin of that Ridge.*" Second communication. By Prof. Eug. Dubois. (Communicated by Prof. Bakhuis Roozeboom).

Further researches in that part of the Hondsrug, considered in my former communication, led to the following results.

At a short distance north-east of pit LI, the boulder-sand bed of which, up to a depth of 1.5 M., shows an irregular mixing with brown clay, there is on the highest part of the Buiner Veld (and the Hondsrug in those parts), under 0.5 to 0.8 M. of boulder-sand, a yellowish red boulder-clay bed of 1 M. thickness. It is situated at about 1 K.M. south of Buinen and measures about two hundred Meters in every direction.

The clay found in pit XVII extends, as shewn by borings, only some 50 Meters in different directions.

Another patch of boulder-clay is found south of the Zuider Esch of Eksloo on the southern Hooge Veld, in an oak-underwood, under about 0.5 M. of boulder-sand. This patch too is of small dimension. The same is the case with another on the Zuider Veld of Eksloo.

Farther, in the neighbourhood of Valthe, a clay bed is found on the Kwabben Veld, under ± 0.5 M. of boulder-sand, 1.5 M. thick, at least, of about 300 M. dimension in every direction and extending still somewhat farther south-east on the Nieuwe Esch; a smaller one exists south-east of the Kampen Veen.

The four latter clay patches are situated, with the two first mentioned, pretty well in one direction, from north-west to south-east, but they are separated by large intervals in which the boulder-sand rests immediately on preglacial stratified white Rhine-sand. The mutual distances of these clay patches are resp. 2, 3, 1, 2, 1.5 K.M. With the only exception of the small clay patch on the Noorder Veld, all these, though situated very near to the eastern border of the Hondsrug, are on the highest parts of that ridge.

The stratified white Rhine-sand is, amongst other localities, to be seen in a sand digging on the Kleine Esch of Eksloo (under ± 0.4 M. of boulder-sand) in a sand digging at the northern border of that Esch (under 0.3 M. of boulder-sand) and on the Zuider Veld, near to the southern border of the Achter Esch; further at the Valther Schans (under 0.3 or 0.4 M. of boulder-sand), in a sand digging east of the Kampen Veen (under a bed of boulder-sand of the same thickness) and further, along the great Bourtangher Peat-moss, from Valthe to Weerdinghe.

The western boulder-clay, on the contrary, forms a long and broad strip, which from Ees to Emmen seems not to be interrupted and is 1 to $1^1/_2$ K.M. wide. It has probably in its whole length a thickness of 2 or 3 M. and is covered by 0.7 to 1 M. of boulder-sand.

The origin of the Hondsrug according to the hypothesis indicated in the former communication can thus only be applied to that western strip of boulder-clay. Other facts now observed have brought to my mind, besides the already mentioned factors, others which may have been of still greater importance in the formation of the Hondsrug.

Beyond the Hondsrug also, even as far west as Hoogeveen, the underground consists of preglacial "Rhine-Diluvium". In the Peat-moss of Ees it is covered by at most 1 M. of boulder-sand. In the Elders Veld between Schoonoord and Schoonloo the preglacial Rhine-sand is of a yellowish grey colour, on account of its intimate mixing with parts of the upper bed. The occurrence of small water-worn pebbles of white quartz and lydite, repeatedly stated to a depth of 2 M., serves to show, that here too we have chiefly before us old Rhine-alluvia, which only later on were mixed with the bottom-moraine. At Schoonloo, in a sand digging, a kind of "Mixed Diluvium" (*Gemengd diluvium*) is to be observed; water-worn pebbles of white quartz and lydite are seen in the sand side by side with Scandinavian granites. On the Elders Veld boulder-clay is only found in single small patches, such as the one at 1.5 K.M. south-west of Schoonloo.

In the midst of the Peat-moss of Ees, at a distance of 4 K.M. exactly south from Westdorp, a round hillock rises above the perfectly level environs, not unlike a small volcanic island above the sea. With a basis of about 30 M. of diameter and a height of circa 5 M. it resembles a very large tumulus; it is the renowned Brammershoop.

The constitution of this hillock, however, is inconsistent with the idea, which presents itself at first sight, that we have before us a work of mans making. It is indeed composed of white quartz-sand with well rounded small pebbles of white quartz and lydite, the same preglacial Rhine-sand, which also constitutes the underground of the surrounding region with a mantle of glacial boulder-sand only 0.2 to 0.5 M. thick.

Still less than in the case of the Hondsrug it will do here, to attribute the origin of the elevation to pressure of the pushing ice; for how could the motion have been directed from all sides towards that single point! As it appears to me, the only way to explain how only there the soil was pressed upward, in the form of an isle, is to suppose that a minimum of pressure of the ice, has existed there, most probably in consequence of a former *Gletschermühle* (*moulin*) in the period of the melting of the ice.

Not improbably then we have, partially or perhaps chiefly, to impute the elevation of the preglacial Rhine-sand in the Hondsrug to a similar minimum of ice-pressure, at the place of a large river-bed, formerly occupied by melting water, and carved in the surface of the ice in the direction from north-west to south-east, or may-be to a large and long crack in the same direction.

Zoology. — "*On the Shape of some Siliceous Spicules of Sponges*"; by Dr. G. C. J. Vosmaer.

The perplexing amount of variety exhibited by sponge spicules has since long made it desirable 1st to designate certain spicules by special terms, and 2nd to divide the spicules into groups. The first attempt to such a classification was made by Bowerbank in 1858; later, in 1864, modified by the same author. Bowerbank divided (1864 p. 13) the spicula into "essential skeleton spicula" and "auxiliary spicula". It is obvious that this primary classification is not based on morphological characters. Since Kölliker (1864) has pointed out the morphological value of the axial canal or, more correctly, the axial thread ("Centralfaden"), Oscar Schmidt has rightly based his classification of siliceous spicula on the presence of one or more of such axial threads, which after all represent the axes of the spicula. Schmidt distinguishes (1870 p. 2—6) four types of spicules:

1. „Die einaxigen Kieselkörper."
2. Die Kieselkörper, deren Grundform die dreikantige reguläre Pyramide."
3. Die dreiaxigen Kieselkörper."
4. Die Kieselkörper mit unendlich vielen Axen."

Neither Gray (1873, p. 203—217), nor Carter (1875, p. 11—15) understood the fundamental value of Schmidt's classification. My attempts to draw attention to it (1881 *a* and 1884 p. 146—168) have had but little influence. Thus, in 1887, Ridley & Dendy divide the spicula of the Monaxonids in the first place into Megasclera and Microsclera, a classification which practically agrees with those of Bowerbank and Carter. The example was followed by Sollas in spite of his being well aware of the fact that the distinction is far from "absolute". This author quite correctly remarks (1888, p. LIII): the microscleres and megascleres pass into each other by easy gradations, so that it is not possible to say where one ends and the other begins, indeed there would be a certain convenience in accepting a third division of intermediate or middle-sized spicules, which we might call mesoscleres." Finally, in 1889, Schulze & Lendenfeld accept Schmidt's primary division into "polyaxone, tetraxone, triaxone, and monaxone Nadeln."

I do not intend to discuss here the triaxons and tetraxons; for the present I only wish to draw attention to some monaxons and some spicules hitherto generally considered as polyaxons.

In the group of the monaxons, i. e. spicula with one single axis, two fundamental divisions may be distinguished, according to the fact whether the ideal axis lies in a plane or not. In the former case the line may of course be straight, curved, bent, flexuous etc.; in the latter case the line is a screw helix [1]). The spicula belonging to the former case I propose to call *pedinaxons* [2]), the others *spiraxons* [3]). To the group of the pedinaxons belong e. g. oxea, styles, tylostyles, some of the "amphidisci", some of the "toxa". It is, however, to the spiraxons, that I wish more especially to draw attention.

Again we can distinguish here two cases: *α*. the screw line is formed on the surface of a circular cylindre or *β*. on that of an elliptical cylinder. The former group I wish to call *α-spiraxons*; the pitch is here generally large. The latter I call *β-spiraxons*; the pitch is here small.

Let us first examine the *α*-spiraxons. To this group belong the spicula known as sigmaspires, toxaspires, spirules; further those which are usually called spirasters and which are by the majority of spongiologists erroneously considered as modified asters. This mistake is due, I believe, to OSCAR SCHMIDT. „Eine blosse Modification dieser Kugelsterne," he says, 1870, p. 5, „sind die Spiralsterne oder Walzensterne. Sie werden zwar in manchen Spongien nur allein, d. h. nicht untermischt mit den Kugelsternen angetroffen (*Spirastrella cunctatrix* Sdt. *Chondrilla phyllodes* N.), häufiger aber, wie wir unten in die Specialbeschreibung (z. B. von *Sphinctrella horrida* N. und *Stelletta hystrix* N.) hervorheben werden, liegen alle Uebergange von den normal centralen Sternen zu den gezogenen Spiralsternen vor." Unfortunately did SCHMIDT not keep his promise; for in the description of *Sphinctrella horrida* we find nothing more about it, and *Stelletta hystrix* is forgotten altogether. SCHMIDT failed, therefore, to give any proof whatever for his statement that "Spiralsterne" are modified "Kugelsterne". SCHMIDT's suggestion has nevertheless generally been accepted, myself not excluded.

SOLLAS (1888, p. LXI) distinguished two chief series of spicula (microsclera): "the radiate or astral, and the curvilinear or spiral." The former are called "asters," the latter "spires." With some astonishment we further read that the asters are divided into two

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[1]) These terms are to be taken cum grano salis. No biological formation will ever be absolutely mathematical; thus it may be that the axis of a flexuous or undulating spiculum is not exactly lying in a plane, without, however, being in any way comparable to a screw helix.

[2]) πεϑινός, plane, even.

[3]) σπεῖζα (lat. spira), everything which is twisted.

subsections: "the true asters or euasters, and the streptaster or those in which the actines do not proceed from a centre but from a larger or shorter axis, *which is usually spiral*". Evidently one should expect that those "streptasters" were arranged under the "spires." As a matter of fact neither SOLLAS, nor any other author has given very striking arguments to consider the spiraster as a modification of the euaster. We know examples of very young stages of spirasters; they always possess the twisted character. But no instance is known of spirasters originating from or forming transitions to true asters. It is true that such supposed transitions are mentioned by some authors; but probably we have here to do with a mistake due to optical delusion. For instance, SCHMIDT described (1862, p. 45) a *Tethya bistellata*, possessing in addition to ordinary asters, double ones ("Doppelsterne"). But LENDENFELD described (1897, p. 55—58) a *Spirastrella bistellata* (which he considers identical with *Tethya bistellata O.S.*), in which he found that the supposed asters are true "spirasters". Judging from what I saw in a type specimen of SCHMIDT's sponge, I have no doubt that LENDENFELD is right. Quite correctly LENDENFELD believes that SCHMIDT has been misled by an optical delusion, "da diejenigen Spiraster deren Axen im Preparat aufrecht stehen und daher verkürzt gesehen werden, häufig wie Euaster aussehen"..... I fail to find a single proof that spirasters are modified euasters, either in previous papers, or in my preparations. On the contrary, everything speaks in favour of the view that "spirasters" are a sort of a-spiraxons. The fact that in some cases it is difficult to get certainty about the twisted shape, is no proof against my suggestion in general. For in the great majority of cases the twisted nature is certain, as can be demonstrated by allowing the spiculum to roll in the preparation when observed through the microscope.

Let us proceed now to examine the *different sorts* of a-spiraxons.

1. *Sigmaspira.*

SOLLAS (1888, p. LXII) gives the following definition of the sigmaspira: "a slender rod, twisted about a single revolution of a spiral"; he adds that it appears in the form of the letter C or S, according to the direction in which it is viewed. Te definition of the "toxaspire" runs as follows: "a spiral rod in which the twist a little exceeds a single revolution. The pitch of the spiral is usually great and the spicule consequently appears bowshaped when viewed laterally".... It seems to me not quite exact when SOLLAS pretends that the bowshaped appearance is in the first place due to the number of revolutions.

Considering the facts that these spicula are generally very small, and that consequently a microscope of very high power is wanted to understand the true shape, it is evidently not easy to determine the number of entire revolutions or parts of it; the same may be said of the pitch of the „spiral" — or rather of the screw helix.

In order to obtain certainty about this I constructed wax models, the axis of which were screw helices of various length and various pitch, of course all drawn on the same circular cylinder. The diameter of the models I made in accordance to the relative size observed in the spicula. Such a set of models ought to be carefully studied *in projection.* This can be done by looking at them with one eye, or, which is far better, by studying the shadows of the models in various positions. These projections are then compared to the camera-drawings or microscopical projections of the spicula themselves. This method most clearly shows 1st that the bow-shape can be obtained with models of less than one revolution; 2nd that the C- or S-shape can be obtained with models of more than $1^1/_2$ revolution. This depends both on the length and the pitch of the screw helix, as is shown by the following table [1]):

Number of revolutions.	Pitch.			
	10°	20°	30°	40°
$^2/_3$	C — —	C [S] (⋏)	C [S] ⋏	
$^3/_4$	C [S] —	C S (⋏)	C S ⋏	
$^5/_6$	C (S) [⋏]		C S ⋏	C S ⋏
1	[C] (S) [⋏]	(C) S ⋏	C S ⋏	C S ⋏
$1^1/_6$	— [S] (⋏)	(C) S ⋏	C S ⋏	
$1^1/_4$	— (S) ⋏	(C) S ⋏		C S ⋏
$1^1/_3$	— (S) ⋏	C S ⋏	C S ⋏	
$1^1/_2$	— (S) ⋏	(C) (S) ⋏		C (S) ⋏
$1^3/_4$	— [S] (⋏)	— [S] ⋏	— — ⋏	— [S] ⋏
$1^5/_6$			— — ⋏	
2	— — —	— — —		— — [⋏]

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[1]) C, S or ⋏ means: C-shape, S-shape or bow-shape distinct; ( ) means indistinct; [ ] means very indistinct. A dash — means that the shape cannot be obtained with the wax model.

This result leads us to a dilemma. Either the definitions of sigmaspira and toxaspira will have to be modified, or we have to drop the distinction between the two forms of spicula. I believe that it follows from the above table that the latter way out of the difficulty is preferable. We may maintain the name sigmaspira for smooth, i. e. not spined *a*-spiraxons of no more than $1^1/_2$ revolution.

Lendenfeld (1890 p. 425) has another conception of the sigmaspira: "ein einfach spiralig gewundener oder bogenförmiger Stab." Hence he seems to accept two different kinds, instead of considering them as belonging to one sort, the shape of which simply differs according to the direction in which it is viewed. Since he says that his "spirul" has "mehr wie eine Windung", he seems to accept no more than one revolution for the sigmaspire. This is not in accordance with my observations, as laid down in the above table.

2. *Spirula.*

Although Carter did not give a special definition of the spirula, it is clear enough what he understands by this name. In his paper on the "spinispirula" (1879 *a* p. 356) he calls the spiculum which he formerly (1875 p. 32) described as "sinuous subspiral", simply "the smooth form of the spirula" and he refers to an illustration of the spicule as it occurs in *Cliona abyssorum* (1874, Pl. XIV, p. 33). Obviously the term spirula used by Carter is an abbreviation of "spinispirula", not as terminus technicus. Ridley & Dendy (1887 pp. XXI and 264) introduce the term spirulae as synonym with spinispirulae of Carter, adding that "these are more or less elongated, spiral or subspiral forms, which may be either smooth or provided with more or less numerous spines." Sollas creates (1888 p. LXII) the term polyspire for spirula, stating that it is "a spire of two or more revolutions", adding, however, that he is inclined to adopt the term spirula. In the list given by Schulze & Lendenfeld (1889 p. 28) we find a "spirul" described as "spiral gewundene Nadel mit mehr als einer Windung". Consequently we learn that the term spirula by some authors is used both for smooth and for spined forms, whereas others leave the question open. Lendenfeld (1890 p. 426) proposes the name for smooth spicula only: "eine schlanke und glatte, spiralig gewundene Nadel mit mehr wie einer Windung". I herein agree with Lendenfeld and I understand by spirula: a smooth *a*-spiraxon of at least $1^3/_4$ revolution.

3. *Spinispira.*

As long as the *a*-spiraxons are smooth it will as a rule not create any difficulty to distinguish sigmaspirae and spirulae. But there are a quantity of spined α-spiraxons. Evidently such spined α-spiraxons will exhibit the twisted nature the less distinctly the more the spines are developed. It is, therefore, not practical in this case to make distinctions, based on the number of revolutions. Especially not because there exists a great diversity with many transitions. I prefer, therefore, to propose for spined α-spiraxons the general term spinispirae, to which I bring the spicula called by previous authors spirasters, metasters, plesiasters, and also (partly) spinispirules, sanidasters etc.

SOLLAS (1888 p. LXIII) has given the following definition of the spiraster: "a spire of one or more turns, produced on the outer side into several spines." SCHULZE & LENDENFELD (1889 p. 28) say that it is a „leicht gewundener gestreckter Aster mit dickem, dornenbesetztem Schaft", a definition which LENDENFELD (1890 p. 426) modified into: „ein kurzer und meist dicker, leicht spiralig gewundener Stab mit starken, meist dicken und kurzen, kegelförmigen Dornen". SOLLAS distinguished "metasters" and "plesiasters" from his spirasters, but he acknowledges himself that: "the three forms present a perfect gradational series, so that it is frequently difficult when they all occur associated in the same sponge, to distinguish in every case one variety from the other". Now it happens very frequently indeed that they all occur associated in the same sponge and that all gradations are met with. One only needs to read SOLLAS' own descriptions and to compare them with his illustrations, e. g, of the many "species" of *Thenea*, *Poecillastra*, *Sphinctrella* i. a. in order to become convinced that it is practically impossible to distinguish spirasters, metasters and plesiasters. SCHULZE & LENDENFELD, therefore, did not adopt the latter two terms.

I am of opinion that the name spinispira can be likewise applied to the spicula which SOLLAS calls amphiaster; at any rate to such amphiasters as are said to occur in *Stryphnus niger* SOLL.[1]) A great confusion exists, with regard to the word amphiaster. The name is first used by RIDLEY & DENDY (1887 pp. XXI and 264), who say that the amphiaster is composed of „a cylindrical shaft bearing a single toothed whorl at each end; occurring for example, in *Axoniderma mirabile...*" The authors give an illustration by fig. 9 on their Pl. XXI, and a further explication saying: "amphiastra = birotulates (Bowerbank); amphidisks (auctorum)." But SOLLAS says (1888 p. LXIV) of *his* amphiaster "the actines form a whorl at each extremity of the axis, which is straight"; herewith a woodcut on p. LXI.

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[1]) In his preliminary account on the Challenger-Tetractinellids (1886 p. 193) SOLLAS calls this spiculum "amphiastrella".

Schulze & Lendenfeld (1889 p. 8) have about the same conception of the spiculum: „gestreckter Aster; ein Schaft, von dessen beiden Enden Strahlen abgehen." Comparing now the three quoted illustrations, it becomes evident that there are important differences between them. Notwithstanding Schulze & Lendenfeld illustrate a spicule with a long „Schaft" and long pointed „Strahlen", we find in the definition of Lendenfeld (1890, p. 419) that the amphiaster is: „ein in die Länge gezogener Stern, die aus einem *kurzen*, geraden Schaft besteht, von dessen Enden mehrere *kurze* Strahlen abgehen". Indeed: tot capita tot sensus. If, therefore, I bring certain amphiasters to the spinispirae, only such are meant as Sollas describes e. g. in *Stryphnus niger*.

Carter (1879 *a*, p. 354—357) has introduced the term „spinispirula" for spiniferous spirally twisted spicules." Such spicula are, according to Carter exceedingly polymorph. They may be „long and thin" or „short and thick". The spines may be „long and thin . . . or long and thick . . . or obtuse . . . The spines may be arranged on the spicule in a spiral line, corresponding with that of the shaft . . . or they may be scattered over the shaft less regularly . . . Lastly, the shaft may consist of many or be reduced to one spiral bend only . . ."

Instead of chosing one of the various terms mentioned above, I prefer the new term spinispira, which is then simply: a spined *a*-spiraxon. If in future it happens become to a desideratum to have more than one name for such spicula, one might distinguish two groups of spinispirae, viz. forms with long spines and such in which the spines are small, in comparison to the total length of the spiculum. In the former group the ratio between the length of the spines and the total length is usually no more than 1 : 3; very seldom as much as 1 : 7; the number of revolutions is generally not more than $1^1/_2$. In the latter group this ratio is usually at least 1 : 10; the number of revolutions as a rule more than two.

4. *Microspira.*

In some sponges very minute spicula occur, especially in the superficial (dermal) layers and lining the canals, which are either distinct *a*-spiraxons, or modifications by reduction. For obvious reasons it can only be made out with a microscope of very high power and in favourable situation in the preparation, whether they are smooth or minutely spined. In such small spicula it is not always possible to distinguish with certainty whether they are minute spinispirae, sigmaspirae or spirulae. Moreover they show generally manifold transitions in one and the same sponge specimen. This is e.g. the case in *Placospongia* *carinata.* And still, we want to designate them with a name; I propose to use for this the term microspira.

5. *Sterrospira.*

In the remarkable genus *Placospongia* the stony cortex and axis are almost entirely composed of spicula, which very strikingly resemble the sterrasters of Geodidae. Keller (1891*a*, p. 298) was the first to demonstrate that these spicula are of quite a different nature; whereas the sterrasters develop from true asters, the cortical spicula of *Placospongia* take their origin from "Spirastern". This observation is confirmed by Lendenfeld (1894*d*, p. 115). Hanitsch (1895, p. 214—216) found the same for the corresponding spicula of *Physcaphora (= Plancospongia) decorticans;* as they possess in this species an elongated, somewhat crescent-shaped appearance Hanitsch called them „selenasters". In 1897 Lendenfeld, not acquainted with the paper of Hanitsch, proposed the name "pseudosterrasters" for the cortical and axial spicula of *Plancospongia graeffei (=Physcaphora decorticans Han.).* If one wishes to apply the rules of priority in this case, the spicula under consideration have to be called selenasters. I am, however, of opinion that these rules, excellent as they are for specific nomenclature, need not to be applied in other cases and I propose, therefore, the name sterrospira, which at the same time reminds us of the sterrasters (of the Geodidae) and the spiraxons. [1])

In the group of the *β-spiraxons* the ideal axis of the spiculum is a line drawn on an elliptical cylinder. The simplest type of such a spiculum is

1. *Sigma.*

This term is introduced bij Ridley & Dendy (1887, pp. LXIII and 264) for spicula called by Bowerbank "bihamate", "contort bihamate" and "reversed bihamate". The authors say that the sigma consists of a "slender, cylindrical shaft, which is curved over so as to form a more or less sharp hook at each end. The two terminal hooks may curve both in the same direction, when the spicule is said to be simple ... or they may curve in different directions, when it is said to be contort ... There is, however, no real distinction between the two, and, as a matter of fact, the spicules are nearly always contort to some extent". Sollas (1888, pp. LXII) modified the definition into "a slender rod-like spicule curved in the form of the letter *C.* This spicule is not spiral though it probably arises

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[1]) For details I refer to a paper on Placospongia from Dr. Vernhout and myself, to appear within a short time (Siboga-Expeditie. Monogr. VI. Porifera).

from a sigmaspire by increase in size and loss of the spiral twist". **Schulze** & **Lendenfeld** (1889, p. 28) stick to the contorted nature: "gewundene, eine halbe Spiralwinding bildende Nadel". Finally the definition is again somewhat modified by **Lendenfeld** (1890, pp. 426): "einfach spiralig gekrümmter oder bogenförmiger Stab."

The spicula belonging to this type, appear, like the sigmaspirae in the shape of the letter *C* or *S*, or as a bow. Here too these various appearances depend on the direction in which the spiculum is viewed. According to my conception only such forms belong to this group, which are contorted, not such in which *really* the "hooks curve both in the same direction". The latter are curved pedinaxons, the former are spiraxons. The axis, as a rule, has less than one, but more than half a revolution, which is easily proved by wax models.

As a derivation or modification of the sigma we have

2. *Chela.*

Bowerbank has already shown (1858, p. 304—305; reprinted 1864 p. 47—48) that the chelae develop from sigmata. This observation is confirmed and enlarged by **Ridley** & **Dendy** (1887, p. XX), **Levinsen** (1886 and 1894), H. W. **Wilson** (1894), **Pekelharing** & **Vosmaer** (1898, *a* p. 36—38). We remarked (l. c. p. 37): "not only can we confirm this but we can give a new strong argument in favour of it. This lies in the fact that the anisochelae of *Esperella syrinx* are twisted." I can add now that this twisted nature is found in isochelae as well as in anisochelae. Consequently we may regard both as β-spiraxons.

3. *Diancistra.*

According to **Ridley** & **Dendy** (1886, p. XIX) the spicula, which **Bowerbank** called "trenchant contort bihamate", and for which they propose the name diancistra are "usually . . . more or less contort, the two hooks lying in two different planes". My own observations confirm this statement and I bring the diancistra, therefore, likewise to the β-spiraxons.

Resuming we may divide the monaxons into the following primary groups:

I.	*Pedinaxons.*	Monaxons the axis of which lies in a plane; (oxea, styles, tylostyles, etc.).
II.	*Spiraxons.*	Monaxons the axis of which is a screw helix.
A.	*α-Spiraxons.*	The axis is a line drawn on a circular cylinder; the pitch is generally great, to this group belong:

1.	*Sigmaspira.*;	smooth α-spiraxon of no more than $1^{1}/_{2}$ revolution.
2.	*Spirula*;	smooth α-spiraxon of at least $1^{3}/_{4}$ revolution.
3.	*Spinispira*;	spined α-spiraxon.
4.	*Microspira*;	very minute, smooth or spined α-spiraxon; it unites the characters of 1 and 3 diminutively, and frequently forms transitions and reductions.
5.	*Sterrospira*;	the young stages are spinispirae, from which develop by secondary soldering together of the spines the adult forms.
B.	β-*Spiraxons.*	The axis is a line, drawn on an elliptic cylinder; the pitch is always small; always less than one revolution. Hereto belong:
1.	*Sigma;*	smooth β-spiraxon.
2.	*Chela;*	the young stages are sigmata; in course of development very complicated siliceous processes grow out; we distinguish two sorts, viz. isochelae and anisochelae.
3.	*Diancistra;*	the young stages are (probably) sigmata from which develop the adult ones by outgrowth of siliceous processes.

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Physics. "*Statistical electro-mechanics.*" *II.* By Dr. J. D. VAN DER WAALS Jr. (Communicated by Prof. VAN DER WAALS.)

The distribution of the energy over the different periods in quasi-canonical ensembles.

In equation (8) of my previous communication [1]) a distribution of the energy over the different periods is included. If therefore this equation really represents the condition of a space filled with "black radiation", then a complete spectral formula for black radiation may be derived from it with the aid of the law of WIEN on the shifting of the wave-length with the temperature.

Instead of discussing the rather intricate equation (8) I have taken a simpler equation which I expected to yield the same distribution of the energy over the different periods. This simpler equation, however, proves to include a distribution which does not at all agree with the distribution of the energy which is found in black radiation. Now it is possible that the distribution, determined by the simpler equation does not agree with that, determined by equation (8). But it is also possible and for the present this seems more likely to me, that equation (8) does not represent the condition of a space filled with black radiation, or in other words that the nature of black radiation is not correctly determined by the suppositions that ε, φ and χ have a most probable value, and that for the rest the distribution is as irregular as possible. If this second explanation is the true one, the systems are still subjected to other conditions, besides those concerning the most probable values of ε, φ and χ, or, what comes to the same, the distribution of the systems of an ensemble in which the conditions for the values of ε, φ, and χ are satisfied, are moreover still partially ordered.

The simplification I have applied to equation (8) is the following. In the first place I have omitted $\frac{\omega}{\vartheta_2}$; this will no doubt have very

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[1]) These Proceedings IV, p. 27.

little influence on the distribution of the energy. Then I have confined myself to treating one dimension only, and this has induced me to omit the terms $\frac{\Omega_e+\Omega_m}{\delta_1}$. If, however, we admit electric and magnetic masses into the space, statical forces may occur. When analysed with the aid of FOURIER's integrals these statical forces actually yield a distribution of the energy over the different wave-lengths. Yet they do not contribute to the propagation of radiation, the distribution of which we wish to investigate. It is for this reason that I have preferred a distribution in time to one in space.

So we consider the component f in a certain point during the time between the moments $t=0$ and $t=t_1$. This time we think divided into n equal parts τ and the values of f during those parts we call respectively $f_1, f_2, f_3, \ldots f_n$. Then the index of probability gets the following value:

$$\eta = \frac{\psi}{\vartheta} - \frac{1}{\vartheta}\int_0^{t_1} f^2\, dt - \frac{1}{k}\int_0^{t_1} \frac{df}{dt}\, dt \quad . \quad . \quad . \quad . \quad . \qquad (8a)$$

If we wish to make the agreement of this equation with equation (8) as great as possible, we have to give to k in this equation $4\pi V^2$ times the value it has in equation (8); this follows from the equations (10) and (15).

Now we will proceed to the investigation of the distribution of the energy over the different periods, included in equation ($8a$). To that purpose we represent f as a function of t during the space of time between $t=o$ and $t=t_1$, by means of the integrals of FOURIER. As we will begin with treating f as a discontinuous function, determined by the n values $f_1, f_2 \ldots f_n$, we will represent the integral as a sum, which only becomes an integral if we make n assume the limiting value ∞. Therefore in the expression

$$f(t) = \iint f(u)\,\{sin\,(uq)\,sin\,(qt) + cos\,(uq)\,cos\,(qt)\}\,du\,dq, \quad . \quad . \qquad (26)$$

in which the limits for u are 0 and t_1 and those for q are 0 and ∞, we will replace u by $\frac{t_0}{n}\,v$ or by τv and du by τ where v represents the series of the integers between 0 and n.

So we get

$$f(t) = \tau \sum_{v=0}^{v=n} \int f_v\,\{sin\,(\tau v q)\,sin\,(qt) + cos\,(\tau v q)\,cos\,(qt)\}\,dq.$$

If we wish to separate in this equation the energy for a determined period we must give q a determined value p and then take the square of the amplitude for this vibration. So we find:

$$A_p = \boldsymbol{\tau}^2 \left\{ \sum_{v=0}^{v=n} f_v \, sin \, (\boldsymbol{\tau} vp) \right\}^2 + \boldsymbol{\tau}^2 \left\{ \sum_{v=0}^{v=n} f_v \, cos \, (\boldsymbol{\tau} vp) \right\}^2 .$$

In what follows we may omit the limits as all summations are to be executed between 0 and n; and we may omit the constant factor $\boldsymbol{\tau}^2$ as it is only our aim to determine the relative values of quantities A_p for different values of p. So we get:

$$A_p = \Sigma\Sigma \, f_v \, f_{v'} \{ sin \, (\boldsymbol{\tau} vp) \, sin \, (\boldsymbol{\tau} v'p) + cos \, (\boldsymbol{\tau} vp) \, cos \, (\boldsymbol{\tau} v'p) \}$$

$$A_p = \Sigma\Sigma \, f_v \, f_{v'} \, cos \, (v - v') \, \boldsymbol{\tau} p \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; , \qquad (27)$$

For this quantity A_p we seek the mean value for all systems of the ensemble. To this purpose we have to multiply the value of equation (27) with the probability that the quantities $f'_1 \ldots . f'_n$ have a determined, arbitrarily chosen value and consequently we have to integrate according to $df'_1 \ldots . df'_n$ between the limits $-\infty$ and $+\infty$. To that purpose we will represent $\frac{df}{dt}$ by $\frac{f_{v+1} - f_v}{\boldsymbol{\tau}}$, and we get:

$$A_p = \int e^{\frac{\psi - \boldsymbol{\tau} \Sigma f_v'^2}{\vartheta} - \frac{\Sigma (f'_{v+1} - f'_v)^2}{k \boldsymbol{\tau}}} f'_v \, f''_v \, cos \, (v - v') \, \boldsymbol{\tau} p \, df'_1 \ldots . df'_n \quad . \qquad (28)$$

If we bring the factor $e^{\frac{\psi}{\theta}}$ outside the integral sign as well the exponent of e as the other factor under the integral sign are homogeneous quadratic functions. By the introduction of other variables we may transform both functions to terms of n squares and in the same time it is possible to choose the variables in such a way, that all coefficients which occur in the exponent are unity. So we may bring the integral into the following form:

$$\int e^{-(\varphi_1^2 + \varphi_2^2 \ldots . \varphi_n^2)} (\beta_1 \varphi_1^2 + \beta_2 \varphi_2^2 + \beta_3 \varphi_3^2 \ldots \beta_n \varphi_n^2) \, \Delta \, d\varphi_1 \ldots d\varphi_n \qquad (29)$$

where Δ represents the determinant of JACOBI. The linear substitution required to get this form may be thought to be executed in two operations: 1st a substitution which yields

$$\chi_1^2 + \chi_2^2 \ldots \chi_n^2$$

for the exponent and:

$$a_{11} \chi_1^2 + a_{22} \chi_2^2 + \ldots . a_{nn} \chi_n^2 + 2 \, a_{12} \chi_1 \chi_2 \ldots . + 2 \, a_{(n-1)n} \chi_{n-1} \chi_n$$

for the other factor; 2nd an orthogonal substitution in consequence of which both functions assume the form they have in equation (29).

The determinant of JACOBI for the total substitution is the product of the determinants for the partial distributions. The determinant for the orthogonal substitution has the value unity; so only the determinant for the first partial substitution remains. This substitution has been chosen without taking into account the form of the second factor. The coefficients which determine this substitution depend therefore only on the coefficients of the exponent; as p does not occur in these coefficients, the determinant also cannot be a function of p, and so we may omit it in what follows.

The integral (29) can easily be integrated and yields:

$$C\,\Sigma\,\beta$$

So we have only to calculate the sum of the coefficients β. These coefficients may be found by the solution of the following equation of which they represent the n roots:

$$\begin{vmatrix} a_{11}-\beta & a_{12} & a_{13} & \dots & a_{1n} \\ a_{21} & a_{22}-\beta & a_{23} & \dots & a_{2n} \\ a_{31} & a_{32} & a_{33}-\beta & \dots & a_{3n} \\ \dots & \dots & \dots & \dots & \dots \\ a_{n1} & a_{n2} & a_{n3} & \dots & a_{nn}-\beta \end{vmatrix} = 0 \; . \quad . \quad . \qquad (30)$$

The sum of the coefficients β is the sum of the roots of this equation, i.e. the coefficient of β^{n-1}. Only the product of the elements of the diagonal of the determinant yields terms containing β^{n-1}; and as is obvious, the coefficient of β^{n-1} will be

$$a_{11} + a_{22} + a_{33} + \; . \; . \; . \; a_{nn}$$

In order to determine this sum we have to find an arbitrary substitution for which the exponent assumes the form $\Sigma\chi^2$ and then we must substitute the new variables χ into the second factor. A substitution fulfilling this condition may easily be found. The exponent namely may be written as follows:

$$\frac{\tau}{\vartheta}\,\Sigma f_v^2 + \frac{1}{k\tau}\,\Sigma\,(f_{v+1}-f_v)^2 = \Sigma\,(\alpha f_v - \beta f_{v+1})^2$$

where:

$$\alpha^2 + \beta^2 = \frac{\tau}{\vartheta} + \frac{2}{k\tau} \quad \text{and} \quad -2\,\alpha\beta = -\frac{2}{k\tau}\,.$$

So we find for α and β:

$$\alpha = -\tfrac{1}{2}\sqrt{\frac{\tau}{\vartheta}} + \tfrac{1}{2}\sqrt{\frac{\tau}{\vartheta}+\frac{4}{k\tau}}\;,\quad \beta = \tfrac{1}{2}\sqrt{\frac{\tau}{\vartheta}} + \sqrt{\frac{\tau}{\vartheta}+\frac{4}{k\tau}} \qquad (31)$$

Now we choose as new variables:

$$\alpha f_v - \beta f_{v+1} = \chi_v\,.$$

This substitution does not yield the accurate coefficients for f_1^2 and f_n^2 for, in order to get n quantities χ, we have to take as one of the new variables $\chi_n = \alpha f_n - \beta f_1$; so we introduce moreover a term $2\,\alpha\beta f_1 f_n$ which does not occur in the exponent. As however the exponent consists of an infinite number of infinitely small terms, these three terms which have not the proper coefficients will be of little importance.

These new variables are now to be introduced into equation (27). Yet it is not necessary to execute the substitution completely, for, as we have only to determine the sum of the coefficients of the squares χ_v^2, we may leave the coefficients of the products $\chi_v \chi_{v'}$ out of account. In the first place we have to express the old variables f in the new variables χ. We have:

$$\begin{aligned}\chi_1 &= \alpha f_1 - \beta f_2 \\ \chi_2 &= \qquad\qquad \alpha f_2 - \beta f_3 \\ \chi_3 &= \qquad\qquad\qquad\qquad \alpha f_3 - \beta f_4\end{aligned}$$

From this follows:

$$f_1 \begin{vmatrix} \alpha & -\beta & 0 & 0 & 0 \dots & 0 \\ 0 & \alpha & -\beta & 0 & 0 \dots & 0 \\ 0 & 0 & \alpha & -\beta & 0 \dots & 0 \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ -\beta & 0 & 0 & 0 & 0 \dots & \alpha \end{vmatrix} = \begin{vmatrix} \chi_1 & -\beta & 0 & 0 & 0 \dots & 0 \\ \chi_2 & \alpha & -\beta & 0 & 0 \dots & 0 \\ \chi_3 & 0 & \alpha & -\beta & 0 \dots & 0 \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \chi_n & 0 & 0 & 0 & 0 \dots & \alpha \end{vmatrix}$$

or $f_1 (\alpha^n - \beta^n) = \chi_1 \alpha^{n-1} + \chi_2 \alpha^{n-2} \beta + \chi_3 \alpha^{n-3} \beta^2 + \dots \chi_n \beta^{n-1}$

In the same way we find for f_v

$$\begin{aligned}f_v (\alpha^n - \beta^n) = \chi_v \alpha^{n-1} + \chi_{v+1} \alpha^{n-2} \beta + \chi_{v+2} \alpha^{n-3} \beta^2 \dots \\ \dots \chi_n \alpha^{n-1} \beta^{n-v} + \chi_1 \alpha^{v-2} \beta^{n-v+1} \dots \chi_{v-1} \beta^{n-1} \quad . \quad . \quad . \quad . \quad . \quad (32)\end{aligned}$$

In determining the products $f_v f_{v'}$ we shall always suppose that $v' > r$, and so we shall integrate v between the limits 0 and v'; v' between the limits 0 and ∞. In this way we get only one half of the quantity we have to determine. In order to find the amount contributed by the product $f_v f_{v'} \cos (v' - v) \tau p$ to the coefficient of χ_r^2, we have to distinguish three different cases:

1st. $0 < r < r$. Then the coefficient has the following form:

$$\alpha^{v+v'-2r-2} \beta^{2n+2r-v-v'} \cos (v' - v) \tau p$$

2nd. $v < r < v'$. Then:

$$\alpha^{n+v+v'-2r-2} \beta^{n+2r-v-v'} \cos (v' - v) \tau p$$

3rd. $v' < r < n$. Then:

$$\alpha^{2n+v+v'-2r-2} \beta^{2r-v-v'} \cos (v' - v) \tau p.$$

We have to seek the sum of these quantities, when r gets successively the value of all integers 1st. between 0 and v, 2nd. between v and v' and 3rd. between v' and v. v has all values between 0 and v', and v' those between 0 and n. We may write these sums in the form of integrals, if we put:

$$\tau v = u \qquad \tau v' = u' \qquad \tau r = w \qquad \tau n = t_1$$

$$\alpha^{1/\tau} = a \quad \text{and} \quad \beta^{1/\tau} = b.$$

The integration according to w may directly be executed. It yields for the three cases:

$$\int {\frac{a}{b}}^{-2w} dw = \frac{-1}{2l\frac{a}{b}} {\frac{a}{b}}^{2w}$$

If we substitute in this equation for each case the proper limits and if we then add the results for the three cases, then we get:

$$\int_0^{t_1}\!\!\int_0^{u'} \frac{-1}{2l\frac{a}{b}} \Big[b^{2t_1} \{ a^{-u+u'}\, b^{u+u'} - a^{u+u'}\, b^{-u-u'} \} + \\ + a^{t_1} b^{t_1} \{ a^{u-u'}\, b^{-u+u'} - a^{-u+u'}\, b^{u-u'} \} + \\ + a^{2t_1} \{ a^{u+u'-2t_1} b^{-u-u'+2t_1} - a^{u-u'} b^{-u+u'} \} \Big] \cos p\,(u'-u)\, du\, du'.$$

In the exponent of a we have neglected the term 2τ as it is small compared with the other terms. If we arrange the terms in another way and again suppress the constant factors we may write the integral in the following form:

$$\int_0^{t_1}\!\!\int_0^{u'} (a^{t_1}b^{t_1} - a^{2t_1}) \left(\frac{a}{b}\right)^{-u'} \left(\frac{a}{b}\right)^{u} \cos p\,(u'-u)\, du\, du' +$$

$$+ \int_0^{t_1}\!\!\int_0^{u'} (b^{2t_1} - a^{t_1}b^{t_1}) \left(\frac{a}{b}\right)^{u'} \left(\frac{a}{b}\right)^{-u} \cos p(u'-u)\, du\, du' \quad . \quad . \quad . \quad (33)$$

Integrating partially we find:

$$\int_0^{u_1} \left(\frac{a}{b}\right)^{u} \cos p(u'-u) du = \frac{1}{l\frac{a}{b}} \left[\left(\frac{a}{b}\right)^{u} \cos p(u'-u) \right]_0^{u_1} - \frac{p}{l\frac{a}{b}} \int_0^{u_1} \left(\frac{a}{b}\right)^{u} \sin p(u'-u)\, du =$$

$$= \frac{1}{b\frac{a}{b}} \left[\left(\frac{a}{b}\right)^{u} \cos p(u'-u) \right]_0^{u_1} - \frac{p}{l^2 \cdot \frac{a}{b}} \left[\left(\frac{a}{b}\right)^{u} \sin p(u'-u) \right]_0^{u_1} - \frac{p^2}{l^2\frac{a}{b}} \int_0^{u_1} \left(\frac{a}{b}\right)^{u} \cos p(u'-u) du$$

From which follows:

$$\int_0^{u_1} \left(\frac{a}{b}\right)^{u} \cos p(u'-u) du = \frac{l\frac{a}{b} \left\{ \left(\frac{a}{b}\right)^{u'} - \cos pu' \right\} - p \sin pu'}{l^2\frac{a}{b} + p^2}$$

In the same way we have:

$$\int_0^{u_1} \left(\frac{a}{b}\right)^{-u} \cos p(u'-u) du = \frac{l\frac{a}{b} \left\{ -\left(\frac{a}{b}\right)^{-u'} + \cos pu' \right\} - p \sin pu'}{l^2\frac{a}{b} + p^2}$$

If we introduce these values into expression (33), it assumes the following form:

$$\frac{1}{l^2\frac{a}{b}+p^2}\int_0^{t_1}\Bigg[(a^{t_1}-b^{t_1})\,l\frac{a}{b}-\left\{a^{t_1}\left(\frac{a}{b}\right)^{-u'}-b^{t_1}\left(\frac{a}{b}\right)^{u'}\right\}l\frac{a}{p}\,cos\;pu'\,-$$

$$-\left\{a^{t_1}\left(\frac{a}{b}\right)^{-u'}-b^{t_1}\left(\frac{a}{b}\right)^{u'}\right\}p\;sin\;pu'\Bigg]\,du'$$

Integrating this equation we get:

$$\frac{1}{l^2\frac{a}{b}+p^2}\Bigg[(a^{t_1}-b^{t_1})\,l\frac{a}{b}\,t_1-(a^{t_1}-b^{t_1})\,l\frac{a}{b}\,p-(a^{t_1}+b^{t_1})\,l^2\frac{a}{b}+$$

$$+(a^{t_1}+b^{t_1})\,l^2\frac{a}{b}\,(sin\;pt_1+cos\;pt_1)+(a^{t_1}-b^{t_1})\,p\,l\frac{a}{b}\,(sin\;pt_1-cos\;pt_1)\Bigg],$$

The fact that the terms with $sin\;pt_1$ and $cos\;pt_1$ occur, shows that the distribution depends on t_1. We might have expected this, specially as we have chosen $\alpha f_n-\beta f'_1$ as one of new variables for the substitution and therefore introduced the condition that f'_1 and f_n have about the same value. If however we take a considerable value for t_1 then the term $(a^{t_1}-b^{t_1})\,l\frac{a}{b}\,t_1$ will have decisive influence. If we now consider a region of the spectrum of some, though it be an extremely small extension and not a rigorously simple wave, then we have to admit slight variations in the value of p. The terms $sin\;pt_1$ and $cos\;pt_1$ will then have alternately the positive and the negative sign and yield zero on an average.

If t_1 has a sufficiently great value then the course of the function is principally determined by the factor $\frac{1}{l^2\frac{a}{b}+p^2}$. This expression does not present a well defined maximum value, but it has its greatest value for $p=o$ (i.e. for infinite wave-lengths), it decreases gradually with increasing p and is zero for $p=\infty$ (i. e. for infinitely small wave-lengths).

So this equation does not at all represent the distribution of black radiation. I only communicate these calculations in order to show that equations analogous to (8) or (8*a*) determine in fact a distribution of the energy over the different periods and to indicate a method for analysing such like equations.

Physics. — *"Ternary systems."* V. By Prof. J. D. VAN DER WAALS. (Continued from pag. 21).

If the temperature is so low that there is no question of critical phenomena, and if therefore both liquid sheet and vapour sheet cover the whole triangle, v_{21} is for all points either positive or negative, and the given rules for the displacement of the curves of equal pressure will therefore be followed by all points of these curves. If on the other hand the temperature is chosen so high, that the surface of saturation does not cover any longer the whole triangle, and if therefore the liquid sheet and the vapour sheet pass into each other above a certain locus in the triangle, v_{21} vanishes for the phases represented by this locus.

We may form an idea of the shape of the surface of saturation with the aid of fig. 11 (Cont. II, p. 135). Let us imagine that this figure represents a section by the vertical plane which contains the X-axis of the triangle and let us take a similar section by the vertical plane which contains the Y-axis. The value of T is then chosen such that $T > (T_{cr})_2$, and also $T > (T_{cr})_3$. In the figure mentioned P is the point, where a vertical tangent may be drawn, so this point represents a phasis which is in critical point-of-contact circumstance, and for which $v_{21} = 0$. The point C represents the plaitpoint. If we now imagine different planes which contain the axis erected in the point 0 normal to the plane of the triangle, these planes will cut the surface of saturation, and the sections will be analogous figures, which however change their shape fluently from that which they have in the POX-plane to that which they have in the POY-plane. If the pressure is lower than the lowest pressure of the points P, the two branches of the curves of equal pressure are perfectly separated lines which, if the pressure is increased, will be displaced according to the rules given above. If however the pressure has risen till the pressure of a point P has been reached, then the two branches are still separated, but on the vapour branch occurs a point for which $v_{21} = 0$. Such a point is not displaced when the pressure increases. The locus of these points forms the limit of the mixtures which may be splitted up into two phases at the given temperature. From a geometrical point of view it is the envelope of the projections of the horizontal sections of the surface of saturation, or the envelope of the projections of the curves of equal pressure. If the pressure has been increased till it has attained the value of the lowest of the pressures of the point C, then the two branches of the curves of equal pressure pass continuously into one another. But if we continue to call those phases represented by the lower sheet, vapour phases, and those phases represented by the higher sheet, liquid phases, then the vapour phases do not reach the point, where the connection of the two branches has taken place (the plaitpoint), but only the point where the value of v_{21} is zero, i. e. the point, where two successive curves of equal pressure intersect. For all points lying on one of the sides of that point of intersection, — e.g. on the side where the plaitpoint occurs, — v_{21} is positive.

These points will be displaced towards the conjugated point, when the pressure is increased; all points on the other side of the point of intersection will move away from the points, representing coexisting phases. If we, therefore, continue to use the expressions "liquid phasis" and "vapour phasis" with the same meaning as we have done till now, we must say that for points between the plaitpoint and the point for which $v_{21} = 0$ two liquid phases coexist. If for the two pairs of the ternary system we had a course of the pressure as is represented in Cont. II, p. 135, fig. 12, the above rules would continue to hold; but in this case we find a series of vapour phases coexisting with vapour phases between the plaitpoint and the point, for which $v_{21} = 0$. For these points we have then retrograde condensation of the second kind. We may expect that it will be easier to observe this phenomenon for a ternary system, than for a binary one. In order that retrogade condensation may be easily observed a rather great distance between the two sheets of the surface of saturation is required; and the distance between the sheets will be more considerable in the middle than at the ends, where we have to deal with a binary mixture, because the requirements for stability and coexistence for a ternary mixture are stricter than those for a binary mixture (See Vol. IV, p. 577). But then we have to avoid the case that a real maximum pressure occurs, for in that case we have also in the middle of the figure a point in which the two sheets touch each other.

c. *Curves of slope and nodal envelopes.*

If for a binary mixture we have construed the curves $p = f(x_1)$ and $p = f(x_2)$, we have at the same time answered the question, what phases may coexist with each other. Every line parallel to the X-axis joins a pair of coexisting phases. If on the other hand we have construed the two sheets of the surface of saturation for a ternary system, this is not sufficient in order to answer the question which phasis coexists with a given phasis. It is true that we know that the pressure must be the same, and that therefore the second phasis will be found on the other sheet at the same height as the first phasis, but as the section of the second sheet by a plane at a height equal to p is a curve and not a point, the question is not yet perfectly determined. Therefore, besides the series of curves of equal pressure, which are already given as the points which have the same height, still another series of curves must be traced on the surface of saturation which pass from lower to higher pressure and whose properties enable us to answer the question, which phasis of one of the sheets corresponds with a given phasis of the other sheet. We will again begin with treating the simplest case, in which maximum-pressures are excluded, as well for the pairs of components of which the ternary system consists, as for the ternary system itself, so the case for which the lowest pressure is equal to p_1 and the highest to p_3. The question is then, what systems of curves, starting at the point where the pressure has the lowest value and ending in the point where the pressure has the highest value, may be traced on one of the sheets or on both sheets of the surface of saturation which enable us to find, what phases coexist with each other. Such a system of curves will be found in the course of a person who would climb the inclined sheet, e. g. the liquid sheet, always moving in such a direction that he has the phasis, coexisting with the point, where he is at the moment, just in front of him. If we now project the tangent to the way which he has followed on a horizontal plane, the point in which this projection cuts the vapour sheet will indicate the coexisting phasis. The projection of such curves on the plane of triangle OXY has therefore the property that the tangent passes through the conjugate point, and is therefore the chord, joining the points 1 and 2; from this follows again that these projections are the envelopes of these chords. If therefore in the plane of the triangle we have drawn the two branches of the curves of equal pressure, and if we have joined a pair of nodes by a chord, an element of the curve in question will be represented by an infinitely small part of this chord. Let the point from which we start represent a liquid phasis and be its coordinates x_1 and y_1. The projections of the element of the way followed are then the quantities dx_1 and dy_1. At the end of the elementary way the second phasis is also changed, of course, and the consequence of this will be that we have to follow a curve. But the direction of the infinitely small way will always be the same as that of the chord joining the nodes; and the differential equation will therefore be given by:

$$\frac{dx_1}{x_2-x_1}=\frac{dy_1}{y_2-y_1}.$$

For these curves on the surface of saturation I have chosen the name of "curves of slope". This series of curves begins and ends with the following curves: 1st the curve $p=f(y_1)$ for the pair (1, 3), and 2nd the curve consisting of a $p=f(x_1)$ part for the pair (1, 2) and of a corresponding part for the pair (2, 3). If we draw these curves on the vapour sheet, we must imagine that we descend instead of ascending. For the projection of these curves on the plane of the triangle I have chosen the name of "nodal envelope". The outmost curves of this series are: 1st one of the sides of the triangle, adjacent to the right angle, namely that one corresponding to the third component, and 2nd a line consisting of the other side adjacent to the right angle and the hypothenuse of the triangle.

For the solution of the differential equation of these curves it is required that we may express x_2 and y_2 in x_1 and y_1. This is possible (p. 7) when the second phasis is a rare gas phasis, if we namely assume the functions μ'_{x_1} and μ'_{y_1} to be known. For that case the equation we have to integrate may be written:

$$\frac{dx_1}{x_1\left\{(1-x_1)\left(e^{\mu'_{x_1}}-1\right)-y_1\left(e^{\mu'_{y_1}}-1\right)\right\}}=\frac{dy_1}{y_1\left\{(1-y_1)\left(e^{\mu'_{y_1}}-1\right)-x_1\left(e^{\mu'_{x_1}}-1\right)\right\}},$$

or

$$\frac{dx_1}{x_1\left\{(1-x_1-y_1)\left(e^{\mu'_{x_1}}-1\right)+y_1\left(e^{\mu'_{x_1}}-e^{\mu'_{y_1}}\right)\right\}}=\frac{dy_1}{y_1\left\{(1-x_1-y_1)\left(e^{\mu'_{y_1}}-1\right)-x_1\left(e^{\mu'_{x_1}}-e^{\mu'_{y_1}}\right)\right\}},$$

$$\text{or}\quad \frac{dx_1}{x_1}\left(e^{\mu'_{y_1}}-1\right)-\frac{dy_1}{y_1}\left(e^{\mu'_{x_1}}-1\right)=\left(e^{\mu'_{y_1}}-e^{\mu'_{x_1}}\right)\frac{d(1-x_1-y_1)}{1-x_1-y_1},$$

$$\text{or}\quad \left(e^{\mu'_{y_1}}-1\right)\left\{\frac{dx_1}{x_1}-\frac{d(1-x_1-y_1)}{1-x_1-y_1}\right\}=\left(e^{\mu'_{x_1}}-1\right)\left\{\frac{dy_1}{y_1}-\frac{d(1-x_1-y_1)}{1-x_1-y_1}\right\}.$$

The last equation may also be written as follows:

$$\left(e^{\mu'_{y_1}}-1\right)d\,log\frac{x_1}{1-x_1-y_1}=\left(e^{\mu'_{x_1}}-1\right)d\,log\frac{y_1}{1-x_1-y_1}.$$

For the case that the liquid sheet is a plane, $e^{\mu'_{y_1}}-1$ and $e^{\mu'_{x_1}}-1$ are constant, and equal to $\frac{p_3-p_1}{p_1}$ and $\frac{p_2-p_1}{p_1}$ and so the equation of the nodal envelope will be given by:

$$\left(\frac{x_1}{1-x_1-y_1}\right)^{\frac{p_3-p_1}{p_1}}=C\left(\frac{y_1}{1-x_1-y_1}\right)^{\frac{p_2-p_1}{p_1}},$$

or
$$x_1^{\left(\frac{p_3-p_1}{p_1}\right)} = C\, y_1^{\left(\frac{p_2-p_1}{p_1}\right)} (1-x_1-y_1)^{\left(\frac{p_3-p_2}{p_1}\right)},$$
an equation in which all exponents are positive as appears from the values of p_1, p_2 and p_3.

For $C=0$ this equation is satisfied by $x_1=0$ and therefore the nodal envelope coincides with the Y-axis. For $C=\infty$ either y_1 or $1-x_1-y_1$ is zero, and for this value of C the nodal envelope coincides with the X-axis and the hypothenuse. For the special case, for which $p_2 = 2\,p_1$ and $p_3 = 3\,p_1$ the equation assumes the following shape:

$$x_1^2 = C\, y_1\, (1-x_1-y_1).$$

This is the equation of a conic section which touches the X-axis and the hypothenuse in the points in which they cut the Y-axis. Whatever the values of p_1, p_2 and p_3 may be, the curve will touch the X-axis and the hypothenuse in the points mentioned, if only the condition $p_1 < p_2 < p_3$ be satisfied, and the same would hold true if on the other hand $p_1 > p_2 > p_3$ be fulfilled. The nodal envelope for which $C=0$ will of course be an exception to this rule.

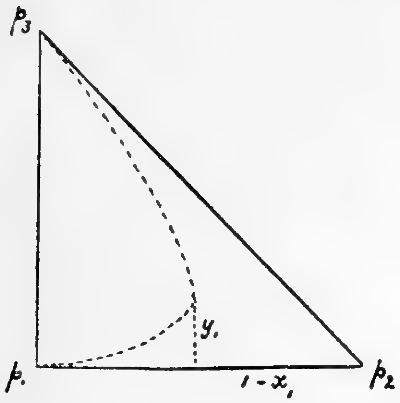

Fig. 13.

In the adjoined figure 13 the general course of the nodal envelope is represented in the above described circumstances. Though the calculated formula only holds for μ'_{x_1} and $\mu'_{y_1}=$ constant the shape of the curve will agree in main features with the one, drawn here, always if neither on the sides, nor anywhere in the middle of the surface of saturation a maximum pressure occurs.

Only the details are different. For the locus of the points where the tangent of the nodal envelope is parallel to the Y-axis for instance, we find in the case that μ'_{x_1} and μ'_{y_1} are constant a right line passing through the intersection of the X-axis and the hypothenuse. For $\frac{dy_1}{dx_1} = \infty$ for such points and so $dx_1 = 0$. But then also $x_2 - x_1 = 0$.

As follows from the equations (p. 11).

$$\frac{x_2-x_1}{x_1} = \frac{(1-x_1)\,(e^{\mu'_{x_1}}-1) - y_1\,(e^{\mu'_{y_1}}-1)}{1 + x_1\,(e^{\mu'_{x_1}}-1) + y_1\,(e^{\mu'_{y_1}}-1)}$$

and

$$\frac{y_2-y_1}{y_1}=\frac{(1-y_1)\left(e^{\mu'_{y_1}}-1\right)-x_1\left(e^{\mu'_{x_1}}-1\right)}{1+x_1\left(e^{\mu'_{x_1}}-1\right)+y_1\left(e^{\mu'_{y_1}}-1\right)}$$

we have:

$$x_2-x_1=0$$

if

$$1-x_1=y_1\frac{e^{\mu'_{y_1}}-1}{e^{\mu'_{x_1}}-1}$$

This equation represents a right line, if the factor of y_1 is constant, and it yields $x_1=1$ if $y_1=0$. If the surface of saturation is a plane, i.e. if $e^{\mu'_{x_1}}=\frac{p_2}{p_1}$ and $e^{\mu'_{y_1}}=\frac{p_3}{p_1}$, then the equation of this right line is:

$$1-x_1=y_1\frac{p_3-p_1}{p_2-p_1}.$$

This right line coincides with the liquid branch of the projection of the curve of the pressure p_2. (See our previous communication, p. 14).

If μ'_{x_1} and μ'_{y_1} are not constant, i.e. if the factor of y_1 is variable, then the locus of the points for which $x_2-x_1=0$ is of course not straight, but it will be a curve, which, however, if the condition $\mu'_{y_1}>\mu'_{x_1}$ continues to be satisfied, will start from the same angle of the triangle. In this case the line for which $x_2-x_1=0$ does no longer coincide with the line for which the pressure is equal to p_2. If we put in equation (7) of p. 12.

$$1-x_1=y_1\frac{e^{\mu'_{y_1}}-1}{e^{\mu'_{x_1}}-1}$$

then we find:

$$\log\frac{p}{MRT}=\mu_{x_1y_1}+(1-x_1)\mu'_{x_1}-y_1\mu'_{y_1}-1.$$

If we denote the value of μ for $x=1$ and $y=0$ by μ_{10}, then we have:

$$\log\frac{p}{p_2}=\mu_{x_1y_1}+(1-x_1)\mu'_{x_1}-y_1\mu'_{y_1}-\mu_{10}.$$

The second member of this equation represents the distance between the point of intersection of the tangential plane to the μ-surface and the vertical axis of the second component, and between the ordinate μ_{10}. If the whole surface lies below the tangential plane, as is probable, then the second member is positive and $p>p_2$, and the difference between p and p_2 increases, if the point of intersection lies at a greater distance from the second component, and if the deviation of the surface μ from a plane surface is more considerable.

The succession of the values of the pressures p_1, p_2 and p_3 involves that the condition $y_2 - y_1 = 0$, which would lead to:

$$1 - y_1 = x_1 \frac{e^{\mu'_{x_1}} - 1}{e^{\mu'_{y_1}} - 1}$$

cannot be fulfilled, for in that case the factor of x_1 would be less than unity, and the equation:

$$1 - y_1 = x_1 \frac{e^{\mu'_{x_1}} - 1}{e^{\mu'_{y_1}} - 1}$$

with constant value of μ'_{x_1} and μ'_{y_1} would then in fact represent a line through the summit of the triangle; but a line outside the triangle. But we will return to this condition presently.

These nodal envelopes have an analogous significance as that of the lines of force in the magnetic field. In the same way as the tangents of the lines of force determine the direction of the force, but not its intensity, so the tangents of the envelopes determine the direction in which the second phasis is to be found; but they do not indicate the distance between the points 1 and 2. This distance, however, is perfectly determined if also both branches of the curves of equal pressure and triangle OXY are drawn. Then we find the second phasis which coexists with a given liquid phasis, by drawing in the point representing the liquid phasis the tangent to the nodal envelope of that point; the point of intersection of this tangent and the vapour branch for the pressure of the liquid phasis represents the second phasis. If we do this for all points of the same nodal envelope then we get a new locus, which we may call conjugated curve of the nodal envelope. In order to give the equation of this conjugated curve we must be able to express x_1 and y_1 as functions of x_2 and y_2 and we must substitute these functions in the equation of the envelope. In general, however, we are not able to do this, not even in the case that the second phasis is a rare gas phasis. Only in the case that μ'_{x_1} and μ'_{y_1} may be considered as constants it can easily be executed. If we write the equation of the envelope as follows:

$$\left(\frac{x_1}{1-x_1-y_1}\right)^{(e^{\mu'_{y_1}} - 1)} = C \left(\frac{y_1}{1-x_1-y_1}\right)^{(e^{\mu'_{x_1}} - 1)},$$

which only may be admitted for constant value of μ'_{x_1} and μ'_{y_1}, and if we take into account that:

$$\frac{x_1}{1-x_1-y_1}=\frac{x_2\,e^{-\mu'x_1}}{1-x_2-y_2}$$

and
$$\frac{y_1}{1-x_1-y_1}=\frac{x_2\,e^{-\mu'y_1}}{1-x_2-y_2}$$

then the substitution into the equation of the envelope yields the following formula:

$$\left(\frac{x_2\,e^{-\mu'x_1}}{1-x_2-y_2}\right)^{(e^{\mu'y_1}-1)}=C\left(\frac{y_2\,e^{-\mu'y_1}}{1-x_2-y_2}\right)^{(e^{\mu'x_1}-1)},$$

or
$$\left(\frac{x_2}{1-x_2-y_2}\right)^{(e^{\mu'y_1}-1)}=C'\left(\frac{y_2}{1-x_2-y_2}\right)^{(e^{\mu'x_1}-1)}.$$

From this follows that the conjugated curve of a nodal envelope of liquid phases, is, in the chosen circumstances again a nodal envelope, with another value of the constant, namely:

$$C'=C\left(\frac{p_2}{p_1}\right)^{\frac{p_3-p_1}{p_1}}\left(\frac{p_1}{p_3}\right)^{\frac{p_2-p_1}{p_1}}.$$

If $p_1 < p_2 < p_3$, the factor of C is greater than unity and the conjugated curve is therefore to be found nearer the hypothenuse. Only in the case that $p_2=p_3$ we have $C''=C$; but then the system is only apparently a ternary one, and the envelope degenerates into a straight line with the equation:

$$x=Cy:$$

It appears therefore that the conjugated curve in this case always coincides with the envelope.

We might also have considered the nodal envelope for vapour phases. Then we consider the projection of the way which we should follow, if we descend on the vapour sheet from the point where the pressure has the highest value towards the point, where it has the lowest value, always moving in such a direction that we have the liquid phasis just in front. We find the equation of this curve if we express the values of x_1 and of y_1 as functions of x_2 and y_2 and if we substitute those functions into:

$$\frac{dx_2}{x_1-x_2}=\frac{dy_2}{y_1-y_2}$$

This is only possible if μ'_{x_1} and μ'_{y_1} are constant as we have already mentioned several times. With the aid of the equations:

$$\frac{x_1}{1-x_1-y_1}=\frac{x_2}{1-x_2-y_2}\,e^{-\mu'x_1}$$

and
$$\frac{y_1}{1-x_1-y_1}=\frac{y_2}{1-x_2-y_2}\,e^{-\mu'y_1},$$

we find a differential equation, which differs from the one treated p. 124 in so far that x_2, y_2, dx_2 and dy_2 are substituted for x_1, y_1, dx_1 and dy_1, and that $-\mu'_{x_1}$ and $-\mu'_{y_1}$ are substituted for μ'_{x_1} and μ'_{y_1}. In the integral found there the same substitutions must of course be performed. So we find:

$$\left(\frac{x_2}{1-x_2-y_2}\right)^{(e^{-\mu'_{y_1}}-1)} = C\left(\frac{y_2}{1-x_2-y_2}\right)^{(e^{-\mu'_{x_1}}-1)}$$

or

$$\left(\frac{x_2}{1-x_2-y_2}\right)^{\left(\frac{p_1}{p_3}-1\right)} = C\left(\frac{y_2}{1-x_2-y_2}\right)^{\left(\frac{p_1}{p_2}-1\right)}$$

This equation may also be written in the following form:

$$x_2^{\frac{p_2}{p_1}\frac{p_3-p_1}{p_1}} = C_2\, y_2^{\frac{p_3}{p_1}\frac{p_2-p_1}{p_1}} (1-x_2-y_2)^{\frac{p_3-p_2}{p_1}}$$

For $C_2=0$, we have also $x_2=0$, and the Y-axis is therefore the first of the envelopes, just as was the case for the liquid phases. For $C_2=\infty$ we have $y_2=0$ and $1-x_2-y_2=0$. The last of the envelopes is therefore also here the X-axis and the hypothenuse. Though the equation of the two series of envelopes is different, the course is in many respects analogous. These envelopes also touch the hypothenuse in their beginning and touch the X-axis in their final point. They have a tangent parallel to the Y-axis, and the locus of the points where this is the case, is found from the equation:

$$x_1-x_2=0$$

or

$$1-x_2=y_2\frac{1-e^{-\mu'_{y_1}}}{1-e^{-\mu'_{x_1}}}$$

or

$$1-x_2=y_2\frac{p_2}{p_3}\frac{p_3-p_1}{p_2-p_1}.$$

This locus coincides with the vapour branch of the curve of pressure p_2. This nodal envelope has a conjugated curve, which is again a nodal envelope with greater value of the constant, just as is the case for the liquid phases.

Before we proceed to the discussion of the nodal envelopes in more complicated cases, namely in those in which a maximum pressure occurs either on the sides of the triangle or for a point inside the triangle, we will make some general observations about peculiar points of these curves, which, however, only apply to the case that the second phasis is a rare gas phasis.

From the equation:

$$\frac{x_2}{1-x_2-y_2}=\frac{x_1}{1-x_1-y_1}e^{\mu'_{x_1}}$$

$$\frac{y_2}{1-x_2-y_2}=\frac{y_1}{1-x_1-y_1}e^{\mu'_{y_1}}$$

we deduce that the nodal envelopes have tangents which pass through the angles of the triangle, if either μ'_{x_1}, or μ'_{y_1}, or $\mu'_{y_1} - \mu'_{x_1}$ are equal to zero. The tangent contains the angle representing the third component, if $\mu'_{x_1} = 0$; that representing the second component if $\mu'_{y_1} = 0$; and that for the first component if $\mu'_{y_1} = \mu'_{x_1}$.

The conditions that a tangent of the envelope is parallel to one of the sides of the triangle may be deduced from the values of $x_2 - x_1$ and $y_2 - y_1$. So from $x_2 - x_1 = 0$ follows the condition that the tangent is parallel to the side of the first and the third components. This condition has the following form:

$$\frac{y_1}{1-x_1} = \frac{e^{\mu'_{x_1}} - 1}{e^{\mu'_{y_1}} - 1}.$$

Now $\frac{y_1}{1-x_1} = \tan\alpha$, where α represents the angle enclosed between the radius vector drawn from the second component, and the X-axis. As α must be less than 45°, we get for the condition for the existence of points where the tangent is parallel to the Y-axis:

$$\tan\alpha = \frac{e^{\mu'_{x_1}} - 1}{e^{\mu'_{y_1}} - 1}$$

and $\mu'_{x_1} < \mu'_{y_1}$, if both are positive.

The condition that the tangent is parallel to the X-axis may be derived from $y_2 - y_1 = 0$ and has the following form:

$$\frac{x_1}{1-y_1} = \frac{e^{\mu'_{y_1}} - 1}{e^{\mu'_{x_1}} - 1}$$

As $\frac{x_1}{1-y_1} = \tan\beta$, where β represents the angle, enclosed between the radius vector drawn from the third component, and the Y-axis, we may write this condition as follows:

$$\tan\beta = \frac{e^{\mu'_{y_1}} - 1}{e^{\mu'_{x_1}} - 1}$$

and $\mu'_{x_1} > \mu'_{y_1}$, if both are positive.

The condition that the tangent is parallel to the hypothenuse may be derived from:

$$\frac{y_2 - y_1}{x_2 - x_1} = -1.$$

From this we deduce:

$$\frac{y_1}{x_1} = -\frac{e^{\mu'_{x_1}} - 1}{e^{\mu'_{y_1}} - 1}$$

Therefore a tangent of the nodal envelope parallel to the hypothenuse can only occur in the case that μ'_{x_1} and μ'_{y_1} have different sign.

All these relations apply only to the case that μ'_{x_2} and μ'_{y_2} may be equated to zero; and the given rules will require corrections when the temperature is increased and approaches one of the critical temperatures. If T has reached a value higher than $(T_{cr})_3$ for instance, and consequently the surface of saturation does not cover the whole triangle any more, the envelopes can no longer pass through the angle of the third component. Even without knowledge of the equation of the envelopes we can understand in the following way what peculiarity will then come into the shape of those curves. The surface of saturation has in the vertical plane containing the Y-axis, and also in that containing the hypothenuse still the shape of fig. 11, Cont. II. The first curve of slope lies in the first mentioned vertical plane and consists of that part of the p curve of the figure mentioned which extends to the maximum, i.e. to the point C. All other points of this pressure-curve, as well those between C and P as those forming the lower branch, represent coexisting phases and belong to the conjugated curve of this curve of slope. The last of these curves of slope lies above the X-axis and above the hypothenuse, but above the hypothenuse it also extends only to the projection of the point of maximum pressure. Every intermediate nodal envelope has initially the shape of fig. 13, has also still a vertical tangent, but ends in a point (the projection of a plaitpoint) before it has reached the locus which represents the limit of the points above which the surface of saturation extends. Above such a limiting point of the nodal envelope the curve of slope of which it is the projection has reached its highest point. Before the limiting point however the course has been modified. In order to discuss this modification we will derive the second derivative function, namely $\frac{d^2y_1}{dx_1^2}$. From:

$$\frac{dy_1}{dx_1} = \frac{y_2 - y_1}{x_2 - x_1} \text{ follows}$$

$$\frac{d^2y_1}{dx_1^2}\,dx_1 = \frac{(x_2-x_1)(dy_2-dy_1)-(y_2-y_1)(dx_2-dx_1)}{(x_2-x_1)^2},$$

or
$$\frac{d^2y_1}{dx_1{}^2}\,dx_1 = \frac{(dy_2-dy_1) - \dfrac{dy_1}{dx_1}(dx_2-dx_1)}{(x_2-x_1)}$$

or
$$\frac{d^2y_1}{dx_1{}^2}\,dx_1 = \frac{dy_2 - \dfrac{dy_1}{dx_1}\,dx_2}{(x_2-x_1)}.$$

When we write it in this form we see that $\frac{d^2y_1}{dx_1{}^2} = 0$ for that phasis for which dx_2 and dy_2 are zero, so for that phasis which coexists with the critical point of contact. If we write:

$$\frac{d^2y_1}{dx_1{}^2}\frac{dx_1}{dx_2} = \frac{\dfrac{dy_2}{dx_2} - \dfrac{dy_1}{dx_1}}{(x_2-x_1)},$$

then the value of $\frac{d^2y_1}{dx_1{}^2}$ assumes for the plaitpoint, where $x_2 = x_1$, and $\frac{dy_2}{dx_2} = \frac{dy_1}{dx_1}$ a shape which is indefinite. As, however, the points 1 and 2 are situated on opposite sides of the plaitpoint, and the point 2 must always lie on the tangent of 1, and the curve containing the points 1, the nodal envelope will present a point of inflection in the plaitpoint, i.e. in the point where it ends. The further continuation to the locus of the critical points of contact belongs to the conjugated curve, and this must reverse its course either abruptly or fluently, where it meets the locus mentioned.

Let us now pass to the discussion of the course of the nodal envelope in the case that a maximum pressure exists on one of the sides of the triangle. We shall suppose it to occur on the X-axis, so that the succession of the pressures is given by:

$$p_1 < p_2 < p_{12} < p_3.$$

If for a certain value of x_1 a maximum pressure occurs on the X-axis, then $x_2 - x_1 = 0$, and $y_1 = 0$; from which follows that for the point representing the phasis with maximum pressure we have:

$$\mu'_{x_1} = 0\,.$$

The locus, represented by $\mu'_{x_1} = 0$, (see our previous communication p. 9) cuts therefore one of the sides of the triangle adjacent to the right angle, namely that one which joins the angles representing the first and the second component. Inside this triangle therefore also a continuous series of points occurs for which this condition is satisfied. The shape of this locus cannot be determined without the knowledge of the equation of state. It might be derived from the equation on

p. 9, if T_{cr} and p_{cr} were known as functions of x and y. If we assume, that T_{cr} is proportional to $\frac{a}{b}$ and p_{cr} is proportional to $\frac{a}{b^2}$, as follows from the form of the equation of state I have adopted, then we see that $\mu'_{x_1} = 0$ in the case under consideration represents a feebly bent curve, which starting from the X-axis intersects either the Y-axis or the hypothenuse. Which of these lines will be cut depends on the values of $(T_{cr})_1$ and of $(T_{cr})_2$ and on the size of the molecules of the components 1 and 2. As intermediate case the curve $\mu'_{x_1} = 0$ might pass through the angle of the third component. In fig. 14 I have represented it by curve DF, so I have assumed it to cut the hypothenuse. The area of the triangle may be divided into two parts according to the value of μ'_{x_1}. On the left of DF this quantity is positive; on the right of DF it is negative. As the quantity μ'_{y_1} does not change its sign in the case under consideration (the pressure not presenting a maximum on the lines AC and BC), the value of $\frac{\mu'_{x_1} - 1}{\mu'_{y_1} - 1}$ is positive on the left of DF, and negative on the right. The points in which the tangents to the nodal envelopes are vertical, can therefore only be found on the right of DF; tangents parallel to the hypothenuse on the other hand can occur on the left of DF. On the line DF itself the tangents have a direction, passing through the point C. The curve DI represents the locus of the points whose tangent is vertical, and the curve DH that of the points whose tangent is parallel to the hypothenuse. We may easily form an idea of the course of the nodal envelopes themselves in main features if we consider them as slight modifications of the shape they should have if the curve DF were a straight line, directed towards the summit C. In that case namely the course of the envelopes in the left part is the same as that of fig. 13, — with the modification which follows from the fact that one of the sides, adjacent to the right angle is smaller than the other, — and in the right part it is symmetrical with fig. 13 with regard to the Y-axis, — with the modification which follows from the fact that an obtuse angle occurs instead of the right angle. In the left part $AD + DC$ is one of the outmost envelopes; in the right part $BD + DC$.

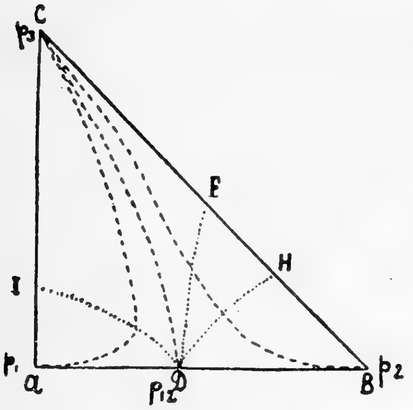

Fig. 14

If also one of the other sides of the triangle presents a maximum pressure, e. g. the Y-axis, then we have to deal with still another locus: $\mu'_{y_1} = 0$. The circumstance whether the two curves $\mu'_{x_1} = 0$ and $\mu'_{y_1} = 0$ intersect or not decides whether for a ternary system a maximum pressure exists or not. The given rules concerning the peculiar points of the envelopes enable us in this and other cases to conclude to the course. But I will no longer dwell upon this subject. I consider the preceding discussion as sufficient to draw attention to the significance of these curves for the knowledge of a ternary system.

d. *The addition of a third component to a given binary system.*

If we have a binary system consisting of $1-x_0$ molecules of the first kind and x_0 molecules of the second kind, and we add to it a third component so that the final composition is given by $1-x-y$, x and y, then we have:

$$\frac{x}{1-x-y} = \frac{x_0}{1-x_0} .$$

From this relation we derive:

$$\frac{x}{x_0} = 1-y ;$$

from which we conclude, that the points representing the ternary system lie on a straight line, which connects the summit of the rightangled triangle with that point on the opposite side that represents the composition of the binary system.

Taking into account the values of $\frac{\partial^2 \zeta}{\partial x_1^2}$, $\frac{\partial^2 \zeta}{\partial x_1 \partial y_1}$ and of $\frac{\partial^2 \zeta}{\partial y_1^2}$ given on p. 5 and substituting the value $-x_0\, dy_1$ for dx_1, we find from formula II of p. 1.

$$\frac{v_{21}}{MRT}\frac{dp}{dy_1} = (x_2-x_1) \left\{ \frac{-x_0(1-y)}{x_1(1-x_1-y_1)} + \frac{1}{1-x_1-y_1} + \mu''_{x_1y_1} - x_0\mu''_{x_1} \right\} +$$
$$+ (y_2-y_1) \left\{ \frac{-x_0}{1-x_1-y_1} + \frac{1-x_1}{y_1(1-x_1-y_1)} + \mu''_{y_1} - x_0\mu''_{x_1y_1} \right\} .$$

This equation may be simplified to:

$$\frac{v_{21}}{MRT}\frac{dp}{dy_1} = (x_2-x_1) \{ \mu''_{x_1y_1} - x_0\mu''_{x_1} \} + (y_2-y_1) \left\{ \frac{1}{y_1(1-y_1)} + \mu''_{y_1} - x_0\mu''_{x_1y_1} \right\} .$$

In order to get the corresponding equation for the vapour phases, we must interchange the indices 1 and 2; it has the following form:

$$\frac{v_{21}}{MRT}\frac{dp}{dy_2} = (x_1-x_2) \{ \mu''_{x_2y_2} - x'_0\mu''_{x_2} \} + (y_1-y_2) \left\{ \frac{1}{y_2(1-y_2)} + \mu''_{y_2} - x'_0\mu''_{x_2y_2} \right\}$$

If the gas phases are very rarified the latter equation may be simplified to:

$$\frac{1}{p}\frac{dp}{dy_2}=\frac{y_2-y_1}{y_2(1-y_2)},$$

which form is identical with that which applies if a second component is added to a simple substance, and from which accordingly the quantity x'_0 has disappeared. This identity of the form of the *equation* does, however, not justify the conclusion that also the shape of the *curve* $p=f(y_2)$ will be identical. The same form of the *equation* applies also to a binary system, and yet it includes the great variety of curves which the pressure as a function of the composition of the vapour can present. All those differences in shape are to be ascribed to the different ways in which y_1 and y_2 depend upon each other. In the same way every plane section of the vapour sheet for a ternary system by a plane, normal to the plane of the triangle and passing through the summit, will be represented by this equation, though these sections may present an infinite variety of forms, which again may differ from those of a binary system. Yet we may make use of this equation and deduce some general properties from it. So e. g. $\frac{dp}{dy_2}$ will be zero if on the chosen section a point x_2, y_2 occurs for which

$$y_2-y_1=0\ .$$

If the succession of the values of the pressures is $p_1<p_2<p_3$ this can never occur. In this discussion, however, we will think the succession to be changed according to the circumstances in order that we are not obliged to draw the section every time through another angle of the triangle. If the succession is $p_1<p_3<p_2$ a locus occurs indeed, for which $y_2=y_1$ and this locus coincides with that for which the pressure of the vapour phases which occur on the chosen section is maximum or minimum. We might have expected a priori that in general a maximum or minimum would be found on the section which passes through the angle for the component whose pressure lies between those of the other components, and which cuts the opposite side in a point with the same pressure. This maximum or minimum will, however, not have the same significance as that of a binary system. For in the case of a binary system the composition of the vapour is the same as that of the liquid phasis; for a ternary system only y_1 and y_2 are equal, but x_1 and x_2 differ. In such a point the pressure of the liquid phasis is not equal to that of the vapour phasis — as is the case with the maximum pressure of a binary system, — but the pressure of

the liquid is higher than that of the vapour. The two sheets do not touch one another in such points. It is true that the pressure for a point conjugated to such a point is the same, but $\frac{dp}{dy_1}$ is different from zero, as appears from the equation for $\frac{dp}{dy_1}$. If we substitute in this equation $y_1 = y_2$, we find:

$$\frac{1}{p}\frac{dp}{dy_1} = (x_2 - x_1)\{\mu''_{x_1y_1} - x\,\mu''_{x_1}\}.$$

The factor $x_2 - x_1$, which also may be written $\frac{d\mu'_{x_1}}{dy_1}$ depends on the curvature of the μ-surface, and in all cases in which the surface is only slightly bent it will have only a small value; but only in very special cases it will be rigorously zero. In general therefore we may assume, that this locus of the maximum liquid pressures does not deviate much from the locus for which $y_2 - y_1 = 0$. If the projections of the curves of equal pressure are drawn, the points of maximum pressure and the sections discussed by us are of course immediately to be determined, by tracing the tangents, passing through the angles of the triangle.

The value of $\frac{v_{21}}{MRT}\frac{dp}{dy_1}$ assumes exactly the same shape it has for a binary system if either $(x_1 - x_2)$ or $\frac{d\mu_{x_1}}{dy_1}$ are zero. The value of $x_2 - x_1$ vanishes in the first place if the quantity we have denoted by x_0 is zero, and in the second place if it is equal to unity. But in these cases we are really dealing with binary systems; in the first case with the pair 1,3 and in the second with the pair 2,3. In the first case we have:

$$\frac{v_{21}}{MRT}\frac{dp}{dy_1} = (y_2 - y_1)\left\{\frac{1}{y_1(1-y_1)} + \mu''_{y_1}\right\}$$

and in the second case, if

$$1 - x_2 - y_2 = 1 - x_1 - y_1, \text{ or } x_2 - x_1 = -(y_2 - y_1):$$

$$\frac{v_{21}}{MRT}\frac{dp}{dy_1} = (y_2 - y_1)\left\{\frac{1}{y_1(1-y_1)} + \mu''_{y_1} - 2\,\mu''_{x_1y_1} + \mu''_{x_1}\right\}.$$

The quantity $\mu''_{y_1} - 2\,\mu''_{x_1y_1} + \mu''_{x_1}$ has for the pair 2,3 the same signification as μ''_{y_1}, for the pair 1,3, as is easily understood.

The quantity $\frac{v_{21}}{MRT}\frac{dp}{dy_1}$ assumes also this simple shape in the very peculiar points, where $x_1 - x_2 = 0$ either inside the triangle or on one of its sides, and also in the points where $\frac{d\mu'_{x_1}}{dx_1}$ vanishes.

But in general the quantity $(x_2-x_1)(\mu''_{x_1y_1}-x_0\mu''_{x_1})$ will cause a modification in the course of the value of the pressure which is very slight. The value of the pressure depending principally on the term $\frac{y_2-y_1}{y_1(1-y_1)}$.

We will consider more closely this last quantity, which represents the limiting value of $\frac{1}{p}\frac{dp}{dy_1}$ for $y_1=0$ or $y_1=1$, for a binary mixture and which for a ternary system is to be augmented with $(x_2-x_1)_0\frac{d\mu'_{x_1}}{dy_1}$.

We have found before the following value for $\frac{y_2-y_1}{y_1}$:

$$\frac{y_2-y_1}{y_1}=\frac{(1-y_1)(e^{\mu'_{y_1}}-1)-x_1(e^{\mu'_{x_1}}-1)}{(1-x_1-y_1)+x_1e^{\mu'_{x_1}}+y_1e^{\mu'_{y_1}}},$$

From this value we deduce, if we set $y_1=0$ and $x_1=x_0$

$$\frac{y_2-y_1}{y_1(1-y_1)}=\frac{(e^{\mu'_{y_1}}-1)-x_0(e^{\mu'_{x_1}}-1)}{1+x_0(e^{\mu'_{x_1}}-1)}=\frac{e^{\mu'_{y_1}}}{1-x_0+x_0e^{\mu'_{x_1}}}-1$$

where μ'_{x_1} and μ'_{y_1} have the values they have in the point whose coordinates are $x_1=x_0$ and $y_1=0$. This value, which for $x_0=0$ is equal to $e^{\mu'_{y_1}}-1$, has for $x_0=1$ the final value $e^{\mu'_{y_1}-\mu'_{x_1}}-1$, and varies fluently with increasing x_0; and now the way in which $\frac{1}{p}\frac{dp}{dy_1}$ varies depends upon the relation between μ'_{y_1} and μ'_{x_1}. This value may have reversed its sign, either from negative to positive or from positive to negative. The quantity $\mu'_{y_1}-\mu'_{x_1}$ represents the variation of μ for the motion along the hypothenuse towards the summit of the triangle in the same way as μ'_{y_1} represents the variation for the motion along the Y-axis towards the summit. If therefore T_{cr} for the summit is lower than $(T_{cr})_1$, then μ'_{y_1} is positive, and if T_{cr} for the summit is higher than $(T_{cr})_2$ then $\mu'_{y_1}-\mu'_{x_1}$ is negative.

It is not superfluous to point out in how high a degree the value of $\frac{1}{p}\frac{dp}{dy_1}$ depends on the value of μ'_{y_1}, if it represents the initial direction of a curve of equal pressure for a binary system. According to our former observations this value is equal to $e^{\mu'_{y_1}}-1$. If we also draw the vapour curve, then $\frac{1}{p}\frac{dp}{dy_2}=\frac{y_2-y_1}{y_2}$, and so it is equal to:

$\frac{e^{\mu' y_1}-1}{e^{\mu' y_1}}=1-e^{-\mu' y_1}$. If we draw moreover the curve of the double points then we have $\frac{dp}{pdy}=\mu'_{y_1}$. For the case that $\mu'_{y_1}=0$ we always find zero as well for the value of $\frac{1}{p}\frac{dp}{dy_1}$ as for $\frac{1}{p}\frac{dp}{dy_2}$ and $\frac{1}{p}\frac{dp}{dy}$. If μ'_{y_1} is positive, the three lines ascend, and they descend if μ'_{y_1} is negative. If the value of μ'_{y_1} is very small, there is only a small difference in the slope of the three curves. But if μ'_{y_1} has not so very small a value, then there is a very great difference in the slope of the three curves, and the liquid branch ascends exceedingly fast.

As
$$\mu'_{y_1}=-\frac{f}{T}\frac{dT_{cr}}{dy_1}+\frac{d\log p_{cr}}{dy_1},$$
we shall have a great value μ'_{y_1}, if $\frac{dT_{cr}}{dy_1}$ has a considerable negative value, so if the T_{cr} of the second component is much lower, e.g. if we press a permanent gas into a liquid. As in general T_{cr} does not depend linearly on y_1 and $\frac{d\log p_{cr}}{dy_1}$ has a value differing from zero, we shall not find the accurate value for μ'_{y_1}, putting:
$$\mu'_{y_1}=\frac{f}{T}\{(T_{cr})_1-(T_{cr})_2\}$$
but only a more or less approximated value. If we choose for the second component a substance whose T_{cr} is much lower than T and for the first component a substance, whose T_{cr} is much higher than T, we do not take an impossible value for μ'_{y_1}, if we give it the value 14 or 15 for ordinary temperature. In that case $e^{\mu' y_1}$ may in rough approximation be represented by 10^6. If we might apply the results we have obtained, also in the case of water, though its behaviour is specially at low temperatures very abnormal, then we might form an idea of the degree of approximation by means of the absorption coefficients of gases solved in water.

According to our results we find for small values of y_1, if we neglect the vapour pressure of the first component compared with the total pressure:
$$p=p_1\,y_1\,(e^{\mu' y_1}-1).$$

Here p_1 represents the vapour pressure of the first component. Further we have, denoting the absorption coefficient by a, and the molecular weight and the density of that component by m_1 and d_1:

$$y_1 = \frac{m_1}{d_1} \frac{0{,}0013}{28{,}8} \alpha p.$$

If we neglect unity to $e^{\mu' y_1}$, we may derive from these two equations:

$$e^{\mu' y_1} = \frac{d_1}{m_1} \frac{28{,}8}{0{,}0013} \frac{1}{\alpha p_1}.$$

If we put in this equation $d_1 = 1$, $m_1 = 18$ and $p_1 = \frac{4.6}{760}$ Atmospheres, and $\alpha = 0{,}02$ as is the case for N_2, then we find for μ'_{y_1} a value between 16 and 17. This result shows that the equation

$$\mu'_{y_1} = \frac{f}{273} \{(T_{cr})_w - (T_{cr})_{N_2}\}$$

does indeed hold as an approximation.

If we had chosen as second component a substance of small volatility and whose T_{cr} is much higher than $(T_{cr})_1$, then we might form an idea of the value of μ'_{y_1} by making use of the approximation:

$$\mu'_{y_1} = \frac{f}{T} \{(T_{cr})_1 - (T_{cr})_2\},$$

but then we should find a very great negative value for μ'_{y_1} and for $\frac{y_2}{y_1} = e^{\mu' y_1}$ a value which differs only slightly from zero.

When we add a third component to a binary system whose composition is determined by x_0, then we have found for the value of $\frac{1}{p}\frac{dp}{dy_1}$, if y_1 is infinitely small:

$$\frac{1}{p}\frac{dp}{dy_1} = \frac{e^{\mu' y_1}}{1 - x_0 + x_0 e^{\mu x_1}} - 1 + (x_2 - x_1)_0 \{\mu''_{x_1 y_1} - x_0 \mu''_{x_1}\}.$$

The two branches of the pressure-curve of this section do not start in the same point and so they differ already from the beginning from those of a binary system. Only if $(x_2 - x_1)_0 = 0$ they start at the same point. But as the factor of $x_2 - x_1$ depends on the curvature of the μ surface the influence of this term may be neglected specially when μ'_{y_1} is great or when the curvature is considerable. So we find for the value of x_0 for which $\frac{1}{p}\frac{dp}{dy_1}$ vanishes approximately:

$$x_0 = \frac{e^{\mu' y_1} - 1}{e^{\mu' x_1} - 1}.$$

Only when $\mu'_{y_1} < \mu'_{x_1}$ this yields a possible value for x_0 at least if as well μ'_{y_1} as μ'_{x_1} are positive.

Geology. — "*Cambrian Erratic-blocks at Hemelum in the South-west of Frisia.*" By J. H. BONNEMA. (Communicated by Prof. J. W. MOLL).

To the East of Molkwerum, a railway-station between Leeuwarden and Stavoren, stretches a region that from a geological point of view is very remarkable; as was especially shown by the interesting researches of Dr. VAN CAPPELLE. [1])

The road first leads in a North-eastern direction to the village of Koudum, which is situated on elevated ground. As far as here the surface showed alluvial clay only; now we see for the first time diluvial formations. The outer part of this elevation consists of boulder-clay, whereas in two sand-pits it may be easily observed that preglacial layers form the inner part.

A little farther on, when the alluvial grounds are reached again, one comes to the Galama-dams. They are found on the Morra, according to the above-named author a bottommoraine-lake.

About a mile farther upward we again find diluvial soil, and on continuing our journey in the direction of Rijs we see, just before leaving Hemelumer-Oldephaert and Noordwolde, and entering the domain belonging to Gaasterland, in a meadow to the right of the road a large pit 8 metres deep. From this pit for some years boulder-clay has been dug in behalf of the brick-works of the Comp. "Gaasterland", at a short distance, on the other side of the road.

As far as I know, these are the only brick-works in the Northern part of the Netherlands, where bricks are made of boulder-clay.

The boulder-clay, which forms a bottom-moraine here and which must be found very deep in the earth, is coloured blue-grey. Only quite near the humus-layer it has become red-brown, under the influence

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[1]) VAN CAPPELLE, Les Escarpements du „Gaasterland" sur la côte meridionale de la Frise. Extrait du Bulletin de la Société Belge de géologie, de paléontologie et d'hydrologie 1889.

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VAN CAPPELLE, Bijdrage tot de kennis van Frieslands bodem. V. Karteering van 't diluvium van Gaasterland en Hemelumer-Oldephaert en Noordwolde. Tijdschr. v. h. Kon. Nederl. Aardrijksk. Genootschap. 1895.

VAN CAPPELLE, Diluvialstudien im Südwesten von Friesland. Verhandelingen der Koninkl. Akad. v. Wetensch. te Amsterdam. 1895.

of the weather. It contains comparatively few erratic-blocks. They often show very fine glacier-scratches and are mostly of average size.

During the time when this opportunity of gathering erratic-blocks has presented itself, I have several times visited, from Leeuwarden, this loam-pit. The result of these visits is that I brought home rather a large number of erratic-blocks (probably between 300 and 400).

The sedimentary ones are still here at present; after studying them I intend to present them to the Geological Institute at Groningen. The others, whose number is small compared with that of the sedimentary stones, have already been given to this Institute.

Though my collection is still small, it is large enough to confirm my opinion that our knowledge of our sedimentary erratic-blocks leaves much to be desired. I formed this opinion already after examining the erratic-blocks of Kloosterholt. [1])

In gathering erratic-blocks in the Gron. Hondsrug I had gradually come to the conclusion that our sedimentary ones almost exclusively originated from Silurian layers, and that the latter must have shown much resemblance to those of the Russian Baltic-sea provinces, perhaps are still to be found there. On getting acquainted with the erratic-blocks in the boulder-clay of Kloosterholt, however, I could not but see very soon that at any rate this rule does not hold good in all cases. In this place I often found pieces of older and younger formations, while corresponding stones occur as firm rocks in Sweden and Denmark. The very same phenomena, as I hope I shall indicate, are seen in the erratic-blocks of Hemelum. Besides Silurian formations, others, both older and younger, are numerously represented. At the same time all of them show almost exclusively a West-baltic character.

We should then see the remarkable phenomenon that at Groningen, which is situated between Kloosterholt and Rijs, erratic-blocks greatly differ from those of the two places mentioned.

Gradually, however, I am beginning to doubt whether my opinion about the character of the erratic-blocks in the Groningen Hondsrug should be the right one. In the years when I used to gather there, digging was atmost entirely confined to the upper layers, so the chances are, that deeper parts contain other kinds of erratic-blocks.

A few facts seem to indicate this. First of all: while a deep cave was being dug under the brewery called Barbarossa, at Helpman, big blocks of Saltholmlime with Terebratula lens Nilss made their

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[1]) Van Calker. Ueber eine Sammlung von Geschieben von Kloosterholt. Zeitschr. d. Deutsch. Geol. Gesellsch. Jahrgang 1898 p. 234.

Bonnema, De sedimentaire zwerfblokken van Kloosterholt. Versl. v. d. Koninkl. Akad. van Wetensch. te Amsterdam 1898 pag. 448.

appearance. Some pieces of this material are still to be seen in the Geological Institute at Groningen.

Secondly: van Calker[1]), — when the ramparts near one of the gates (Boteringepoort), which ramparts had certainly been made of the boulder-clay from the very deep ditches in that neighbourhood, were dug off, — found some erratic-blocks consisting of kinds of stone such as I never found afterward, and which do not occur in the Russian Baltic-Sea provinces, i.a. slate with graptolites, Faxe-lime and sandy glauconite lime-stone with Terebratula lens Nilss.

Deeper cuts made into the Hondsrug may afterwards give us an opportunity of learning whether my original opinion was entirely right, or is the true one only as far as the outer layers are concerned.

I should now like to tell something about the chief Cambrian pieces that are found in my collection. I am going to treat only of those stones whose age may be more or less precisely determined.

I. Lower-Cambrian Stones.

1. Scolithus-sandstone. Eleven stones consisting of this material are found in my collection. Nine of them are typical grey, quartziferous Scolithus-sandstone, showing a peculiar, fatty lustre on the side where they were broken off. No layers are visible as long as the stone is not changed by the influence of the weather. Only if this takes place, the layers become more or less visible. In one stone they are rather distinct and turn upward (perhaps downward) near the "scolithus." Two other stones, one of which is blue-grey, whilst the other moreover contains red parts, are clearly divided into layers and contain much finer tubes than are found in the typical stone. In the regions from which our erratic-blocks come, Scolithus-sandstone was first seen as firm rock in the isle of Runö near Oscarshamm, where according to Torell[2]) it was discovered by Dr. Holmström. Afterwards it was also met with as such by Nathorst[3]), in the isle of Furön, not far from Runö.

I was wrong when, in treating of the Kloosterholt erratic-blocks, I told that Scolithus-sandstone as firm rock is found in Sweden, in the neighbourhood of Lund and Kalmar. The same mistake was

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[1]) Van Calker, Beiträge zur Kenntniss des Groninger Diluviums. Zeitsch. d. deutsch geol. Gesellsch. Jahrg. 1884 pag. 718 and 727.

[2]) Torell, Petrificata Suecana formationis cambricae. Lunds Univ. Årsskrift. Tom. VI 1869 pag. 12.

[3]) Nathorst, Geol. Föreningens i Stockholm Förhandlingar 1879. Bd IV, pag. 293.

made by SCHROEDER VAN DER KOLK [1]) and by STEUSLOFF [2]). The latter and I probably came to make it unter the influence of what was told by ROEMER [3]) with regard to the origin of this kind of erratic-blocks. With SCHROEDER V. D. KOLK this is certainly the case, as appears from the note at the bottom of the page.

As to their being found at Hardeberga in the neighbourhood of Lund, ROEMER seems to have forgotten the fact that TORELL [4]), though he at first communicated that the Hardeberga sandstone contained worm-shaped bodies probably belonging to Scolithuslinearis Hall, afterwards makes mention of a new kind, viz. Scolithuserrans TORELL [5]). The latter are distinguished for being mostly curbed and running through the stone in various directions.

ROEMER'S information that TORELL describes Scolithuslinearis from an erratic-block found near Lund, and that according to NILSSON Scolithus-sandstone occurs near Calmar (as firm rock), must be attributed to an error. If my imperfect acquaintance with the Swedish language does not deceive me, TORELL [6]) writes that the place where the pictured stone (an erratic-block) was found, cannot be indicated for sure, but that NILSSON thinks he remembers that it was found near Calmar.

In the Northern part of the Netherlands erratic-blocks of Scolithus-sandstone are rather common. In Frisia were found, besides the stone treated of above, one in the Roode klif (Red Cliff) [7]), one in the Mirnsercliff [8]) and one at Warns (see number 3). Among the erratic-blocks of the Gron. Hondsrug [9]) only one piece was found up to this time, whereas I formerly described already two pieces from Kloosterholt [10]) and afterwards gathered more of them there. In the

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[1]) SCHROEDER VAN DER KOLK, Bijdrage tot de kennis der verspreiding onzer kristallijne zwervelingen. Dissertatie pag. 50.

[2]) STEUSLOFF, Sedimentärgeschiebe von Neubrandenburg. Archiv des Vereins der Freunde der Naturgeschichte in Mecklenburg. Jahrg. 45 pag. 162.

[3]) ROEMER, Lethaea erratica pag. 23.

[4]) TORELL, Bidrag till Sparagmitetagens geognosi och paleontologi. Lunds Univ. Årsskrift. Tom. IV. pag. 35.

[5]) TORELL, Petrif. Suec. format. cambric. pag. 12.

[6]) TORELL, Bidrag till Sparagmitetagens geogn. och paleontol. pag. 29.

[7]) VAN CAPPELLE, Bijdrage tot de kennis van Frieslands bodem. II pag. 12.

[8]) VAN CAPPELLE, Les Escarpements du „Gaasterland", pag. 236.

[9]) VAN CALKER, Ueber das Vorkommen cambrischer und untersilurischer Geschiebe bei Groningen. Zeitschr. d. deutsch. geol. Gesellsch. Bd XLIII pag. 793.

[10]) VAN CALKER, Ueber eine Sammlung von Geschieben von Kloosterholt, pag. 235. BONNEMA, De sedim. zwerfblokken van Kloosterholt, pag. 449.

province of Drente VAN CALKER [1]) mentions Buinen, Steenbergen and Zeegse as places where he came across these stones, whereas I myself found some at Odoorn.

2. Grey sandstone with interlaced coloured layers.

A small piece of quartziferous sandstone, 7 centimetres long, is almost entirely grey-coloured. Two systems of coloured layers, varying from red to violet, interlacing under angles of about 30 degrees, are also found. The layers of each system separately run parallel to each other. Surfaces of deposit do not occur and the size of the grains of sand is everywhere the same, so that it is impossible to examine which layer-system runs parallel to them.

This sandstone was made mention of for the first time by NATHORST [2]), who found erratic-blocks consisting of it in Jungfrun in the Kalmarsund. With DAMES [3]) he found the same kind of stone in Oeland, a few years after. Later on the latter writer [4]) could tell about this kind of erratic-block occurring in diluvial layers in the neighbourhood of Berlin.

As one of the pieces found there contains Scolithus-tubes, he could also draw the conclusion that their age is the same as that of the above mentioned Scolithus-sandstone. This conclusion is confirmed by means of a piece of Scolithus-sandstone that I found at Warns a short time ago. Through the grey piece of sandstone run on one side a few violet-coloured layers, which are intersecting the Scolithus-tubes under an angle of 60 degrees, while the latter always stand perpendicularly on the surfaces of deposit, which are not seen here.

That this stone also occurs in the Dutch diluvium, was already shown by VAN CALKER [5]); he proves that it is found in the erratic-blocks of the Gron. Hondsrug.

II. Mid-Cambrian Stones.

3. Limesandstone with Paradoxides-remains.

In my collection I have also a piece of grey, fine-grained sandstone with a large quantity of calcium-carbonate as binding-material.

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[1]) VAN CALKER, Ueber ein Vorkommen von Kantengeschieben und von Hyolithus- und Scolithus-Sandstein in Holland. Zeitschr. d. deutsch. geol. Gese'lsch. Jahrg. 1890 pag. 583.

[2]) NATHORST, Geol. Föreningens i Stockholm Förhandlingar 1879. Bd IV pag. 293.

[3]) DAMES, Geol. Reisenotizen aus Schweden. Zeitschrift der deutsch. geol. Gesellschaft. Jahrg. 1881 pag. 417.

[4]) DAMES, Zeitschr. d. deutsch. geol. Gesellsch. Jahrg. 1890. Bd XLIII pag. 777.

[5]) VAN CALKER, Zeitschr. der deutsch. geol. Gesellsch. Jahrg. 1891. Bd XLIII pag. 793.

Through the stone run intersecting passages of the same mineral. Here and there are small grains of glauconite and pyrites-crystals. Besides many Paradoxides-fragments arranged in layers, my stone contains remains of horn-shelled Brachiopoda. The former are cream-coloured and do not allow of being further defined. Among the latter are easily found valves of Acrotele granulata Linn.

About this stone I have up to this time nowhere found any information. It is probably of the same age with the layers of Paradoxides Tessini Brongn., or it is a little older than these are.

4. Gravel-stone with Paradoxides Tessini Brongn.

a. It is a piece of fine-grained, hard sand-stone, yellow-grey inside and light grey nearer the surface, whilst the surface itself is brown in some places. With a magnifying-glass some grains of glauconite and a few mica-scales may be distinguished in it.

With muriatic acid applied to it, there is no effervescence; consequently it does not contain calcium-carbonate. There are no layers.

The chief remnant occurring in this erratic-block is a mid-shell, a little more than 1 centimetre long, of a Paradoxides, which mid-shell is visible for the greater part. The cream-coloured shell is still almost entirely present. That this remnant originates from Paradoxides Tessini Brongn., could be easily determined by means of the description and the pictures which Linnarsson [1]) gave us of this kind. Prof. Moberg, to whom I had the honour of showing this erratic-block, when visiting Lund, thought my determination right.

The glabella increases in breadth towards the front; quite near the front it is broadest. The front-edge is rounded off. On each side the glabella has two side-furrows, which in the middle run into those of the other side, which is also the case with Paradoxides Oelandicus. Of smaller furrows, which according to Linnarsson are sometimes found in the latter, nothing is to be seen here. The edge before the glabella is very narrow in the middle and broadens towards the ends. This is characteristic of Paradoxides Tessini, whilst with Paradoxides Oelandicus the breadth of the edge before the glabella is rather considerable, and remains about the same towards the sides.

We also find here a piece of a thorax-ring of a kind of Paradoxides, in which it may be seen that the pleurae first run straightway towards the outside and then turn to the back, forming an almost right angle. This also occurs with Paradoxides Tessini, whereas with Paradoxides Oelandicus this turning to the back takes place gradually.

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[1]) Linnarsson, Om Faunan i Kalken med Conocoryphe exsulans („Coronatus kalken"). Sveriges geologiska undersökning. Series C. N⁰ 35 pag. 6. Scene I fig 1—4.

Finally are found in this erratic-block a few small valves of horn-shelled Brachiopoda, among which is one of Lingula or Lingulella.

b. Besides the piece treated of just now I found a piece of sandstone with Paradoxides-remains, which shows no effervescence when hydrochloric acid is applied to it, and which consequently is gravel-stone.

It is a flat piece, consisting of two parts of a different nature. One of them is formed by sandstone and does not present many layers. This sandstone greatly resembles the material of which consists the erratic-block treated of under *a*, but is a little bluish. Some small mica-scales and glauconite-grains are also present here. The other part shows many more layers and has a dark bluish-grey colour. Sometimes the layers are as thin as paper, so that the material becomes slate-like.

Just as in the other piece of stone, the Paradoxides-remains are cream-coloured here. They are, however, too fragmentary to enable us to draw the conclusion that they originate from Paradoxides Tessini. As up to this time, however, only sandstone with this kind of Paradoxides has been found in diluvial grounds, and the petrographical nature of one part of them bears a great resemblance to that of the previous piece, I think I may suppose this much, and I venture to range this erratic-block under this head.

I think that both pieces originate from a layer-complex of gravel-stone with Paradoxides Tessini-remains, which complex consisted both of slate-like blue-grey parts and of thicker light-coloured layers. The last-mentioned erratic-block may originate from the former, whereas the one treated of under *a* would be a piece of a thicker layer.

If my supposition is not false, it may be easily explained from the difference in firmness and the difference in fitness for being transported issuing from this, why in literature nothing is found about erratic-blocks that should bear resemblance to the last-mentioned piece, whilst two or three communications have been received about the finding of erratic-blocks that most probably are more like the piece treated of in the first place.

The first communication we got from Roemer.[1] It deals with a piece of gravel-stone that was found in a sand-pit of Nieder-Kunzendorf near Freiberg in Silesia. It seems to have been more exposed to the influence of the weather than the erratic-block found by me, the writer mentioned speaking of a ferrugious outer crust, while round my piece such a crust begins to form itself.

Probably I must also range among this kind a piece of sandstone

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[1] Roemer, Zeitschr. der deutsch. geol. Gesellschaft. Bd 9. Jahrg. 1857 pag. 511.

with Paradoxides Tessini-remains that was found in the collection of Groningen erratic-blocks, given to the geological Institute at Lund by Mr. DE SITTER, L. L. D., then burgomaster of Groningen. It was described by LUNDGREN [1]). I am sorry that we do not learn whether it is gravel-stone or lime-sandstone. I wrote to Prof. MOBERG, director of the Institute mentioned above, in order to ask after this, but he could not give me any information concerning the piece just then. I think, however, that it is gravel-stone, LUNDGREN telling us that the colour is „gråhvit”, while according to ROEMER [2]) lime-sandstone with Paradoxides Tessini is dark grey.

While in the previous case it has not yet been with certainty determined which kind of sandstone one has to deal with, REMELÉ [3]) has announced another gravel-stone with Paradoxides-remains having been found. This erratic-block differs from the piece I described under *a* in the fossils being coloured brown by manganite-superoxide. However, I think this of little importance, as it may be just as well a consequence of infiltration that occurred in diluvial grounds or even before that time.

Gravel-stone with Paradoxides Tessini has up to this time not been met with as firm rock. Probably it occurs as such, or did so in former times, in the neighbourhood of Oeland; for on the Western coast of this isle is found, in several places, lime-sandstone with the same kind of trilobites.

III. Upper-Cambrian Stones.

5. Alum-slate with Agnostus pisiformis L. var. socialis Tullb.

One time I was so fortunate as to find a piece of black slate, in which are scattered the grey head- and tailshields, preserved in relief, of a kind of Agnostus. They have a length and a breadth of 3 millimetres at most.

The head-shields are moderately vaulted. The dorsal furrows meet in front, and a tongue-shaped glabella is bounded by them. At the front-part of the glabella is on each side a lateral furrow. The two lateral furrows run into each other and in this way cut off a small part in front. At the foot of the glabella two small lobes are separated from the rest by means of two lateral furrows slanting backward. The central, largest part of the glabella shows

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[1]) LUNDGREN, Geologiska Föreningens i Stockholm Förhandlingar. 1874. II N⁰ 2 pag. 44.

[2]) ROEMER, Lethaea erratica, pag. 29.

[3]) RÉMELÉ, Zeitschr. der deutsch. geol. Gesellschaft. Bd 35. Jahrg. 1883 pag. 871.

in the midst a wedge-shaped elevation. The cheeks are in front separated by a furrow running from the front of the glabella to the edge-furrow.

The tail-shields are much more vaulted. This is especially the case with the rhachis, which broadens towards the back and stretches nearly as far as the edge. Consequently, the lateral parts of the pygidium, which are already narrow, become even more so towards the back part. They are not separated by a furrow, as it is the case with those of the head-shields. The pygidia have at the back-edge on either side a little cog pointing backward. The rhachis of the pygidia is clearly divided into three parts. The back-part is the largest by far and is particularly swollen. The lateral furrows of one side do not meet those of the other, as they are separated by a wedge-shaped elevation passing on from the second part to the first and ending towards the back in a blunt point slanting upward.

From the properties mentioned it may be easily seen why this kind of Agnostus was described by TULLBERG [1]) as Agnostus pisiformis L. var. socialis. Pictures of it have been given by BRÖGGER [2]) and POMPECKI [3]).

Up to this time this erratic-block is the only piece of alum-slate with Agnostus pisiformis L. var. socialis that was found in our diluvial grounds. In Germany they also seem to be very rare. Only GOTTSCHE [4]) mentions such a piece from SCHULAU. This one also contains, however, remains of Olenus truncatus Brünn. As firm rock such alum-slate with this variety of trilobites occurs in Sweden (Oeland and Bornholm included), in different places, as I learned from Prof. MOBERG, to whom I showed a piece of the erratic-block.

Microbiology. — "*Accumulation experiments with denitrifying bacteria*". By G. VAN ITERSON JR. (Communicated by Prof. M. W. BEIJERINCK).

The great signification of the denitrifying bacteria for the circulation of nitrogen in organic life and the important biochemisms to which they give rise, made the study of these organisms very attractive.

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[1]) TULLBERG, Om Agnostus-arterna i de Kambriska aflagringarne vid Andrarum. Sveriges geologiska Undersökning. Ser. C. N⁰ 42 pag. 25.

[2]) BRÖGGER, Die Silurischen Etagen 2 und 3 im Kristianiagebiet und auf Eker. Pag. 56. Taf. 1. fig. 10 a b c.

[3]) POMPECKI, Die Trilobiten-Fauna der Ost- und Westpreussischen Diluvialgeschiebe. Beiträge zur Naturkunde Preussens herausgegeben von der Physikalisch-Oekonomischen Gesellschaft zu Königsberg. Pag. 15, Taf. IV, fig. 24 a b.

[4]) GOTTSCHE, Die Sedimentär-Geschiebe der Provinz Schleswig-Holstein, pag. 11.

In the first place it was necessary to subject their distribution in nature and their isolation to an investigation, because the literature thereon offers but very deficient data. The best way to attain this object seemed to try whether the method of "accumulation" gave in this case, as in so many others, any definite result, and that for the following reasons.

The character of this way of experimenting is the cause, that many biological properties of the species there by accumulated may be predicted;

it renders it possible, in a simple way, directly and with certainty to isolate from nature a determined species; this is of special interest inasmuch the cultures of most bacteria, by being kept in the laboratoria, change their character to such a degree as to become irrecognisable, so, that the descriptions, found in bacteriological literature, according as they are made after newly isolated or long kept material, may be wholly different;

it teaches us to recognise the sought- for species in the different varieties occurring in the material used for infection, as these varieties are bound to corresponding culture conditions;

the identification and synonymy of the bacteria, which are always extremely difficult, even in case we possess good descriptions, made of freshly isolated cultures, are much facilitated by good "accumulation experiments";

these may, moreover, be controlled by anyone, and render the investigator independent from material isolated by others.

For the arrangement of my experiments I have followed the example given by Dr. H. H. GRAN [1]) of Bergen in his researches in the Bacteriological Laboratory at Delft on denitrifying sea bacteria. By exclusively using nitrate as source of nitrogen in the culture liquid, which was contained in a cotton-plugged flask, so that the air could freely enter, he succeeded to restrict considerably the number of developing species of bacteria, when taking fresh sea-water for infection, bringing the denitrifying species to vigorous growth. He furthermore selected, as source of carbon the calciumsalts of organic acids, by which the prejudicial alkaline reaction, which appears in bouillon in consequence of the decomposition of the alkalinitrate, was avoided. Mostly calciummalate was used, which is a very good bacterial food, and has moreover the advantage of solving only to 0,8 °/₀ at 25° C., so that it can be added to an excess, whence, as the salt is oxidised, a new quantity is solved.

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[1]) Studien über Meeresbacteriën I. Bergens Museums Aarbog 1901 N⁰. 10.

After 2 or 3 successive inoculations in the same liquid a constant bacterial mixture was obtained.

I tried to apply these principles to the isolation of denitrifying land-bacteria, and so-doing I succeeded indeed, when using calcium-tartrate as source of carbon, to accumulate *Bacillus vulpinus*, hereafter to be discussed.

It proved however to be a fundamental improvement wholly or partly to exclude the access of air as thereby the growth of the denitrifying bacteria is not in the least impeded, whilst a number of other aerobic bacteria are very much hindered in their development.

Of the numerous methods of culture under exclusion of air I have followed the simplest, namely the "bottle method", long since in use in the Bacteriological Laboratory at Delft for the examination of the sulphate reduction by microbes and the lactic-acid fermentation. For my experiments this method proved perfectly adapted, as the quantity of air which finds access, can thereby easily be regulated. An ordinary, narrow-mouthed stoppered bottle, with an exactly fitting stop, is quite or partly filled with the culture liquid, and after sterilising or not, according to circumstances, the bottle is placed in the thermostat for culture.

1. *Historical.*

The reduction of nitrates by bacteria constantly begins with the formation of nitrite. This may be further converted in five different ways, viz.:

1st. It may be reduced to ammonia.

2nd. It may be converted into unknown, nonvolatile nitrogen compounds.

3rd. If in the liquid acid is formed simultaneously, it may give rise to the development of nitrogen-oxygen compounds.

4th. It may be decomposed in alkaline solution under formation of nitrogen-oxygen compounds.

5th. The nitrite may, in alkaline solutions, give rise to the development of nitrogen without the production of nitrogen-oxygen compounds. This is *denitrification proper*, of which here is only question.

Already in 1814 Davy [1]) states that during putrefaction of animal matter nitrogen as such is freed. "Here it is again seen," says in 1860 G. J. Mulder [2]), from whom I borrow this particular, "if one wishes

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[1]) Elemente der Agriculturchemie, Berlin 1814, S. 309.

[2]) De Scheikunde der Bouwbare Aarde, 1860, dl. 3, blz. 58.

truly to give the cuique suum in this part of science, one often must retrograde half a century."

Not before 1856 the problem was again taken into research. In that year Reiset [1]) pointed out, that at the putrefaction of dung and flesh free nitrogen is produced. Later investigators have not been able to observe free nitrogen under these circumstances, in asmuch as no nitrate or nitrite are present, but the putrefaction of albuminous matter as such has still remained an open question from this point of view.

It was Pelouze [2]), who in 1857, for the first time, with certainty stated the disappearance of nitrate during the putrefaction of animal matter.

Boussingault [3]) observed in 1858 the disappearance of salt-peter in the soil. He ascribed it "à une cause purement accidentelle, à une action réductrice, exercée par de la matière végétale morte".

From the year 1873 date very interesting observations of Schloesing [4]) on nitrification. By studying the influence of oxygen on this process, he was led to the examination of denitrification. He found that nitrification in the soil was still very active, when it was held in a current of gas, which contained but 1,5 $^0/_0$ oxygen. If he worked in a current of pure nitrogen, there not only occurred no nitrification, but even the nitrate, originally in the soil, disappeared entirely. He furthermore proved that at this decomposition nitrogen is formed.

Experiments of Pasteur and the well known investigation of Schloesing and Münz on nitrification, induced Gayon and Dupetit [5]) to ascribe denitrification to the action of micro-organisms. In 1882 they communicated their first results and these put the bacterial nature of the process out of all doubt. Their elaborate and excellent researches on this subject were published in 1886 [6]).

Our compatriots Giltay and Aberson [7]) isolated, for the first time, in 1892 a denitrifying ferment, and the prescription given by them for the artificial culture liquid has been followed by various later investigators.

The attention of bacteriologists was again fixed on these ferments

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[1]) Expériences sur la putréfaction et sur la formation des fumiers. C. R. 1856, T. 42, p. 53.

[2]) Remarques de M. Pelouze. C. R. 1857, T. 44, p. 119.

[3]) Nouvelles observations sur le développement des *hélianthus* soumis à l' action du salpètre donné comme engrais C.R. 1858, T. 47, p. 807.

[4]) Etude sur la nitrification dans les sols, C.R. 1873, T. 77, p. 203.

[5]) Sur la fermentation des nitrates, C.R. 1882, T. 95, p. 644.

[6]) Recherches sur la réduction des nitrates par les infiniments petits. Nancy. 1886.

[7]) Recherches sur un mode de dénitrification et sur le schizomycète qui la produit. Arch. Neerl. T. 25, 1892, p. 341.

by interesting agricultural experiments of P. WAGNER [1]) in 1895, which seemed to point out a danger produced by these bacteria for agriculture.

His experiments gave direct cause to the research of BURRI and STUTZER [2]), who, in the same year, elaborately described two denitrifying bacteria.

From that time this group has been laboriously studied and at present a number of twenty denitrifying species have been described [3]).

To these I for my own part might add some ten species more, but of these I will only discuss those, for which I can point out an accumulation experiment, which gives a constant result.

2. *General considerations.*

The hitherto isolated denitrifying bacteria are all aerobic. In liquids containing nitrate or nitrite, they can, however, grow vigorously with a very slight or without access of air, so that in this case they behave like anaerobic bacteria. They then transfer the oxygen of the nitrate or the nitrite to the organic compounds present in the culture liquid. Thence nitrogen is freed and the metals of the salts pass into carbonates or bi-carbonates, which process may be represented by the formulae:

$$5\,C.. + 4\,KNO_3 + 2\,H_2O = 4\,KHCO_3 + 2\,N_2 + CO_2$$

$$3\,C.. + 4\,KNO_2 + H_2O = 2\,KHCO_3 + K_2CO_3 + 2\,N_2$$

The correctness of this representation has been proved by the observations of GAYON and DUPETIT, GILTAY and ABERSON, PFEIFFER and LEMMERMANN, AMPOLA and ULPIANI, and also by my own researches.

We see from this, that in a liquid, simultaneously with the nitrate, the rate of organic substances decreases, and accordingly also the permaganate number. From a practical point of view this must necessarily be of signification for the explanation of the processes on which is based the biological purification of sewage and water [4]).

My experiments have furthermore convinced me that denitrification is inseparably connected with the growth, for which traces of free oxygen are always necessary.

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[1]) Die geringe Ausnützung des Stallmiststickstoffs und ihre Ursachen, Landw. Presse, 1895, S. 92.

[2]) Ueber denitrifizierende Bakterien. Centrbl. f. Bakt. Abt. II, Bd. 1, 1895, S. 257.

[3]) O. LEMMERMANN. Kritische Studiën über Denitrifikationsvorgänge. Jena. 1900. C. HÖFLICH. Vergleichende Untersuchungen über die Denitrifikationsbakt. etc. Centrbl. f. Bakt., Abt. II, Bd. 7, 1902, S. 245.

[4]) Dr. JENNY WEYERMAN. Biologische stelsels tot reiniging van rioolvocht, enz. Vragen des Tijds. Febr. 1901, Sep., blz. 38.

In 1897 Weissenberg [1]) pronounced the hypothesis, that, at the reduction of nitrate to free nitrogen, nitrite constantly appears as interphase. I can perfectly well share this view, and that for the following reasons:

1st. All denitrifying species which I have studied in the course of this research could, in as much as they produced free nitrogen from nitrate, do the same from nitrite.

2nd. Like Burri and Stutzer (l.c.) I have been able to isolate a species, which does convert nitrite into free nitrogen, but leaves nitrate intact, so that from a mixture of nitrite with a little nitrate, all the nitrite is removed by this bacterium, whilst the nitrate remains unchanged.

Here I must however observe, that at the conversion of nitrate into free nitrogen, not always nitrite can be detected in the culture. This fact has already been stated by Sewerin [2]) and Künnemann [3]). It is however by no means in contradiction with Weissenberg's hypothesis, for if the course of the second process: decomposition of nitrite, is quicker, or as quick as the first: reduction of nitrate, the nitrite-phase is no more to be demonstrated.

Künnemann observed this fact in a variety of *B. stutzeri,* which observation I have been able to confirm; however, in my opinion, the cultural conditions played in this experiment a much more important part than the character of the variety. In bouillon with 0,1 $^0/_0$ KNO_3, I could often point out no nitrite, whilst here a strong development of gas took place. On the other hand, I obtained with 4 and 5 $^0/_0$ KNO_3 only a slight gas development, but a strong reaction of nitrite.

For the investigation of a colony on its denitrifying power, sterile test-tubes were filled with 10 à 15 Ccm. of bouillon, as well with 0,1 $^0/_0$ KNO_3 as with 0,1 $^0/_0$ KNO_2 and then inoculated. Denitrifying bacteria grow therein sufficiently, after 24 hours to produce a distinct turbidity, whilst, at the surface they form a scum-layer. Sometimes the scum is wanting, but is produced at shaking the test-tube.

Besides were used solutions of calcium-salts of organic acids, decocts of pease-leaves with 2 $^0/_0$ cane-sugar, and decocts of potatoes, likewise with 0,1 $^0/_0$ KNO_3 or KNO_2.

In this case a control experiment was made to decide, whether without addition of nitrate or nitrite, these solutions might cause

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[1]) Studien über Denitrification. Arch. f. Hygiene. 1897, Bd. 30, S. 274.

[2]) Zur Frage über die Zersetzung von Salpetersauren Salzen durch Bakterien. Centrbl. f. Bakt. Abt. II, 1897, Bd. 3, S. 504.

[3]) Ueber denitrifizierende Mikro-organismen. Landw. Versuchs-Stat. 1898, Bd. 50, S. 65.

development of gas, which proved never to be the case with denitrifying bacteria.

In order to obtain perfectly convincing results, to the said culture liquids 10 °/₀ gelatin often was added and, when in the boiled solution, at about 30° C., some of the culture had been suspended, it was poured into a test-tube and solidified. The developing gas then remains as bubbles, nearly at the place of its origin, in the gelatin. This method ("tube-culture") produces a sharp reaction on denitrification, especially when controlled by a parallel experiment, using the same culture gelatin, without nitrate or nitrite.

This principle may also be used for a rough computation of the number of denitrifying germs in any material. So it was proved that circa 2000 of these organisms occur in 1 gr. of garden soil, and circa 100 in 1 gr. of canal water.

In these experiments the potassium-salts may be replaced by natrium- or magnesium-salts; calcium-nitrate, on the other hand, prevents even in dilute solution the growth of many bacteria.

Before passing to the description of the different accumulation experiments, I have to make a general remark about their arrangement.

Which species finally becomes most common in the used culture liquid depends on many circumstances, difficult to control, in particular on the mutual numerical proportion of the individuals and the nature of the different species in the material originally used for the infection, and likewise on the condition of the microbes themselves in consequence of previous circumstances.

This explains why, when using different materials of infection for the accumulation of one and the same species, it is sometimes necessary to modify the cultural conditions in accordance with the nature of that material.

I insist on this circumstance in particular to explain the different accumulation experiments described under *B. stutzeri*, on the one hand from water by using tartrate, on the other hand from soil by using malate.

3. *Accumulation of Bacterium stutzeri*, LEHMANN and NEUMANN [1]).

This interesting bacterium was isolated in 1895 from straw by BURRI and STUTZER (l.c.), whilst in 1892 BRÉAL [2]) had already shown the presence of denitrifying bacteria thereon.

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[1]) LEHMANN u. NEUMANN. Bakteriologie. München 1896, S. 237.

[2]) De la présence dans la paille d'un ferment aérobie, réducteur des nitrates. C.R. 1892, T. 114, p. 681.

In 1898 KÜNNEMANN (l.c.) isolated the same species from soil and a variety from horse-dung and straw.

By accumulation experiments, logically carried out, I have succeeded in obtaining this bacillus from soil, canalwater, sewage-water and horse-dung.

The following experiment always led practically to a pure culture from canalwater:

A bottle of about 200 Ccm. is partly filled with fresh canalwater with addition of 2 °/₀ calcium-tartrate, 2 °/₀ KNO_3 and 0,05 °/₀ K_2HPO_4 [1]), computed after the whole capacity. Then the bottle is filled up to the neck with canalwater and the stop is loosely put in, so that a little water is pressed from the bottle. In this way it is filled without a single bubble of air and, after shaking, put in a thermostat of 25° of 28°. The calcium-tartrate solves at this temperature for only 1 °/₀, so that this salt remains for a great part at the bottom.

Commonly already after one day a feeble production of gas is to be observed, issuing from the non-solved calcium-tartrate at this bottom. The process gets into full course after three or four, sometimes only after five days. So much gas thereby is produced that a coarse, slimy scum originates at the surface and a great quantity of the liquid is pressed out of the bottle. The gas containing only nitrogen and carbondioxyd, the culture remains anaerobic. The liquid grows turbid by the growth of the bacteria and the fine, cristalline calcium-tartrate changes into coarsely granular calcium-carbonate. After a week, in consequence of the scum formation, the bottle is nearly half void, and after about 12 days the reaction is at an end, in as much, corresponding with the chosen quantity of tartrate, all nitrate has disappeared.

If a vigorously growing culture is sown on broth gelatin, a mixture is obtained of colonies of various different species, from which *B. stutzeri* can easily be isolated, if we are once acquainted with it.

From such a bottle some drops are inoculated into a bottle of about 50 ccm. capacity [1]), which, after sterilisation, is filled for ³/₄ with the following sterile culture liquid:

Tap-water, 2 °/₀ calcium-tartrate, 2 °/₀ KNO_3 and 0,05 °/₀ K_2HPO_4.

After inoculation the bottle is quite filled up with the same liquid in the above described way, and after the lapse of two or three days, the same phenomena appear as in the first bottle.

If now, once more, of this transport a plate culture on broth gelatin is made, the great diminution in the number of species is

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[1]) The capacity of the bottle is not indifferent.

surprising. All liquefying colonies, and most fluorescents have disappeared, whereas, among two common and some less frequently occurring species, *B. stutzeri* developes in great numbers and is easily recognised by the characteristic properties of its colonies.

By repeating the said transport this bacterium may still be more multiplied, so that, after three or four successive inoculations, practically a pure culture of this species is obtained.

From soil of the garden of the Bacteriological Laboratory I regularly obtained the same bacterium, in the course of the winter of 1901—2 by applying the "bottle method" with this liquid:

Tap-water, 2 $^0/_0$ calcium-malate, 1 $^0/_0$ KNO_3 and 0,05 $^0/_0$ K_2HPO_4.

In the spring, however, though there were constantly some colonies of the species, the number of its germs proved so small that they were replaced by other denitrifying bacteria, particularly *B. denitrofluorescens,* of which more presently.

A detailed description of *B. stutzeri* is given by BURRI and STUTZER (l. c.), as well as KÜNNEMANN (l. c.). It will therefore be sufficient here to give the chief characteristics by which this species is directly recognised.

The bacterium is a short, thick rodlet with a peculiar vibrio-like motion.

The colonies on gelatin are extremely characteristic (see Plate). After three or four days they have a diameter of about 0.5 mm. and after a week they attain 1 to 1.5 mm. When magnified they then resemble a rosette, or have an irregularly folded or crispate, greyish surface. The peculiar structure appears only distinctly, when the glass-dish which contains the plate culture, is reversed and the colony is seen through the bottom with about a 30-fold magnification. The most frequent shapes are represented in figures 1—4.

But it may happen that the crispate character becomes still more conspicuous and then the image is as in fig. 5.

Commonly it seems as if regularly arranged smaller colonies are situated in the larger ones, which may often be observed till in the outer border, and points to a peculiar periodicity of the mucus secretion in the interior of the colony.

In the colonies moreover a fine deposit is observed, and sometimes very distinct crystals, which may also be found in the gelatin around.

All these characteristics are particularly marked when the cultures have been recently isolated, but they may in the course of time get lost or become indistinct. Another property however remains always quite distinct, i.e. the adhering to the gelatin. Young colonies can only be removed in one piece, and of the older always part remains behind.

Very characteristic also is the growth of this bacterium on a sterilised slice of potato, where the curled and folded structure of the colonies is quite distinct, in consequence of the large dimensions they attain. The colour changes thereby into flesh-red. Old cultures grow soft in consequence of a dissolving process the slimy substance.

The compounds which can provide the carbon and nitrogen nutrition of this species were determined by means of the auxanographic method [1]), this giving in a simple way a measure for the difference in assimilability of the nutritive substances.

With KNO_3 as source of nitrogen, a feeble growth was observed with glucose and maltose. Kalium-succinate, malate, malonate, citrate and calcium-tartrate, gave rise to a vigorous growth. No growth was obtained with cane sugur, milk sugar, mannite, galactose and oxalic acid.

The auxanograms prove that tartrate belongs to the best assimilable substances, which explains why its use in the accumulation experiment with canal water produces such good results.

With kalium-citrate as source of carbon, NH_4Cl, KNO_3, KNO_2, asparagin, kalium-asparaginate and pepton, could serve as source of nitrogen.

B. stutzeri produces no invertin, does not split indican and ureum but it secretes diastase, although in very slight quantity. This latter fact explains the possibility of denitrifying by this species in solutions containing, besides the salts, only amylum and KNO_3. In broth no indol and no sulphureted hydrogen are produced.

B. stutzeri produces much alkali; even the presence of glucose does not prevent the production of it in a plate of broth gelatin.

Very remarkable is the behaviour of *B. stutzeri* towards free oxygen.

If the arrangement of the moving individuals under the influence of the oxygen of the air [2]) is examined in the glassroom, we find an accumulation in a line at rather great distance from the meniscus. On the other hand, growth is only observed [3]) in the meniscus itself. Hence, in this respect the bacterium behaves quite in accordance with the aerobic spirilla.

B. stutzeri is a very active denitrifying species; to broth could be added up to 4°/₀ KNO_3, and up to 1°/₀ KNO_2, without thereby preventing the development of gas. If in the before described way a "tube

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[1]) Beyerinck. L'auxanographie ou la méthode de l'hydrodiffusion dans la gélatine appliquée aux recherches microbiologiques. Arch. Neerl. 1889, T. 23 p. 367.

[2]) Engelmann, Zur Biologie der Schizomyceten. Botanische Zeitung 1882, Bd. 40, S. 320.

[3]) Beijerinck, Ueber Atmungsfiguren beweglicher Bakteriën. *Centr.bl. f. Bakt.* 1893, Bd. 14, S. 827.

culture" in broth gelatin is made, with 0,1 °/₀ KNO_3, after two or three days the gas bubbles will appear over the whole length of the tube, and herein this species differs from *B. vulpinus,* where the gas bubbles originate at some distance from the meniscus only.

I will finally make mention of an instructive experiment I performed with *B. stutzeri.* Some garden soil was mixed with tapwater with 0,05 °/₀ K_2HPO_4, and a thin layer of this mixture in an ERLENMEYER-flask exposed to a temperature of 25° C. Under these circumstances the production of nitrate becomes very marked after two weeks. If now the whole content of the ERLENMEYER flask is poured into a stoppered bottle, which thereby is quite filled, whilst *B. stutzeri,* is used for infection, soon a development of gas sets in and the nitrate disappears completely. Hence it follows that according as the air enters our culture liquid well or not, nitrification or denitrification may occur. This is quite in accordance with older experiences described by SCHLOESING (l. c.) in regard to the soil in general.

4. *Accumulation of Bacillus denitrofluorescens n. sp.*

SEWERIN (l. c.) found in 1897 that *B. pyocyaneus* belongs to the denitrifying ferments. But the group of fluorescents proper was long fruitlessly examined as to their denitrifying power, first by LEHMANN and NEUMANN and afterwards by WEISSENBERG (l. c.). In 1898 KÜNNEMANN isolated for the first time a denitrifying bacterium, which liquefied gelatin and fluoresced.

Though in my experiments I often obtained fine cultures of a similar species, I did not succeed in finding a satisfactory accumulation experiment for it. On the other hand I found such an experiment for a non-liquefying fluorescent *Bacillus,* which I named *B. denitrofluorescens.*

The culture liquid for the accumulation of this species is:

Tap-water, 2 °/₀ calcium-citrate, 1 °/₀ KNO_3 and 0,05 °/₀ K_2HPO_4.

In a bottle of 50 Ccm. capacity, 1 to 2 gr. fresh garden soil is put; it is then quite filled up with the culture liquid, in the way described under *B. stutzeri.* The culture is made at 25° C.

When sowing on broth gelatin the 2nd or 3rd transport, successively kept in the same culture medium, I always obtained cultures containing almost exclusively colonies of that species.

In horse-dung, canal water and sewage water, I also observed this bacterium, but it is with more certainty to be isolated from soil.

In exterior appearance of the colony this species differs in no respect from one of the most common fluorescents, characterised by lacking, on the culture gelatin, the smoothly spreading border. In young broth gelatin cultures, the pigment fluoresces blue, and after some time a white precipitate forms in the gelatin.

Examined auxanographically, KNO_3 as source of nitrogen proved to cause a feeble growth with mannite, a vigorous one with kalium-malate, citrate, malonate, succinate and tartrate, as well as with glucose and levulose. On the other hand no growth is seen with cane-sugar maltose, milk-sugar, and raffinose.

In broth, with 2 $^0/_0$ glucose, this bacterium, like all fluorescents, produces acid. Broth with 2$^0/_0$ cane-sugar, becomes however strongly alkaline, which is observed also in all other fluorescent secreting no invertin.

This bacterium neither produces diastase, nor can it hydrolise indican or ureum. In broth it forms no sulphureted hydrogen and no indol.

In its behaviour towards free oxygen it likewise corresponds with the fluorescents, i.e. with the cover-glass culture in the humid room, both motion and growth cause accumulation in the meniscus.

This makes the bacterium strongly contrast with *B. stutzeri* and *B. vulpinus*, whose motion figures show the spirillum type.

As to the energy of its denitrifying power *B. denitrofluorescens* corresponds with *B. stutzeri.* At the "tube experiment" with broth gelatin with 0,1 $^0/_0$ KNO_3, the bubbles form over the whole length of the tube, quite in the same way as with *B. stutzeri.*

5. *Accumulation of Bacillus vulpinus n. sp.*

Already in my introductory observations I remarked, that an accumulation experiment with full access of air, when using tartrate and nitrate, produced this species, but the accumulation obtained in this way was still very imperfect. By cultivating under *partly* exclusion of air, I succeeded in improving the experiment very much. I obtained this result by enclosing in the culture bottle with the liquid a determined volume of air, and reinoculating from bottle to bottle under the same conditions three or more times. It is true that thereby not all other species are totally removed, but this is no obstacle to the recognition of *B. vulpinus,* whose colonies are extremely characteristic, possessing a quite unique brown-red pigment.

The experiment is as follows:

Into a bottle of 50 Ccm. 1 to 2 grams of fresh garden soil is put, and further it is filled up with the following culture liquid, whilst leaving on air bubble of 2 Ccm: Tap-water, 2 $^0/_0$ Calcium-tartrate, 0.1 $^0/_0$ KNO_2, and 0.05 $^0/_0$ K_2HPO_4.

Here likewise the culture is effected at 25°.

With observation of the said proportion and operating as described under *B. stutzeri*, the different varieties of *B. vulpinus* can also be obtained from canal water.

The denitrification sets in very slowly and the development of gas gets not by far the intensity perceived in the preceding species. Here, too, by the complete disappearance of all liquefying bacteria already at the first transport, the isolation of the wished for species is much facilitated. Although at sowing the crude cultures on broth gelatin some *B. vulpinus* colonies may already be perceived, they multiply so much in the transports, that plates therewith prepared, appear, so to say, quite covered with the large, flatly spread, transparent, fox-coloured colonies of this species.

If for the accumulation other organic salts than tartrate are used, or a higher rate of nitrate than 0.2 $^0/_0$, not a single colony of *B. vulpinus* is detected, though it was certainly present in the infection material as it is universally, distributed in the soil.

By their growth the colonies strongly remind of the flatly spread variety of *B. fluorescens non liquefaciens*, but of fluorescence nothing is seen. In shape and motility the bacterium corresponds with *B. stutzeri.*

An interesting property of *B. vulpinus* is, that the brown pigment only develops under the influence of light. If simultaneously two cultures of this species are made on broth gelatin, and one, wrapped in black paper, is put in the dark, and the other in the light, for the rest in equal conditions, a great difference is perceptible. This becomes more obvious still, when making reinoculations or transports of either culture, likewise keeping these respectively in the dark and the light. So-doing a perfectly colourless culture can be obtained, but if this is again inoculated in the light, the brown colour returns. The pigment formation only takes place at growth, so that colonies, full-grown in the dark do not colour when exposed to light.

B. vulpinus belongs to the group of real chromophores [1]), i. e. the pigment is bound to the bacterial body, and the behaviour towards light is, in my opinion, another indication that in this group the pigment has a biological function.

The auxanographic examination proved, that with nitrate for nitrogen nutrition, a feeble growth is obtained with kalium-malonate, a vigorous one with levulose, glucose, maltose, kalium-citrate, succinate

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[1]) See BEIJERINCK, La biologie d'une bactérie pigmentaire. Arch. Néerl. 1892, T. 25, p. 227.

acetate and tartrate, whereas cane-sugar, milk-sugar, mannite and raffinose produce no growth at all. Ammonium-chloride may also serve as source of nitrogen, when using tartrate for carbon nutrition.

Pepton, asparagin, and kalium-asparaginate may simultaneously serve as C and N nutriment.

The bacterium secretes neither invertin nor diastase and does not split indican or ureum. In broth it produces no sulphureted hydrogen but a little indol.

In the "tube experiment" in broth gelatin with 0,1 % KNO_3, bubbles of nitrogen are exclusively seen to form at a little distance from the meniscus, and moreover, the culture of this species not succeeding in a bottle *wholly* filled with a culture liquid containing nitrate, we must needs conclude, that *B. vulpinus* wants considerable quantities of oxygen for the denitrification.

As regards the other species, which form gas bubbles also in the depth of the tube, I have come to the conviction that they too, want traces of free oxygen to this end.

Notwithstanding this different behaviour towards free oxygen, the motion figure, like that of *B. stutzeri,* shows the spirillum type.

By modifying the nutrient liquids and temperatures I have succeeded, as observed above, in accumulating various other denitrifying bacteria, beside those described. Thus I obtained, at 37° C. with calcium-citrate and 0,2 % KNO_3, under exclusion of air, and using garden soil for material of infection, the spirillum-like *B. indigoferus* VOGES [1]), which denitrifies only feebly, but is interesting by its indigo-like pigment. When using sewage water, I obtained a strongly denitrifying, liquefying, blue pigment bacterium, not yet described.

Of all these experiments however, the result is not constant enough to be inserted here.

6. *Summary and conclusions.*

1st. The fundamental principle of my accumulation experiments was partly or completely to prevent the access of air. By this means I have succeeded, by cultivating in solutions of organic salts and nitrate, only by repeated transports in the same liquid, in bringing many denitrifying bacteria to a more or less perfectly pure culture.

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[1]) CLAESSEN. Ueber einen indigoblauen Farbstof erzeugenden Bacillus aus Wasser. Centrbl. f. Bakt. 1890, Bd. 7, S. 13.

VOGES. Ueber einige im Wasser vorkommende Pigmentbacteriën, Centrbl. f. Bakt. 1893, Bd. 14, S. 301.

Of these experiments three always gave constant results, and produced respectively *B. stutzeri* NEUMANN and LEHMANN, *B. denitrofluorescens* n. sp. and *B. vulpinus* n. sp.

2nd. *B. stutzeri* deserves attention on account of the unique structure of its colonies, as seen in Fig. 1—5 on our Plate.

3rd. *B. denitrofluorescens* is the first example of a denitrifying, non liquefying fluorescent.

4th. *B. vulpinus* is a chromophorous pigment bacterium, whose pigment only forms at growth in the light.

5th. *B. stutzeri* and *B. vulpinus* behave towards free oxygen like aerobic spirilla, *B. denitrofluorescens* behaves like an ordinary aerobic bacterium.

6th. Like in soil and dung, in which it had also been found by other experimentators, I have established the general distribution of denitrifying bacteria in canal and sewage water.

7th. The denitrifying bacteria can, even with the slightest quantities of various organic substances, cause the disappearance of determined quantities of nitrate under development of free nitrogen.

8th. In one and the same culture medium, where nitrification is produced during aeration, denitrification may be caused by exclusion of air, this holds good also in regard to the soil.

At the end of this paper I want to express my sincere thanks to Professor Dr. M. W. BEIJERINCK for his kind, invaluable guidance and efficacious assistance, afforded me in these researches.

Delft, July 1902.

Physics. — *"An Hypothesis on the Nature of Solar Prominences."*

By Prof. W. H. JULIUS.

The introduction of the principle of anomalous dispersion into solar physics makes it possible to form an idea of the Sun's constitution from which necessarily follow i.a. a great many peculiarities of prominences, which, until now, it has been impossible to deduct in a satisfactory manner from other physical laws. This I will show in the following pages.

In my paper on "Solar Phenomena, etc." read Febr. 24, 1900. I put forth the following hypothesis with respect to that part of the solar atmosphere, situated outside what is called the photosphere 1):

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1) W. H. JULIUS, Solar Phenomena, considered in connection with Anomalous Dispersion of Light, Proc. Roy. Acad. Amsterdam, II, p. 585.

G. VAN ITERSON Jr. „Accumulation experiments with denitrifying bacteria."

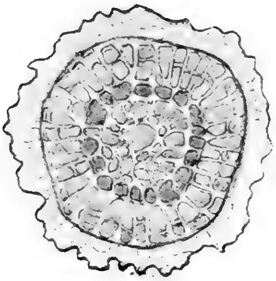

Fig. 1.

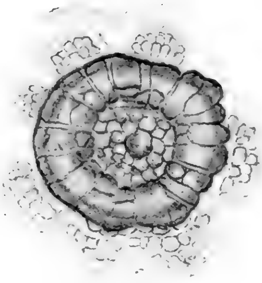

Fig. 2.

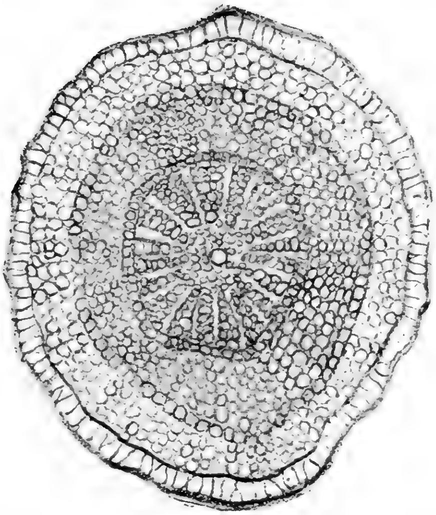

Fig. 3.

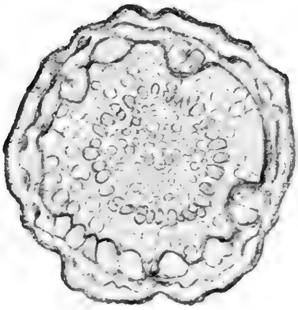

Fig. 4.

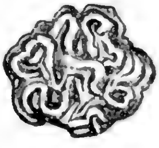

Fig. 5.

"The various elements, whose presence in that atmosphere has been inferred from spectral observations, are much more largely diffused in it than has generally been assumed from the shape of the light phenomena; they may be present everywhere, up to great distances outside the photosphere, and yet be visible in few places only; their proper radiation contributes relatively little to their visibility (with perhaps a few exceptions); the distances, at which the characteristic light of those substances is thought to be seen beyond the Sun's limb, are mainly determined by their local differences of density and their power to call forth anomalous dispersion."

How we were to imagine the condition of the matter inside the photosphere, was not considered there. Our hypothesis on the origin of the light of the chromosphere was kept free from any special conceptions as to the nature of the photosphere. Only where the principle of anomalous dispersion was made use of also to explain spectral phenomena observed in sunspots [1]), we had to fall back upon A. Schmidt's theory [2]), according to which the Sun is an unlimited gasball, so that the apparent surface of the photosphere should not be considered to be the real boundary of a body, but to correspond to a "critical sphere", defined by the property that its radius equals the radius of curvature of horizontal rays, passing through a point of its surface.

At present, however, in working out the problem of the nature of the chromosphere and the prominences, we likewise will take as a starting point the first of the three Theses, in which Schmidt sums up the main points of his theory. Accordingly, we suppose the Sun to be an unlimited mass of gas, in which the density and luminosity (not considering local irregularities) gradually diminish from the centre outward. But our conception of the properties and composition of this gaseous body can in a certain respect be much simpler than would be the case, if we accepted the whole of Schmidt's theory.

Indeed, Schmidt explains both the edge of the Sun's disk by the laws of regular refraction (or ray-curving) in a stratified medium, and the prominences by refraction in "Schlieren" [3]); but in order to account for the fact that the light from the prominences as well as that from the chromosphere, instead of being white, shows a bright line spectrum of varying appearance, he supposes the strongly radiat-

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[1]) l. c. p. 585.

[2]) A. Schmidt, Die Strahlenbrechung auf der Sonne. Ein geometrischer Beitrag zur Sonnenphysik. Stuttgart 1891.

[3]) A. Schmidt, Erklärung der Sonnenprotuberanzen als Wirkungen der Refraction in einer hochverdünnten Atmosphäre der Sonne. Sirius XXIII S. 97—109, Mai 1895.

ing mass of gases in its outer parts to be composed so as to emit almost exclusively hydrogen-, calcium-, heliumlight, whilst the radiations of sodium, magnesium, titanium, iron are supposed to originate in deeper layers, a.s.o. [1]. We, on the contrary, by the introduction of anomalous dispersion are permitted to suggest, that throughout the gaseous body, as well inside as outside the critical sphere, the various elements are altogether intrinsically mixed (granting that in the mixture the quantity of materials with greater specific gravity must grow with the depth). For wherever there are local differences of density in the mixture, caused by currents, whirls etc., the conditions for irregular ray-curving are present, and it is evident that specially those elements of the mixture, which possess an exceptionally high dispersing power for certain waves of the transmitted light, will be able to reveal their presence even at great distances from the disk, while other substances, though also present at the same places, remain invisible there. Thus a purely optical explanation may be given of the fact, that the different gases of the sun are *seen* separated, even though we suppose them to *be* thoroughly mixed.

And surely this last supposition is the simpler by far; it even necessarily follows from the fundamental idea, that the Sun may be considered as a rotating, heat-radiating mass of gas, for in such a body the constituent parts must continually mix.

A few months ago the main character of the motion that must go on in a sun, supposed to be gaseous, has been discussed by R. EMDEN [2]. He applies to the Sun the same mathematical deductions, which had been devised by VON HELMHOLTZ for investigating the kind of motion which in our terrestrial atmosphere must result from the united influence of heating by the Sun and of the daily rotation [3]. Though EMDEN supposes the gaseous Sun to be limited by a well-defined surface, and so far accepts the prevailing views on the constitution of this celestial body, still his mathematical formulae are absolutely independent of the existence of a boundary surface, and so are fully applicable to a sun, such as we are considering here.

Radiation causes the outer layers to cool down soonest; they sink inwards and are replaced by ascending hotter gases, so that,

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[1] As appears from a paper in the Physik. Zeitschr. 3. S. 259—261: entitled „Ueber die Doppellinien im Spectrum der Chromophäre" SCHMIDT adheres to this conception, even after having taken into consideration the possibility of explaining the light of the chromosphere by anomalous dispersion.

[2] R. EMDEN, Beiträge zur Sonnentheorie. Ann. d. Phys. [4] 7, p. 176—197.

[3] H. VON HELMHOLTZ, Gesammelte Abhandlungen I, p. 146, III p. 287—355.

if the Sun did not rotate, we could only expect radial convection currents. But the rotation of the sun completely changes this form of motion; the angular velocity of descending masses increases, of ascending masses diminishes; there will be found side by side gaslayers of different densities, and rotating at different speeds.

It has been shown by von Helmholtz, that during a certain time such gaslayers can flow side by side, sharply separated by a so-called surface of discontinuity (i. e. by a surface, on passing which the values of the velocity and the density change with a leap); but gradually the friction causes this surface to undulate; the waves advance with the more swiftly moving layer, they grow steeper, overhang and break, forming whirls; and thus, by the mingling of the adjacent parts of the two layers a new layer is formed between them, the properties of which will be intermediate between the corresponding properties of the original layers.

From the conditions of the problem we may deduce the position of the surfaces of discontinuity. This has been performed by von Helmholtz with regard to the air-currents in our atmosphere, and by Emden for the rotating layers of the Sun. He arrives at the conclusion, that in the Sun the surfaces of discontinuity must in the main have the shape, figured in the accompanying sketch and reminding us of hyperboloids of revolution [1]).

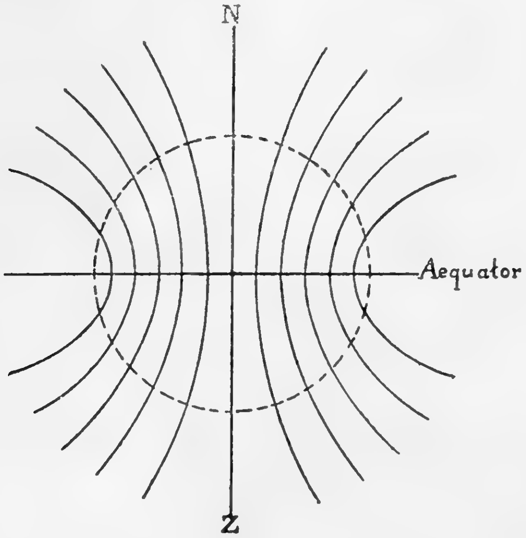

Fig. 1.

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[1]) Emden draws the intersections of the surfaces with the plane of the paper only inside the circle, representing the sun's boundary. I have dotted this circle, with a view to indicate, that the border is only a seeming one; accordingly I prolonged the intersections outward.

In every annular layer, bounded by two consecutive surfaces of discontinuity, the moment of rotation of unit mass ($\Omega = \omega r^2$) as well as the so-called potential temperature θ are constant; but in a following layer, farther from the Sun's axis, Ω has a greater and θ a smaller value. Within every layer there exists a velocity potential, but at the separating surfaces the linear velocity changes discontinuously, the difference between the velocities on each side of one and the same separating surface increasing as that surface approaches the axis.

The waves, that are formed in the separating surfaces, will proceed in the direction of the rotation, and when, after growing steeper and steeper, they break, the resulting vortices will have their core-lines perpendicular to the direction of motion of the waves, i.e. coinciding with the generatrices of the surfaces of discontinuity. So, the curves in our figure also give an idea of the position of the vortex-cores.

From the theory follows, as we already mentioned, that at each definite surface of discontinuity the leap of the velocity is greater at a short than at a long distance from the Sun's axis; therefore, the transition from a wave into a whirl must, as a rule, begin in those parts of that wave, which are nearer to the axis, and appear afterwards in the outer parts.

Further it is clear that, because every whirling leads to mingling of the adjacent parts of two layers and to the formation of two new surfaces of discontinuity, there will never exist a complete surface, such as indicated by our sketch. Everywhere we shall meet with pieces of surfaces of discontinuity; only their main character and the average direction of the vortex-cores will correspond to the sketch. And in spite of the continual mixing of layers, which leads to equalization of differing rotational velocities, the motion still remains nearly stationary; for within each layer, temporarily enclosed between two surfaces of discontinuity, the convection currents carry cooled matter inwards and hot matter outwards, by which process the differences in rotational velocity are renewed.

Forced as we are to admit, that such an uninterrupted mixing process is going on in the Sun, the advantage of explaining the chromosphere and the prominences by anomalous dispersion of white light, must appear to us very obvious. All other explanations, that I know of, must start from the hardly tenable supposition, that the different gases of the chromosphere are separately present in large quantities.

Emden has succeeded in deducing many properties of sun-spots from the supposition, that the spots show us the places, where huge whirls attain the Sun's surface. It seems to me that Emden's views on sun-spots would become even much more acceptable, if the notion of a real surface of the Sun were given up and if the consequences of normal and anomalous refraction (better ray-curving) in those whirls were allowed for. But to this subject I desire to come back on another occasion.

For the present we will confine our attention to those parts of the whirls, optically projecting beyond the edge of the Sun's disk, and we propose the hypothesis, that the whole chromosphere with all its prominences is nothing but this system of waves and whirls, made visible within shorter or longer distances from the Sun's edge by anomalous dispersion of light, coming from deeper layers.

(Perhaps the structure of the corona, with its polar streamers, arches, etc., might tell us something about the course of the surfaces of discontinuity at very great distances outside the critical sphere; this point too, however, I will only hint at here).

So we ascribe the chromosphere to the smaller vortices, to the continual rolling up of the surfaces of discontinuity; in the prominences we see the whirling, in which the rarer, very large waves of the solar ocean dissipate.

The particular structure of the chromosphere, suggesting the comparison with a grass-field in vertical section, follows immediately from this hypothesis. Prominences likewise nearly always show a tissue of stripes, bands and filaments [1]). These, according to our view, indicate the position of the whirl-cores. In the whole region, where whirling is going on, the density will, of course, vary in a very irregular way; we therefore may expect to find in the spectrum of that region as well the light on the red as that on the violet side of the absorption lines, i. e. the chromospheric and flash lines must be double lines [2]).

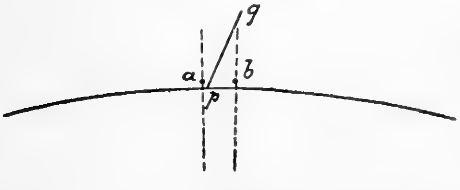

Fig. 2.

Along the core of a vortex the density is a minimum. If, now, a vortex intersect the apparent limb of the sun obliquely, as in Fig. 2, where *pq* represents the core-line, the light coming from a point *a* must differ from the light, coming from *b*. Indeed, following in *a* the Sun's radius

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[1]) J. Fényi S. J., Protuberanzen, beobachtet in den Jahren 1888, 1889 und 1890 am Haynald—Observatorium, p. 5. (Kalocsa, 1902).

[2]) W. H. Julius. On the Origin of Double Lines in the Spectrum of the Chromosphere, Due to Anomalous Dispersion of the Light from the Photosphere. Proc. Roy. Acad. Amst. Vol. III, p. 193.

outward, we at first get into layers of increasing density, whereas, ascending from *b*, we meet with layers of decreasing density. Consequently, in the spectrum of *a* the "violet-facing" components of the double lines must be prominent and in the spectrum of *b* the red-facing ones. If the slit be placed tangentially, through the points *a* and *b*, the two cases will be seen at a short distance on the same spectral lines. And when during a total eclipse of the Sun the chromosheric arc itself functions as a slit (the prismatic camera being used), the same phenomenon may be met with on numerous places of the crescents. Many instances thereof are visible on the plates, obtained in Sumatra by the Dutch expedition for observing the total eclipse of May 18th 1901.

With large prominences the phenomenon sometimes appears very intensely. In the important work by Fényi, mentioned before, we read for instance on p. 121, in the description of a carefully observed prominence, the following passage:

. . . . „Im unteren Teile zeigte die Protuberanz am Anfange ihrer Entwickelung eine grosse Störung in der H_α Linie. Bei engem (tangentiell gestelltem) Spalte reichten zwei Spitzkegel über denselben hinaus, der eine, grössere erstreckte sich gegen rot, der andere kleine gegen blau und stand etwas südlicher. Die Grösse des ersteren betrug 9″ im Gesichtsfelde; auf Grund einer neuen Bestimmung der thatsächlichen Dispersion des Spektroskops ergibt sich daraus für diese Stelle der Protuberanz eine Bewegung *von* uns mit der Geschwindigkeit von 240,4 Klm. in der Secunde. Die Verschiebung gegen blau betrug nach dem Augenmaasse etwa die Hälfte der ersteren gegen rot.

Die entgegengesetzten Bewegungen neben einander und die Kegelförmige Form des veränderten Lichtes würden unschwer die Deutung auf eine Wirbelbewegung am Grunde der Protuberanz gestatten. Aus der Ungleichheit der Kegel würde ein Vorschreiten des Wirbels *von* uns mit der Geschwindigkeit von 180 Klm. sich ergeben. Die Beobachtung steht auch nicht allein da; eine ähnliche Erscheinung wurde von Young am 3. Aug. 1872 (The Sun, p. 210) eine andere von Thollon in Nizza (C. R. XC p. 87, XCI p. 487) beobachtet; ähnliches wurde auch von mir bei anderen Gelegenheiten beobachtet."

Thus, interpreting the light on both sides of the hydrogen-line after Doppler's principle, Fényi arrives at the very astonishing conclusion, that the whirling mass of hydrogen moves at a speed of 180 kilometers per second. Moreover, there is a much greater difficulty, not even mentioned by Fényi, viz. that the coherent outbuds of the line impose upon him the necessity of supposing that velocity to be very different for the various parts of the whirl, adjacent pieces of the prominence not even taking any part in the enormous motion along the line of sight.

The above-given explanation of the phenomenon by anomalous dispersion solves all these mysteries.

It occurs very seldom that prominences show a rapid sideward motion, i.e. a motion in the meridian of the Sun. FÉNYI mentions as an exceptional case a sideward velocity of 25 kilometers per sec[1]). As, on the other hand, velocities of 250 kilometers and more in the direction of the parallel (calculated after DOPPLER) are by no means a great exception, we meet with contradictions — as is admitted also by FÉNYI — from which it appears impossible to escape, unless we doubt the reality of the velocities.

It is surprising and satisfactory to see how nearly all the peculiarities in the behaviour of prominences, as described by YOUNG, FÉNYI and many others, appear quite intelligible as soon as we look at these phenomena from our point of view.

Let us choose only a few more examples out of the vast material.

FÉNYI says (l. c. p. 115): „Schon seit Jahren habe ich bemerkt, dass helle hervortretende Punkte in der Chromosphäre, welche eine kleine Verschiebung gegen blau zeigen, der Ort sind, wo alsogleich der Aufstieg einer Flamme oder einer kleinen Protuberanz erfolgt."

Now the process of whirl-formation in a surface of discontinuity proceeds, as a rule, from the inner parts of the Sun outwards. In the axis of a whirl the density is a minimum. Consequently, at the moment the whirling reaches the apparent edge af the Sun, a minimum of density will be found just projecting beyond the edge. Here we have a place, where the density increases from the photosphere outward and where, therefore, the violet-facing component of the chromospheric double-line temporarily prevails: it seems as if a shifting towards the violet occurs. Shortly afterwards the more distant parts set a whirling and the prominence appears.

In the description of a great prominence, observed by FÉNYI on the 18th of Aug. 1890, we read i.a. the following particulars[2]):

„Ein ganz besonderes Interesse verleihen dieser an und für sich schon grossartigen Erscheinung die Eigenbewegungen in der Gesichtslinie, die an derselben beobachtet wurden. Eine ungefähr zwischen 40″ und 50″ Höhe liegende Schicht, (deren Lage in der beigegebenen Figur genau bezeichnet ist), zeigte eine heftige Bewegung gegen die Erde zu. Das rote Licht des Hydrogeniums ergoss sich daselbst in verworrenen Formen über den Spaltrand gegen blau hinaus ohne

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[1]) FÉNYI, l. c. p. 114.

[2]) FÉNYI, l. c. p. 129.

indessen den Spalt ganz zu verlassen. Die Bewegung war durchaus local, die Umgebung zeigte keine Spur einer Bewegung. Die Geschwindigkeit derselben war keine ungewöhnlich grosse; ich erhielt aus 4 mit dem Fadenmikrometer gemachten Messungen zwischen 11 h. 45 m. und 12 h. 15 m. verschiedene, zwischen 94 und 201 klm. schwankende Werthe. Was aber die Erscheinung zu einer besonders merkwürdigen gestaltet ist der Umstand dass, während diese in der Höhe vor sich gehende ganz locale Bewegung nicht einer Ausströmung zugeschrieben werden kann, dieselbe trotzdem doch eine halbe Stunde lang beobachtet wurde! Nehmen wir als Mittelwerth der Geschwindigkeit 150 klm. per Secunde an, so hätte dieser bewegte Teil der Protuberanz während der zwischenzeit von 30 Minuten gegen 270.000 klm. durchlaufen, also wohl auch den scheinbaren Ort ändern müssen."

Of course this contradiction immediately vanishes if we only suppose, that in the part of the prominence, showing the persistent shift of the hydrogen light towards the blue, the density of the solar matter was increasing in the direction from the photosphere outwards. This supposition is quite in harmony, too, with the fact, that the picture of this prominence shows very important whirling *below* the part in question and no disturbance worth mentioning *above* it.

Observers have often been puzzled at the rapid disappearing of enormous prominences and at the perfect calm in the whole region, including the Sun's surface, a short time after such a violent "eruption" had taken place. It was hardly conceivable that the ejected incandescent gases could loose their huge quantities of heat so rapidly, nor that the eruption had no further visible consequences.

In our theory a large prominence is nothing but the visible token, that whirling is going on almost simultaneously over vast regions. The very important varieties of density in the whirling mass may, however, be annulled by displacements of much matter over relatively small distances, which process, of course, may go on without violent movements and yet be accomplished in a short time. So there is no reason whatever to expect, that a great prominence will leave the medium in a highly disturbed condition.

Whosoever wishes to consider prominences as eruptions, must grant, that it is one of the most difficult problems to account both for the tremendous values of the ascending velocities sometimes observed and for the most capricious way, in which the speed often suddenly changes without any conceivable cause. The 20th of Sept. 1893 Fényi witnessed a prominence ascending 500000 kilometers in a quarter of an hour, that is at an *average* velocity of more than

550 kilom. per sec. In another case, also observed by FÉNYI (July 15th 1889), in the course of 10 minutes the ascending velocity passed through the values 72, 6, 65, 24, 154 kilometers per second; and with the prominence of Oct. 6th, 1890, in 30 minutes' time through the values 33,8, 79,8, 67,6, 72,7, 127,7 275,5, 242,3, 121, 57,3 kilom. per sec.

Considering the problem from the new point of view we see the difficulties disappear in consequence of the observation, that, properly speaking, we have not to do with velocities at all. We may speak of the velocity with which matter moves or with which a disturbance is transmitted by a medium; but neither of these cases is met with here. Wherever the whirling sets in, it results from local conditions and cannot be considered as directly transmitted from places, where whirling was going on a little earlier. Though it is true that, as a rule, the breaking of a wave begins in those parts of a surface of discontinuity, that are nearer to the Sun's axis, and from there proceeds outwards, yet this does not involve that we should have a right to call this process a transmission of matter or of motion in the direction of the vortex-cores. And where there is no transmission, there is no velocity.

When at the sea-shore a wide wave approaches and breaks, now here, then farther and farther, nobody will speak of the „velocity" with which the foam or the whirling is moving along the coast. Every body knows, that the foam, the visible token of the whirling, is successively formed at different places. Such about is the case with the prominences, the visible spots in the breakers of the solar ocean.

Chemistry. — Professor LOBRY DE BRUYN communicates a paper by himself and Mr. J. W. DITO. „*The boilingpoint-curve of the system: hydrazine + water*".

In a previous report[1]) Mr. DITO has communicated the results of determinations of the densities of mixtures of hydrazine and water; the figures showed that a maximum density corresponds exactly (or nearly so) with the composition N_2H_4-H_2O. At the end of that note it was stated that we would endeavour to determine the boiling-point-curve of the system: hydrazine + water.

We have lately been engaged with that determination; the result is given in the following table and annexed curve.

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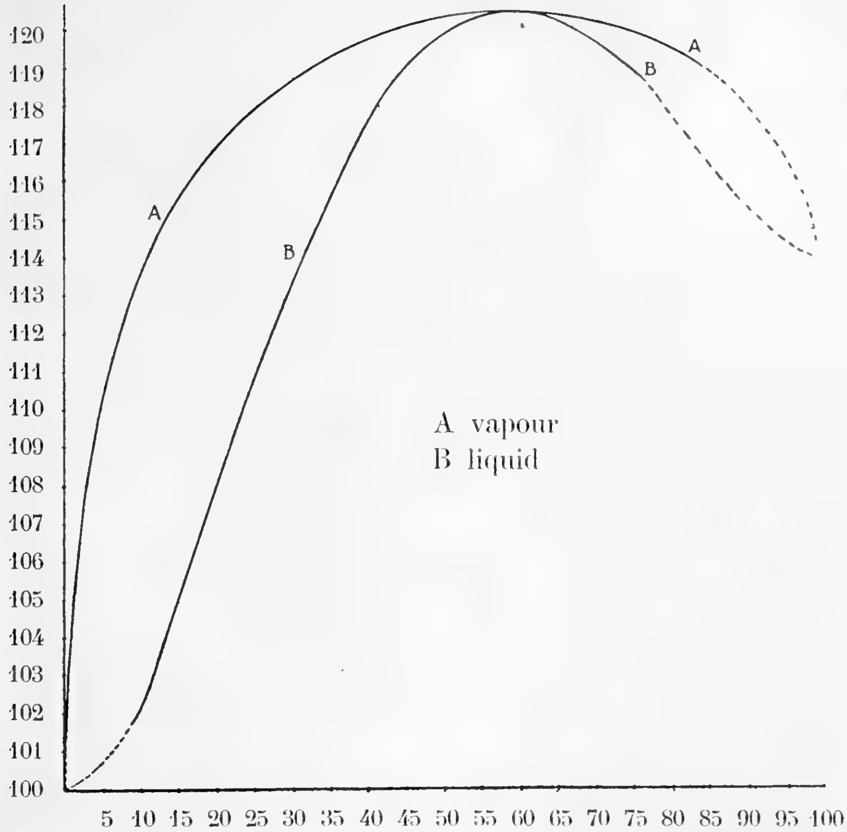
[1]) Proc. of April 19, 1902, p. 838.

Amount of mixture and barometer.	Temp.	Number mols. of N_2H_4 on 100 mols.	
		liquid.	vapour.
	102.2	9.4	0.18
300 grm. 755.5 ↓	104.6	14.2	
〃	105.9		1.6
〃	107.45	19.5	2.7
〃	109.15		3.9
〃	111.0		6.2
〃	114.95	34.0	13.8
〃	117.95	41.7	25.0
85 gr. 768.0	118.6	42.9	30.3
〃	119.2	45.2	34.9
〃	119.8	50.3	41.7
38 gr. 770.8	120.2	51.8	44.6
〃	120.35	53.3	48.75
〃	120.45	54.8	52.8
〃	120.5	56.0	53.5
	[120°5	58.5	58.5]
771.1	120.45	62.5	
〃	120.25	65.8	72
〃	119.9	68.3	75.5
〃	119.5	72.7	81
〃	119.25	73.6	83.7
50 gr. 〃 ↑	118.8	76	

It should be observed beforehand that the figures obtained, particularly those relating to the mixtures rich in hydrazine, cannot possess that accuracy attainable with other mixtures. In the first place free hydrazine is a costly substance; working with a large quantity such as is required for the accurate determination of a boilingpoint curve, therefore, leads to not inconsiderable expenses. Moreover, free hydrazine and its mixtures with little water (also the hydrate $N_2H_4 . H_2O$) are very hygroscopic and also easily oxidisable by the oxygen of the air. During the volumetric determination of the amount of



hydrazine in the liquid and condensed vapour, it was impossible to avoid contact with the atmosphere. The operation was carried out in such a manner that each time after distilling off a certain quantity (10—20 c.c. in the case of the greater concentrations), two portions (3—4 drops) of the condensed vapour and residue were simultaneously collected in tared weighing bottles containing about 5 c.c. of water. On account of the many weighings a certain time necessarily elapsed between the taking of the samples and the titration and, considering that the bottles also contained a little vapour of hydrazine mixed with air, this must have excercised some influence. This explains why the agreement between the various duplicate determinations often left much to be desired; in one case a discrepancy occurred amounting to 2 mols. per 100. Finally, another source of error is found in the fact that on account of the many weighings and titrations, the determinations had to be done on different days, so that the distillations were conducted under different barometric conditions.

Notwithstanding this, the results allow of the construction of a curve, the regular course of which is a guarantee that the figures observed

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express the entire phenomenon with a certain amount of accuracy. As already stated, more correct results can only be obtained by repeating the experiments with larger quantities of hydrazine [1]).

Our experiments have led to the interesting result that hydrazine-hydrate does not at all represent a chemical compound $N_2H_4 . H_2O$ with a constant boilingpoint of about 120°, as hitherto believed. This however is not surprising, particularly after KNIETSCH's experiments on the system sulphurtrioxide + water [2]). The tendency of SO_3 and H_2O to enter into combination is greater than that of N_2H_4 and H_2O. As the boilingpoint curve of the system sulphurtrioxide + water shows a maximum not belonging to the compound H_2SO_4 but to a mixture of 98,5 °/₀ of H_2SO_4 and 1,5 °/₀ of H_2O, it is not at all surprising that in the system hydrazine + water the maximum does not correspond with the composition $N_2H_4 . H_2O$. It is seen from these figures that a liquid boiling at 119°.8 and having the composition 50 mols. N_2H_4 + 50 mols. of H_2O yields a vapour containing about 42 mols. of N_2H_4 and 58 mols. of water, while a vapour of about the composition $N_2H_4 . H_2O$ is given off at 120°.4 by a liquid containing about 54 mols. of N_2H_4 and 46 mols. of water.

From the course of the curve it appears that a maximum boilingpoint of about 120°.5 corresponds with a liquid with about 58 mols. of N_2H_4. The experiment has shown that a mixture of about 58.5 mols. of N_2H_4 and 41.5 mols. of H_2O has a constant boilingpoint of 120°.1 at 760 m.m. In the table 120°.5 therefore corresponds with 771 m.m.

The course of the first half of the curve plainly shows the phenomenon observed by CURTIUS namely, that on boiling dilute solutions of hydrazine the distillate consists at first almost exclusively of water, although the boilingpoint has very sensibly increased. It may be assumed that the same thing happens in the reverse case of much hydrazine and little water; for reasons stated we have not been able to ascertain this.

One of us (DITO) is already engaged with the determination of the viscosity of the system: hydrazine + water; while with the co-operation of Professor ERNST COHEN experiments have already been started, several months ago, on the electrolytic conductivity of the same system and of solutions of salts in hydrazine [3]).

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[1]) Ber. **34.** 4088 (1901).

[2]) CURTIUS states that concentrated solutions of hydrazine attack glass when boiling at ordinary pressure. We did not notice any such action of even highly concentrated solutions on our glass fractional distilling apparatus and condensing tube.

[3]) Recueil **15**, 179.

Chemistry. — Professor Lobry de Bruyn presents, also in the name of Mr. W. Alberda van Ekenstein, a communication on *"Formaldehyd (methylene) derivatives of sugars and glucosides."*

In a previous communication [1]) we have already stated that an aqueous solution of formaldehyde when evaporated with some of the sugars reacts on the same. This was shown by the great changes in the rotation. We then also remarked that attempts to isolate the crystalline compounds from the syrupy mass had not proved successful. These, moreover, are readily dissociated by evaporation in the presence of much water, the pure sugars being left behind. [2])

About the same time [3]) Tollens had prepared a crystallised methyleneglucose by mixing a solution of glucose in formaldehyde with hydrochloric and acetic acids and setting the liquid aside for some months. He obtained a monoformal-derivative which still powerfully reduced Fehling's liquid. Other sugars gave a negative result.

On continuing our researches it appeared that substances, of an apparently different nature and more stable than those occurring in the said syrups, are formed when the dry sugars are melted with polymerised formaldehyde (trioxymethylene). The rotatory power then appears strongly modified and the reducing power decreased: this, however, reaches its normal figure on boiling with dilute acid. From this follows that during the reaction of the sugar with the formaldehyde, the aldehyde groups disappear.

We now succeeded in isolating in the case of several sugars (and glucosides) crystallised compounds or such having a constant boiling point, by introducing the fused mass into sulphuric acid of various concentrations or phosphoric acid and then agitating the liquid with an organic solvent such as chloroform, which dissolves the diformal compounds. In some cases there are formed, simultaneously, monoformal derivatives which are readily soluble in alcohol and water, but sparingly soluble in chloroform and so behave in this respect quite the reverse from the diformal derivatives.

Both the di- and the mono-methylenesugars no longer react with Fehling's solution and behave indifferently toward phenylhydrazine; the carbonyl groups have therefore disappeared during the action of the formaldehyde. After boiling with dilute acids, the reducing power returns. These substances must therefore in the first place

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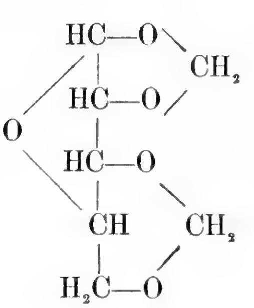
[1]) Proc. 1900. **9**.

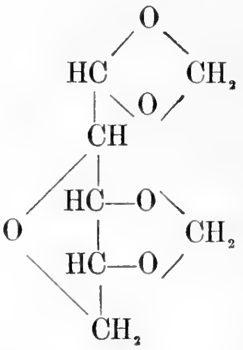
[2]) Ruff and Ollendorff, Ber. **32**. 3236 (1899), have regenerated some sugars from different hydrazines by evaporation with solution of formaldehyde.

[3]) Ber **32**. 2585 (1900); his experiments had commenced some years previously.

be regarded as glucosides, derived from methylenglycol $CH_2\,(OH)_2$ [1]), which is unknown in the free state. Two of the alcoholic hydroxyl groups of the sugar-molecule have also taken part in the formation of the diformal-derivatives. A hydroxyl group is no longer present in formalmethylenexyloside and -arabinoside, for acetic anhydride and benzoyl chloride do not act on these substances. As, according to the analysis, two mols. of water have been eliminated, the following constitutional formulae, for instance, may be drawn up for the said pentose derivatives.



or



Diformalxylose ($C_7\,H_{10}\,O_5$) crystallises very neatly from benzene or light petroleum; melting point 56°—57°, $[\alpha]_D$ ($2^0/_0$ solution in methylalcohol) $= + 25°,7$; may be readily sublimed.

Diformalarabinose is a somewhat oily, colorless liquid which may be distilled in vacuum without decomposition. Boiling point 155° at about 32 m.m. pressure; $[\alpha]_D$ ($2^0/_0$ solution in methylalcohol) $= - 16°$.

With glucose a syrupy diformalderivative may be separated from a solid mono-compound by taking advantage of the said difference in solubility. Neither of these substances have any reducing power or react with phenylhydrazine. They are probably mixtures; the white substance, although crystalline, does not possess a definite melting point (140—150°) and on analysis gives no satisfactory figures, but it could not up to the present be resolved by recrystallisation into components. The diformal-derivative, left in contact with solvents for many months, remained syrupy.

Both compounds still contain one or more free hydroxyl groups;

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[1]) The methyleneglucose obtained by TOLLENS (l.c.) has still a strong reducing action; it appears to us that it should not be regarded as a glucoside (which TOLLENS does); apparently two alcoholic groups of the glucose have taken part in its formation.

the products of the reaction with acetic anhydride and benzoyl chloride could not as yet be obtained in a crystalline form.

They are not liable to fermentation but do not prevent the fermentation of any free glucose, although they retard the same.

The simultaneous formation of various isomeric mono- and diformalglucosides may, as will be easily seen, explain the unsatisfactory result.

Galactose yielded products comparable with those obtained from glucose. The indistinctly crystalline methylenegalactoside (monoformal derivative) seems, however, to be a pure substance as the melting point (203) remained unaltered; $[\alpha]_D$ (in $2^0/_0$ aqueous solution) $= + 124°.8$. It is still being investigated.

Fructose yields a well-crystallised formalmethylenefructoside; when preparing the same a $50^0/_0$ sulphuric acid should be used. Melting point 92°; $[\alpha]_D$ ($2^0/_0$ aqueous solution) $= - 34°.9$.

d-Sorbose yields a derivative melting at 54° and $[\alpha]_D$ ($2^0/_0$ aqueous solution) $= - 25°$. Rhammose yields a product melting at 76° and $[\alpha]_D$ [$0.4^0/_0$ aqueous solution) $= - 18°$; mannose also yields a crystalline derivative.

The (mono)methyleneglucosides also derive a certain importance from the analogy which they show, as regards their properties, with ordinary canesugar. In the same way as the latter has been formed from glucose and fructose, they are also formed, with the loss of two carbonyl groups, from two aldehydes from which one mol. of water has been eliminated. The reducing power is lost; towards phenylhydrazine they have become indifferent. On boiling with dilute acids, however, the components are regenerated.

It cannot be a matter of astonishment that the methylglucosides are quite as capable as the hexites, the oxy-acids and the sugars to give condensation products with formaldehyde. They are formed in abundance by simply melting the powdered glucosides with dry trioxymethylene.

In a properly crystallised state were obtained the formalderivatives of methylmannoside [m.p. 127°, $[\alpha]_D = + 10°.5$], of β-methyl-*d*-glucoside m. p. 136°, inactive] and of α- and β-methyl-*d*-galactoside.

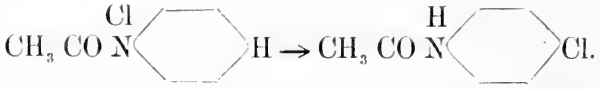
The derivatives of α-methyl-*d*-glucoside and of amyl- and aethyl-*d*-glucoside are viscious liquids.

It is worthy of notice that saccharose melted with trioxymethylene is decomposed with the formation of a mixture of formalderivatives of glucose and fructose, from which the latter was separated in a crystalline condition.

Chemistry. — "*The intramolecular rearrangement in halogen-acetanilides and its velocity*". By Dr. J. J. Blanksma. (Communicated by Prof. Lobry de Bruyn).

In a former paper [1]) attention was called to the fact that the ready bromination, nitration, sulphonation etc. of phenol and aniline derivatives may be explained by assuming that the halogen atom or the groups NO_2 or SO_4H first enter the side-chain and then pass into the nucleus by intramolecular migration. Although a great many compounds are now already known containing groups linked to N or O which, under the influence of certain agencies, shift towards the nucleus, it was in these cases up to the present not proved with absolute certainty that we are really dealing here with a rearrangement of atoms or groups in a molecule and not with a reaction in which several molecules take part, which according to some authors is not improbable [2]). In order to investigate this it became necessary to know the velocity of reaction. If the reaction took place monomolecularly, we should be really dealing with an intramolecular displacement; a bimolecular reaction would point to a double decomposition between two molecules.

As a suitable example for this research, Prof. Lobry de Bruyn pointed out to me the conversion of acetylchloroanilide into parachloroacetanilide under the influence of hydrochloric acid, first discovered by Bender [3])



It is known that the chlorine in acetylchloroanilide may be determined by adding potassiumiodide to its acetic acid solution and titrating the liberated iodine; *p*-chloroacetanilide does not react with K I:

$$C_6H_5NClCOCH_3 + 2HI = C_6H_5NHCOCH_3 + HCl + I_2.$$

The acetylchloroanilide was prepared according to the directions of Chattaway and Orton [4]) by shaking acetanilide with a solution of bleaching powder containing potassium bicarbonate. Within half a minute to a minute it will be noticed that the acetanilide has nearly entirely dissolved; after a few minutes the acetylchloroanilide separates in a crystalline state. Chattaway and Orton state that this

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[1]) Proc. 25 Jan. and 29 March 1902.

[2]) Armstrong, Journ. Chem. Soc. **77.** 1053.

[3]) Ber. **19.** 2273. Slossen, Ber. **28.** 3265.

[4]) Journ. Chem. Soc. **79.** 278.

compound is unstable and is spontaneously converted into *p*-chloroacetanilide. A closer investigation showed me that the cause of this must be attributed to the action of sunlight. After 14 days exposure to the light (May 14-28), the atmosphere being cloudy, this substance was entirely converted into *p*-chloroacetanilide while on a bright day in June the conversion was complete in a day. In the same manner it was shown that the analogous bromo-compound $C_6 H_5 N Br CO CH_3$ had been entirely converted after 3—4 hours exposure to direct sunlight on an afternoon in June and in 70 hours by exposure to incandescent gaslight; in diffuse daylight the conversion was complete after a few days, while both the chlorine and the bromine compound, could be preserved unaltered in the dark.

We therefore see that Br and Cl linked to N, shift to the nucleus under the influence of light. On consulting the literature it was found that BAMBERGER [1]) had already shown that phenylnitramine is converted by sunlight into *o*- and *p*-nitraniline, while he had also found that nitrosophenylhydroxylamine is very rapidly decomposed by direct sunlight and sometimes even explodes. The reaction takes here a more complicated course, the first stage of the reaction is probably the migration of the N O group to the nucleus.

Recently KNIPSCHEER [2]) has shown that azoxybenzene is converted by direct sunlight into *o*-oxyazobenzene.

We therefore see that under the influence of sunlight Br, Cl, NO_2, NO and O attached to N migrate from the side-chain to the nucleus and change place with an atom of hydrogen [3]).

In the previous communication (l.c.) attention was called to the analogy of the CH_3-group with NH_2 and OH. Now however, we notice a difference. Whereas sunlight promotes the entering of atoms or groups into the nucleus of the NH_2-derivatives, it causes the formation of Br and Cl compounds in the side-chain of the CH_3-derivatives, for instance in the bromination or chlorination of toluene [4]).

We may briefly refer to the experiments of SRPEK [5]) and ERRARA [6]) who have proved that on chlorinating parabromotoluene *p*-bromo-

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[1]) Berichte **27**, 364, 1554, **34**, 66.

[2]) Proc. 31 May 1902.

[3]) No experiments showing the effect of light have, as yet, been made with phenol derivatives containing atoms or groups attached to the oxygen. It is probable that sunlight will in this case also excercise an influence on the migration of atoms or groups of the side-chain to the nucleus. This should be borne in mind when preparing these compounds.

[4]) SCHRAMM, Ber. **18**, 608.

[5]) Monatsch. f. Chem. **11**, 431.

[6]) Gazz. Chim. Ital. **17**, 202.

benzylbromide is formed in addition to *p*-bromobenzylchloride; in this case the bromine leaves the nucleus and is introduced into the side-chain [1]. This question merits further investigation.

After several preliminary experiments which showed that the interchange of Cl and H is much promoted by the catalytical action of acids, I determined the velocity of reaction in the following manner. 3—4 grams of the acetylchloroanilide were dissolved in 100 grams of glacial acetic acid (100 %), 10 cc. of hydrochloric acid containing 2,9127 grams of HCl were added and finally the liquid was diluted with water to 500 cc. This solution was put into a black bottle and kept in a thermostat at 25°. As soon as the temperature had reached 25° 50 cc. were removed with a pipette and delivered into 100 cc. of water to stop the reaction. Excess of solution of potassium-iodide was added and the liberated iodine titrated with sodium thiosulphate (0,150 N). The following results were obtained.

t in hours.	cc. $Na_2S_2O_3$.	*k*.
0	49.3	
$^1/_2$	42	0.160
1	35.6	0.162
$1^1/_2$	30.25	0.163
2	25.75	0.162
$2^1/_2$	21.8	0.163
3	18.5	0.160
4	13.8	0.160
6	7.3	0.160
8	4.8	0.162

By applying the formula for the monomolecular reaction $k = \frac{1}{t}\, l \frac{A}{A-x}$ values are found for *k* which may be regarded as constants.

This proves that the reaction is really monomolecular and that we are dealing with an actual intramolecular rearrangement of atoms.

If instead of 10 cc., 20 cc. of hydrochloric acid were added the value for *k* was found to be 0.610; (the average result of eight observations); by using double the quantity of acid the velocity has therefore increased nearly four times. If instead of hydrochloric acid sulphuric acid of the same concentration was used, the conversion was very slow and a good constant was not obtained (32.8 cc. of $Na_2S_2O_3$ at first, 29 cc. after 24 hours).

In glacial acetic acid (99—100 %) the reaction takes place much

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[1] Cf. HANZSCH, Ber. **30**, 2334. THÖL and ECKEL, Ber. **26**, 1104.

more rapidly so that addition of very little hydrochloric acid suffices for the complete conversion.

The substance was again dissolved in glacial acetic acid and 3 cc. of a solution of dry hydrogenchloride in glacial acetic acid were added. The quantity of HCl thus introduced into 500 cc. of the solution amounted to only 0.0135 gram or not quite $^1/_{200}$ part of the quantity present in the experiment with aqueous acetic acid.

The progressive change of the reaction was as follows:

t in hours	cc. $Na_2 S_2O_3$
0	30.3
$^1/_2$	29.7
1	28
$1^1/_2$	24
2	22.6
$2^1/_2$	19.8
3	17.2
$3^1/_2$	14.2
4	12.4
$4^1/_2$	10.5

On calculating k according to the formula $k = \frac{1}{t} l \frac{A}{A-x}$ it will be seen that it keeps on increasing; this shows that the amount of the catalyser increases. On repeating the experiment it was found that, after the reaction, more hydrochloric acid existed (weighed as Ag Cl) than corresponded with the quantity added.

A graphic representation of the above figures plainly shows that we are dealing here with a reaction the velocity of which has been accelerated by an increase of the catalyser [1]. In the experiment with 20 per cent acetic acid the small increase of the relatively large amount of HCl is not perceptible.

Even when we do not add hydrochloric acid but set the acetic acid solution aside in the dark we meet with the same type of progressive change of the reaction. 10 c.c. of a solution in glacial acetic acid were titrated from day to day and took:

13. 12. 9. 6,7 3,7 2,6 1,5 and 1 c.c. $Na_2 S_2 O_3$

which figures again reveal the character of a reaction accelerated by a catalyser. It moreover shows that it is not the glacial acetic acid which starts and continues the reaction, but that the conversion is due to the catalyser formed from the product itself; in the first

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[1] Ostwald, Lehrb. d. allgem. Chem. Bd. II, T. II, 266.

case it ought to be possible to calculate a constant by means of the formula employed for monomolecular reactions.

We are, therefore, dealing here with a case quite analogous to that of the spontaneous decomposition of alkyl sulphuric acid and nitrocellulose mentioned by OSTWALD; it is known that this may be prevented by adding a little K_2CO_3 or $CaCO_3$,

The reaction in the presence of alcohol takes place in a similar manner; on warming on the waterbath it may according to CHATTAWAY and ORTON become so violent that the alcohol begins to boil. This may be prevented by adding a trace of Na_2CO_3 which fact has been noticed by ARMSTRONG (l. c.).

We therefore, see:

1. That the conversion of acetylchloroacetanilide into *p*-chloroacetanilide proceeds like a monomolecular reaction and that it represents a true intramolecular rearrangement of atoms. It may therefore be compared to the case of the transformation of the bromo-amides under the influence of alkalis studied by VAN DAM and ABERSON [1]).
2. That Br, Cl, NO_2, NO, and O attached to N change place, under the influence of sunlight, with an H-atom present in the nucleus.
3. That the conversion of acetylchloroacetanilide in alcoholic or acetic acid solution is caused by the formation of a catalyser which causes the reaction to proceed at an increasing rate (particularly in sunlight); this may be prevented by adding a trace of sodium carbonate or acetate as this removes the catalyser.

The investigation will be continued in various directions.

Chemistry. — *"Galvanic cells and the phase rule."* By Dr. W. REINDERS of Breda. (Communicated by Prof. H. W. BAKHUIS ROOZEBOOM).

NERNST [2]) and, more recently, BANCROFT [3]) have tried to establish a relation between galvanic cells, consisting of a combination of two metals surrounded by electrolytes in communication with each other, and the phase rule. Neither of them, however has paid sufficient attention to the fact that: When the phase *A* is in equilibrium with *B* and also with *C*, then *B* must be also in equilibrium with *C*. They regard the liquid electrolyte, in contact with the metals, as one homogeneous phase, whilst in reality two phases exist which are

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[1]) Recueil **19**. 318 (1900).

[2]) Theor. Chem. 1e Aufl. p. 560, 3e Aufl. p. 660.

[3]) J. of phys. Ch. II 427 (1898).

not in equilibrium with each other; in fact various means are employed to prevent them from forming a homogeneous mixture.

The following contains a new effort to study the galvanic cell from the point of view of phase rule.

Those cells have been considered, which consist of a combination of 2 metallic electrodes, each surrounded by an electrolyte, containing the cation of the metal and connected with each other either directly or by means of an electrolyte.

Equilibrium may exist between both the electrodes and the surrounding electrolyte and when that equilibrium is reached, there exists at the plane of separation a certain potential difference, which is the measure of the energy required to transfer an equivalent of the metal from the one phase into the other.

Bancroft is therefore in error in regarding the E.F. as an independent variable, as a further condition of equilibrium. He says: "In addition to the ordinary conditions of equilibrium there is also the electromotive force."

The variables would then be the n components, temperature, pressure and the potential difference and from this it would follow that for an invariant system $n+3$ phases were required.

This is not the case, for π is completely defined when n phases are present in a system of n components at a given temperature and pressure (for instance by the formula of Nernst when $n=2$ or 3).

There exists, however, no equilibrium between the two electrolytes in the cell. They will tend to form a homogeneous mixture in which case the composition is changed and the equilibrium with the electrode disturbed.

Therefore, there can be no question of a real equilibrium in the whole of the cell so long as both electrodes cannot be in equilibrium with the same electrolyte and the EMF becomes zero. An apparent equilibrium may, however, be got by preventing as much as possible the diffusion of the two electrolytes.

Considering the cell as a combination of two systems consisting of metal and electrolyte, the equilibrium of the separate systems should be discussed before alluding to that existing in the cell.

The equilibrium between the metallic electrode and the surrounding electrolyte and the potential difference at their plane of separation.

A. *The electrode consists of a single metal and the surrounding electrolyte also contains cations of that metal alone.*

When the electrolyte is a fused salt of the metal, we have a system of 2 components in 2 phases which at a given temperature and pressure is completely defined. If the electrolyte is a solution of a salt of the metal, there will be 3 components and, therefore, the concentration must also be given. The potential difference is determined by the formula of NERNST: $\pi = \frac{RT}{n} l \frac{P}{p}$ in which $P =$ the solution tension of the metal, $p =$ the osmotic pressure of the cation and $n =$ the valency of the metal.

B. *The electrolyte consists of two different metallic salts M_1Z and M_2Z and in the electrode both metals of these salts may be present.*

Assuming that the electrolyte forms one homogeneous phase, the following distinction may be made in the equilibria of the electrode and electrolyte.

I. *At the given temperature there is no reaction between the two metals; they form therefore neither a compound nor a liquid or solid solution.*

Starting from the electrolyte, containing only the salt M_1Z (fused or in solution), there is a series of electrolytes with an increasing amount of M_2Z, which can only be in equilibrium with M_1, and another series, starting from M_2Z with increasing quantities of M_1Z, which are only in equilibrium with M_2.

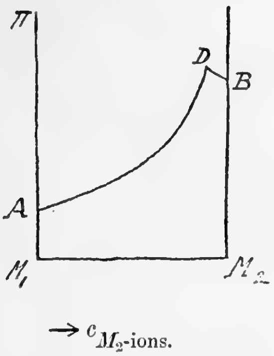
Where these two series meet, we have an electrolyte, which is in equilibrium with both M_1 and M_2. When there is no solvent and we are consequently dealing with a fused salt mixture, there is only one electrolyte which satisfies this equilibrium. We then have 3 phases: electrolyte, M_1 and M_2 and 3 components M_1, M_2 and the acid group Z. The equilibrium at a given t and p is, therefore, completely defined.

If, however, a solvent, and consequently a fourth component is also present, then, according to the quantity of this solvent, there will be a series of electrolytes which satisfy the conditions of equilibrium.

To follow the change in the potential difference, we may imagine, that a part of the ions M_1 in the electrolyte containing M_1Z, has been replaced by M_2, but in such a way, that the total concentration of the ions $M_1 + M_2$ remains constant. The potential difference between M_1 and the electrolyte will increase, because in the equation $\pi_1 = \frac{RT}{n_1} l \frac{P_1}{p_1}$, p_1 becomes smaller and consequently π_1 becomes greater.

The same applies to π_2, the potential difference between the metal M_2 and an electrolyte containing only M_2 cations, when part of these ions is replaced by ions M_1.

Fig. 1.



In fig. 1 AD and BD are the lines giving a graphic representation of the change of π as function of the ratio of the ions M_1 and M_2 at a constant total concentration of the cations. A point on AD, therefore, gives the concentration of the M_1 and M_2 ions in an electrolyte, which is in equilibrium with M_1 and the potential difference at the plane of separation between this electrolyte and the electrode. BD does the same for M_2. Both lines are logarithmic curves. AD, therefore, asymptotically approaches the ordinate M_2B, until it is intersected in D by the line BD.

In D the electrolyte is in equilibrium with the two metals M_1 and M_2. To the left of it, M_1 is precipitated by M_2, to its right, M_2 by M_1. The condition of equilibrium in D is $\pi_1 = \pi_2$

therefore
$$\frac{1}{n_1} log \frac{P_I}{p_1} = \frac{1}{n_2} log \frac{P_{II}}{p_2}$$

or
$$\sqrt[n_1]{\frac{P_I}{p_1}} = \sqrt[n_2]{\frac{P_{II}}{p_2}}$$

and, for metals of the same valency $P_I : P_{II} = p_1 : p_2$.

In words: in this equilibrium the ratio of the concentrations of the cations is equal to the ratio of the solution tensions of the metals.

Owing to the great difference in the solution tensions, p_1 must in most cases be very small and consequently the possibility of the second metal existing in contact with the mixed electrolyte, is limited to very minute concentrations of the first metallic salt; whereas the first metal may be in equilibrium with almost all the electrolytes, whatever the proportions of the two salts may be. The point D is, therefore, situated nearest to the less noble metal and almost coincides with B.

Danneel [1]) has investigated an instance of this equilibrium, namely $2\,HI + 2\,Ag \rightleftarrows 2\,AgI + H_2$. The solution, which is in equilibrium with both Ag and H_2 under 1 atm. pressure, is saturated with AgI ($c = 0{,}567 \times 10^{-8}$) and 0,043 normal in HI.

II. *The two metals form a homogeneous liquid or solid solution.*

This is the case with the liquid amalgams and other fused metals, with Zn—Ag [2]), Sb—Sn [3]) and other alloys.

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[1]) Z. f. Phys. Ch. **33**, 415.

[2]) Heycock en Neville. J. Chem. Soc. 1897, 415.

[3]) Heycock en Neville. J. Chem. Soc. **330**, 387; van Bijlert, Z. f. phys. Ch. **8**, 357 en Reinders Z. f. anorg. Ch. **25**, 113.

Starting with the one pure metal and a solution, containing only the first metallic salt, it is found that on addition of the second metallic salt a small portion of the second metal will be separated and dissolved in the first one until the metallic phase is again in equilibrium with the electrolyte.

This equilibrium requires that $\pi_1 = \pi_2$ or for dilute solutions:

$$\frac{RT}{n_1} \log \frac{P_1}{p_1} = \frac{RT}{n_2} \log \frac{P_2}{p_2}$$

or also

$$\sqrt[n_1]{\frac{P_1}{p_1}} = \sqrt[n_2]{\frac{P_2}{p_1}}$$

in which P_1 and P_2 are the partial solution tensions of the two metals in the homogeneous metal phase. P_1 and P_2 are not constant here, but vary with the composition of the electrode.

This formula was obtained by NERNST [1]) and verified by OGG [2]) by means of the example $Hg + AgNO_3 \rightleftarrows HgNO_3 + Ag$.

The electrode now contains both metals, as may also happen in the case of non-homogeneous mixtures (*D* in fig. 1). The difference, however, is that there the metals form 2 phases and here only one. If the electrolyte is a mixture of fused salts or a solution in which the total concentration of the two cations is constant, then, at a constant temperature and pressure, the system will still be monovariant and the relation $\sqrt[n_1]{P_1} : \sqrt[n_2]{P_2}$ or $\sqrt[n_1]{p_1} : \sqrt[n_2]{p_2}$ may still be variable. Once however, the relation $\sqrt[n_1]{p_1} : \sqrt[n_2]{p_2}$, that is the composition of the electrolyte, having been given, $\sqrt[n_1]{P_1} : \sqrt[n_2]{P_2}$ or the composition of the metal phase, is also determined and consequently also π.

At each temperature a series of two such coexisting phases are possible. The potential difference continuously changes with their composition.

In order to trace the general course of this π-line it must first be ascertained how P_1 and P_2 depend on the composition of the electrode.

If, in the metal phase, there are x atoms of M_2 and $1-x$ atoms of M_1 and x is small, the lowering of the solution tension may be taken as proportional to the number of dissolved molecules of the second metal, which is analogous to the lowering of the vapour pressure in liquid mixtures. If we call the solution tension of the pure metal M_1 P_1, then $P_1 = P_I(1-x)$.

For small concentrations P_2 is proportional to the concentration

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[1]) Z. für phys. Ch. **22**, 539.

[2]) Z. für phys. Ch. **27**, 285.

of the second metal, as has already been proved by the investigations of MEYER [1]), RICHARD and LEWIS [2]) and OGG [3]). Therefore $P_2 = Kx$.

The factor K is unknown. For $x = 1$ it becomes however $= P_{II}$. For small values of x however this is not necessarily the case, for it is to be expected that its value will be influenced by the nature of the first metal.

The condition of equilibrium then becomes:

$$\sqrt[n_1]{\frac{P_I(1-x)}{p_1}} = \sqrt[n_2]{\frac{Kx}{p_2}}$$

or

$$\frac{\sqrt[n_2]{p_2}}{\sqrt[n_1]{p_1}} = \frac{\sqrt[n_2]{Kx}}{\sqrt[n_1]{P_I(1-x)}}$$

and for $n_1 = n_2$

$$\frac{p_2}{p_1} = \frac{K}{P_I}\frac{x}{1-x}.$$

In words: The ratio of the ions in the electrolyte is to that of the atoms in the metal as $K : P_I$.

When the ratio $K : P_I$ is very great, $p_2 : p_1$ will also be great, even when x has but a small value, that is to say that the electrolyte will contain almost exclusively cations of the baser metal even when the concentration of that metal in the electrode is small.

In calculating the potential difference, the concentration of these ions (p_2) may, therefore, be taken as constant. $\pi = \frac{RT}{n_2} l \frac{Kx}{p_2}$ is then a logarithmic function of x and, for small values of x, will increase rapidly with it. $\left(\frac{d\pi}{dx} = \frac{RT}{n_2}\frac{1}{x}\right)$.

The graphic representation of this function is a curve rising rapidly from the potential of the nobler metal at a small distance from the π-axis. As x increases, K approaches to the value P_I, becoming equal to P_I when $x = 1$. The curve, therefore, bends sharply and after a small further rise reaches to the value of the potential of M_2 in a solution of pure M_2Z.

The ratio of the ions in the coexisting electrolyte $\frac{p_2}{p_1+p_2}$ increases from 0 to nearly 1 for quite small values of x. The curve, which represents π as a function of this ratio, runs, therefore, at a slight incline towards the ordinate representing these baser metal, finally approaching it almost asymptotically.

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[1]) Z. f. phys. Ch. 7, 477.

[2]) „ „ „ „ 28, 1.

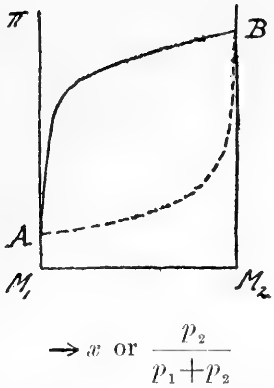
[3]) l. c.

The same results are obtained by considering the equation

$$\pi = \frac{RT}{n_1} l \frac{P_1 (1-x)}{p_1}$$

a. When the two metals form homogeneous mixtures in all proportions, the curves will therefore possess the general form shown in figure 2.

Fig. 2.



The points on these curves, which are situated on the same horizontal line, are coexisting phases. The ordinate of the points gives the potential difference at the plane of separation.

Although it is not impossible, a maximum or minimum will rarely occur, unless the solution tensions of the two components differ very little.

b. If the metals are not homogeneously miscible in every proportion, and the series of mixtures is therefore discontinuous, the two metallic phases, which are in equilibrium with each other (the end points of the break), will also be in equilibrium with the same electrolyte. The potential in this electrolyte must be the same for both metallic phases, for if such were not the case, a current might be generated and the equilibrium would be disturbed.

According to whether the potential difference in this non-variant equilibrium is greater than those of the pure metals in solutions of their salts or intermediate between them, the figures 3 or 4 are obtained.

Fig. 3.

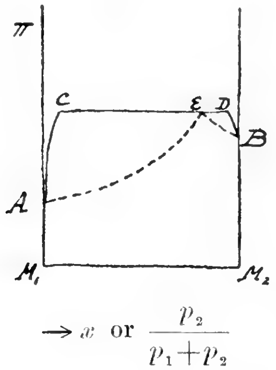
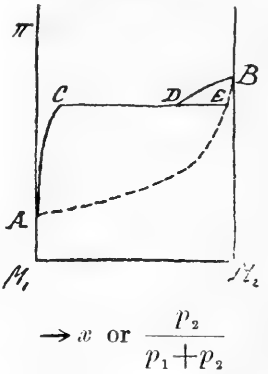


Fig. 4.



C and *D* are the two metallic phases in equilibrium with each other. *E* is the coexisting electrolyte.

The case of fig. 3 becomes identical with that of fig. 1 if *C* and *D* coincide to the right and the left with the π-axis, that is when the metals do not mix.

An example of the case of fig. 4 is found in my investigation [1]) of the equilibrium between fused lead, zinc and their chlorides. At 515° is $C = 89\,\%$ of Pb, 11 % of Zn; $D = 97\,\%$ of Zn, 3 % of Pb; $E = 99{,}9\,\%$ of $ZnCl_2$, 0,1 % of $PbCl_2$ and if π_A is taken as 0 then $\pi_{CED} = 0{,}277$ Volt and $\pi_B = 0{,}283$ Volt.

A second example is found in the cadmium amalgams, investigated by JAEGER [2]) and BIJL [3]). Further researches are those of MEYER and RICHARDS and LEWIS on the dilute amalgams, those of LINDECK [4]) and those of HERSCHKOWITSCH [5]), who met with the case represented by fig. 4 in his investigation of Cd—Sn, Cd—Pb, Zn—Sn, Zn—Bi, Cu—Ag.

In all these cases the concentration of the nobler metal in the electrolyte is very small; to a large extent the curve AEB almost coincides with M_2B.

III. *The two metals form a compound.*

If the compound is present in a pure condition there will only be 2 phases and at least 3 components. Even without solvent the system is still monovariant at constant temperature and pressure. As in case I, if one of the pure metals forms the electrode, a series of solutions exists with varying proportions of the salts M_1Z and M_2Z, which may be in equilibrium with this compound. The limit of this series is reached when the solutions are also in equilibrium with a second metallic phase (one of the pure components, a liquid or solid solution or a second compound).

In order to make use of NERNST's formula to calculate the potential difference, it is necessary to assume that the electrode forms ions of the same composition as the compound, for instance of $AuAl_2$, Zn_2Ag, etc., and to substitute the concentration of these ions in the formula. The solution pressure is then a definite constant for this compound, as it is for every pure metal:

therefore
$$\pi = \frac{RT}{n_{1.2}}\, l\, \frac{P_{1.2}}{p_{1.2}}\,.$$

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[1]) Z. f. anorg. Ch. **25** 126.

[2]) Wied. Ann. **65** 106.

[3]) Inaug. Dissert., Amsterdam 1901.

[4]) Wied. Ann. **35** 311.

[5]) Z. f. phys. Ch. **27** 123.

If the formula of the compound is $M_1^a\,M_2^b$, then owing to dissociation, ions M_1 and M_2 will occur along with ions $M_1^a\,M_2^b$ and between these an equilibrium will exist expressed by the equation:

$$p_1^a\,p_2^b = Kp_{1.2}.$$

When the total concentration of the ions remains constant, $k-p_1$ may be substituted for p_2 and the equation becomes

$$p_1^a\,(k-p_1)^b = Kp_{1\cdot 2}.$$

The maximum value of $p_{1\cdot 2}$ is reached when the first differential quotient with respect to $p_1 = 0$, that is, when

$$a\,p_1^{a-1}\,(k-p_1)^b - b\,p_1^a\,(k-p_1)^{b-1} = 0$$

or

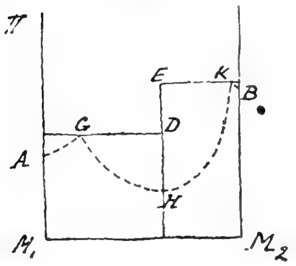
$$a\,(k-p_1) = b\,p_1$$

or

$$p_1 : p_2 = a : b.$$

$p_{1\cdot 2}$ therefore reaches a maximum and π a minimum where the ratio of the ions M_1 and M_2 in the electrolyte is equal to that of the metals in the compound.

Fig 5.



a. If the compound can be in equilibrium with an electrolyte in which the ratio of the cathions is the same as that of the metals in the compound and if in addition to the compound only the metals in a pure condition are capable of existence, then the π-curve will have the form indicated in fig. 5.

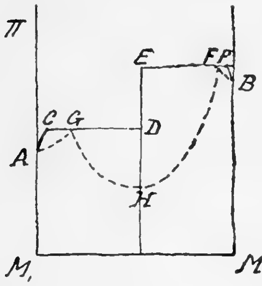
The points on the line AG give the compositions of electrolytes in equilibrium with pure M_1 and the corresponding potential differences. With the electrolyte G both M_1 and the compound are in equilibrium. So long as both metal phases are present, the potential difference remains constant. Should M_1 have entirely disappeared, so that the electrode consists of the pure compound (composition $= D$), the electrolyte may vary from G to K while the potential difference first falls to H and then again rises to K. In K there is again a non-variant equilibrium between the compound, pure M_2 and the electrolyte K and so long as these phases exist the potential difference remains constant. But when the compound has disappeared, it falls to B, while the electrolyte changes from K to pure M_2Z.

From an electrolyte having a composition situated between G and K the compound M_1M_2 is precipitated by M_1 and also by M_2.

Owing to the small rise of the line *AG*, the first case is sure to occur but rarely, as the line *GHK* then stands a chance of not being again intersected by *AG* and this case will pass into that of *b* (see below).

H may be situated higher or lower than *A*.

Fig. 6.



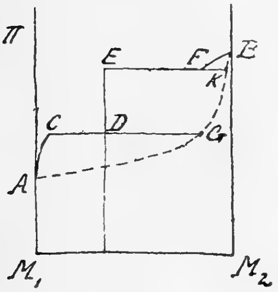
If, in addition to the compound, two solid solutions are possible (M_1 in which a little M_2 and M_2 in which a little M_1 is dissolved), the π-curve takes the course indicated in fig. 6, which differs from fig. 5 in this, that in presence of the electrolytes *A* to *G* pure M_1 is replaced by an electrode of varying composition, represented by the line *AC*, and in presence of the electrolytes *B* to *K* metallic phases *B* to *F* occur.

The line *BF* may either rise or fall [1]).

An example of this case is probably the system Hg, Ag, NO_3, examined by Ogg (l.c.) for dilute solutions of Ag in Hg.

b. If the compound cannot exist in presence of an electrolyte in which the ratio of the cations is the same as that of the atoms in the compound and if we consider the case in which in addition to the compound two solid solutions are possible, we get fig. 7.

Fig. 7.



Metallic phases from *A* to *C* are in equilibrium with electrolytes from *A* to *G*. From *C* to *D* the electrode consists of a mixture of the two phases *C* (a solution of M_2 in M_1) and *D* (the compound). The potential difference is constant.

As therefore, the compound is not in equilibrium with an electrolyte having the same ionic ratio, it will, in contact with such an electrolyte, dissolve with separation of M_1, and tend towards the equilibrium *G*, *D*, *C*. If, before attaining this, *D* has totally dissolved, a metallic phase on the line *AC* and an electrolyte on the line *AG* will remain.

From *D* to *E* the pure compound is in equilibrium with an electrolyte of varying composition, situated on the line *GK*. The potential difference rises. The metallic phase *F* and the compound *E* are in equilibrium with the electrolyte *K*. As long as these three are present, the potential difference is constant. If, however, the electrode reaches a composition to the right of *F*, the compound will have disappeared

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[1]) In fig. 6 to read *K* instead of *F* and *F* instead of *P*.

and there will be equilibrium of the metallic phases F to B with the electrolytes K to B. π rises or falls (as in fig. 3).

It may be expected here as in II, that the line $AGKB$ will to a large extent run close to the π-axis of M_2 and that in consequence the concentration in M_2-ions in G and K will be very small.

When no solid mixtures of the two metals are possible AC and BF coincide with the π-axis. F then lies above B.

If there is more than one compound, the sudden change of potential DE is repeated for such compound. HERSCHKOWITSCH (l.c.) has noticed these sudden rises with Zn_2Cu, Zn_4Ag, $ZnSb_2$, Cu_3Sn, Ag_4Sn and has regarded them as evidence of the existence of these compounds.

We should, however, be careful when drawing such conclusions as to the composition of alloys from measurements of potential difference, for an alloy, obtained by melting together the two components and rapidly cooling the mass, is a badly defined substance and often contains more than two phases which are not at all in equilibrium. When they are brought into contact with an electrolyte consisting of a salt of the less noble metal, the unstable compounds in the alloy may be converted into the more stable ones and this reaction, which is caused by a short circuited element (unstable compound, electrolyte, stable compound), continues until only the two phases, which are really in equilibrium, remain. During this period the EMF observed is not necessarily constant.

The constant cells.

As already stated, there is no equilibrium between the two electrolytes of a cell; they tend to form a homogeneous mixture by diffusion. The potential difference between two electrolytes is, however, generally very small and when the diffusion is small, it will change very little. As, moreover, the EMF of a cell consists of the sum of the potential differences between the two electrolytes and between electrolytes and the electrodes, an apparent equilibrium and consequently a constant EMF may be secured by making the diffusion as small as possible.

To attain this it is necessary that there should be equilibrium between the electrodes and their electrolytes. But, in a constant cell, that equilibrium must not be modified when the current is allowed to flow and an interchange between the phases takes place in consequence. At constant t and p the system must be invariant.

If the electrode consists of a single metal, the concentration of the ions of the metal in the electrolyte must be kept constant. In case the electrolyte consists of a solution of the metallic salt, the presence of this salt in a third phase of constant composition, such as a solid hydrate, is required. These conditions are satisfied in the original form of the Clark cell, which contains on one side Zn and a saturated solution of $ZnSO_4$, $7H_2O$ and on the other side mercury and a saturated solution of Hg_2SO_4.

If the electrode consists of two metals forming only one phase (liquid solution, solid solution or compound), the current will necessarily cause a change in the equilibrium, because the ratio of the metals in the electrolyte is generally different from that in the electrode. The equilibrium will only then become invariant when a second metallic phase appears.

If there is no solvent, and the electrolyte therefore consists of a mixture of the two fused metallic salts, its composition is completely defined by the presence of 3 phases of the 3 components (M_1, M_2 and the common acid radicle). If, however, there is also a fourth component in the form of a solvent, a fourth phase must be present to make the equilibrium invariant such as the crystals of one of the two salts. The choice between the two salts is not an arbitrary one, but is regulated by the required relation of the concentration of the cations and the solubility of the two salts.

From this it follows, that on passing the current, only that metal, the salt of which is present in a second constant phase, can dissolve or deposit on the electrode (which consists of a mixture of the two metal phases). The ratio of the quantities of the two metallic phases must be regulated accordingly.

An example, from among the commonly used normal elements is the Weston cell in which the Cd-electrode consists of a mixture of a liquid phase (Hg with 5 % Cd) and a solid one (Hg with 14 % Cd)[1] while the surrounding electrolyte consists of a solution of $CdSO_4$ and traces of Hg_2SO_4, saturated with $CdSO_4\ \frac{8}{3}\ H_2O$.

The Clark cell in which a zinc amalgam with 10—15% of zinc is used, is clearly a similar combination.

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[1] Byl. l. c.

Astronomy. — *"On the yearly periodicity of the rates of the Standardclock of the observatory at Leyden,* Hohwü *No.* 17." Second part. By Dr. E. F. van de Sande Bakhuyzen.

III. *The period* 1862—1874.

9. As was mentioned, several investigations about the rate of the clock Hohwü 17 during this period have been made by Kaiser. They have been partly published. These published investigations are relative to the period 1862 May—1864 August [1]).

Afterwards, in the autumn of 1870, Kaiser undertook a new investigation founded on the period 1862—1870 [2]). In 1872 this investigation was continued and extended over the last year and a half [3]). Kaiser was engaged in this investigation, the results of which were intended for the 3rd Volume of the Annals of the observatory, till the last months of his life. It was unfinished, however, at his death.

The results which Kaiser had obtained did not wholly satisfy him. Several singular irregularities had shown themselves; moreover he was aware of the fact that the barometer-readings, one of the foundations of the investigation, might still be affected by rather considerable systematic errors, even after they had been corrected as well as possible. These barometer-readings had been derived by him from observations repeated three times every day on an old defective mercury barometer of Butti hanging in his study (during a year and a half on an Aneroid-barometer). The correction of this barometer was derived from simultaneous readings of the barometer in the transit-room. It appeared to be variable with the height of the barometer and increased considerably in the course of the years; moreover the temperature of the barometer was quite uncertain.

For these reasons H. G. van de Sande Bakhuyzen, when in 1873 he planned the continuation of the investigation of the clock, deemed it necessary, first of all to procure better data about the atmospheric pressure to which the clock had been exposed [4]). He intended to derive these by the help of the regular barometer-readings made at the meteorological Institute at Utrecht.

In the first place the constant differences between the barometer-readings at Utrecht and those at Leyden (the barometer in the transit-room) had to be derived. From extensive calculations, which have

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[1]) F. Kaiser l. c.

[2]) *Vide:* Verslag van den staat der sterrenwacht te Leiden. 1870—71 pp. 15 and 16.

[3]) *Vide:* Verslag van den staat der sterrenwacht te Leiden. 1871—72 pp. 14 and 15.

[4]) *Vide:* Verslag van den staat der sterrenwacht te Leiden 1872—73 p. 4.

been continued afterwards, it finally appeared that, when the necessary corrections [1]) and the reduction for difference in altitude had been applied, the mean barometer-readings at both places are in perfect agreement [2]).

After the completion of this preparatory work H. G. VAN DE SANDE BAKHUYZEN has been prevented by want of time from further investigations of the rates of the clock HOHWÜ 17.

10. When last year the investigation of the clock in the period 1862—74, was resumed by me, I have soon given up the attempt to derive trustworthy corrections for the barometer of BUTTI and I too have used the readings at Utrecht. It appeared that in this way we can get a precision sufficient for our purpose, at least for the mean monthly barometer-readings.

I had at my disposal readings of the barometer at Utrecht for 20^h, 2^h and 10^h. From these I derived mean barometerreadings reduced to 0° for the whole of our period [3]). In addition to these, however, we have readings of the barometer at Leyden for the last months. For, to begin with July 1873, the barometer in the transit-room has been regularly read five times a day. From these I could derive, in the same way as I had done for the time after 1877 mean barometerreadings, which afterwards I reduced to 0°. The comparison of the monthly means obtained in the two ways stands as follows:

		L. — U.			L. — U.
1873	July	+ 0.3 Mm.	1873	Dec.	+ 0.3 Mm.
	Aug.	0.0	1874	Jan.	— 0.2
	Sept.	— 0.2		Febr.	+ 0.2
	Oct.	— 0.2		March	+ 0.3
	Nov.	— 0.1		April	+ 0.1

The differences thus appear to be very small. They would have turned out still smaller perhaps, if we had not neglected the hundredth parts of the millimeters in all the computations. The mean value amounts only to + 0,05 Mm.

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[1]) About the errors of the barometer at Utrecht see: J. D. VAN DER PLAATS, „Over den barometer van het K. Nederl. Meteor. Inst." (Meteor. Jaarboek voor 1888). At Leyden the barometer-readings were reduced to those of the standard-barometer of FUESS.

[2]) See also: Annalen der Sternwarte in Leiden. Vol. VI pp. CXIV—CXVI.

[3]) By taking the means of the readings at 10^h, 20^h, 2^h, 10^h and giving half weight to both the extreme values I obtained the daily means from midnight to midnight.

11. For the derivation of the temperature of the clock I had the following data at my disposal.

From 1862 to 1866 May a thermometer hanging at the pier of the clock was read at 8ʰ 30ᵐ in the morning.

Beginning from that time two thermometers suspended in the clock case were regularly read, but from 1866 June to 1873 June these readings were only made at 8ʰ 30ᵐ in the morning. Since 1873 July both thermometers were read five times a day.

From July 1873 it was possible therefore to take daily means of the temperature according to the upper thermometer in the clock case in the same way as was done for the time after 1877.

For former periods I had to find corrections in order to reduce to daily means of the latter thermometer.

For the purpose of finding these corrections I compared:

1st. For the years 1871, 1872 and 1873 the readings at 8ʰ 30ᵐ in the morning of the upper thermometer in the clock case with those of the thermometer at the clockpier;

2nd. for the years 1873—75 the readings at 8ʰ in the morning of the upper thermometer in the clock case with their daily means.

From the two comparisons I found the following monthly means of the differences Δ_1 = clock case — pier and Δ_2 = daily means — readings at 8ʰ, everything being expressed in degrees RÉAUMUR. The index-corrections have been taken into account.

	Δ_1	Δ_2		Δ_1	Δ_2
Jan.	+ 0.21	+ 0.22	July	+ 0.01	+ 0.36
Febr.	.11	.19	Aug.	.19	.41
March	.14	.44	Sept.	.16	.46
April	.15	.48	Oct.	.20	.26
May	.06	.38	Nov.	.16	.29
June	.03	.47	Dec.	.16	.04

For all the months I adopted for Δ_1 the general mean + 0,13. For Δ_2 I adopted

October—February	+ 0.20
March—September	+ 0.43

With the aid of these values and of the index-errors determined at regular intervals the necessary reductions were applied.

Lastly I compared the temperatures according to the upper and lower thermometer, as has been done for the subsequent period, the difference in the two cases being that, for the period now under discussion, the clock was only enclosed in a single case. I will set down only the results which I found for the means of the 5 daily readings in the years 1873—76.

	u.—l.		u.—l.
Jan.	+ 0.32	July	+ 0.44
Febr.	+ 0.34	Aug.	+ 0.40
March	+ 0.38	Sept.	+ 0.34
April	+ 0.42	Oct.	+ 0.30
May	+ 0.44	Nov.	+ 0.31
June	+ 0.44	Dec.	+ 0.31

These differences are corrected for index-errors.

12. With a few exceptions I used for the time before 1872 the same time-determinations from which Kaiser had formed his monthly means of the rates. Some corrections however could be applied. The clock had been set going in June 1861 but I left out the first year and placed the beginning of my investigation at 1862 May, as Kaiser had done. It ends April 1874, a short time before the occurrence of the perturbation.

The observed rates were first reduced to 760 Mm. at 0° and to + 10° R. For the coefficient b I again took $+ 0^s.0140$ (Kaiser in his last investigation found $+ 0^s.0134$) and for c I adopted the value $- 0^s.0174$ which is the mean result of Kaiser's last investigation, allowance being made for the fact that I now reduced the barometer-readings to 0°.

In the following table all the columns have the same meaning as the corresponding ones in the table for the period 1877—1898.

	Obsd D. R.	Bar.	Temp.	Redd D. R. I	Redd D. R. II	O.—C.
1862 May	s — 0.322	759.5	+ 12.7	s — 0.268	s — 0.299	+ 15
June	0.390	58.2	13.0	0.313	333	— 19
July	0.408	60.3	13.8	0.346	350	— 36
Aug.	0 424	60.6	14.5	0.354	341	— 27
Sept.	0.328	62.9	13.0	0.317	290	+ 24
Oct.	0 346	59.4	10.6	0.328	294	+ 20
Nov.	0.245	60.0	6.2	0.314	280	+ 34
Dec.	0.192	61.6	5.0	0.301	281	+ 33
1863 Jan.	0 301	56.9	4.8	0.348	344	— 30
Febr.	0.141	69.1	5.2	0.352	365	— 51
March	0 246	58 4	6.4	0.287	314	0
April	0.237	61 0	8.8	0.272	306	+ 8
May	0 213	61.7	10.8	0.223	254	+ 60
June	0.388	59.9	13 6	0.324	344	— 30
July	0.247	64.3	14.2	0.234	238	+ 76
Aug.	0 415	60.1	15.1	0.327	314	0
Sept.	0.404	58.2	11.8	0.348	321	— 7
Oct.	0.442	58.8	10.3	0.420	386	— 72
Nov.	0.237	63.9	6.4	0.355	324	— 10
Dec.	— 0.277	63.1	6.0	0.390	370	— 56
1864 Jan.	+ 0.032	68.8	0.8	0.251	247	+ 67
Febr.	— 0.165	59 8	2 2	0.298	311	+ 4
March	0 305	54.0	5.1	0.306	333	— 18
April	0.121	63 9	6 9	0.230	264	+ 51
May	0 208	61.4	10 1	0.226	257	+ 59
June	0.342	60.2	12.7	0.298	318	+ 2
July	0.375	62.0	13 9	0 335	339	— 13
Aug.	0 347	63 2	13 2	0.336	323	+ 9
Sept.	0.401	61.2	12.5	0.374	347	— 9
Oct.	0.369	59.0	8.7	0.378	344	0
Nov.	0.268	58.8	4.6	0.345	314	+ 35
Dec.	0 403	63.8	1.2	[0.369]	370	— 15

	Obs^{d} D. R.	Bar.	Temp.	Red^{d} D. R. I	Red^{d} D. R. II	O.—C.
1865 Jan.	$-0^{s}.433$	750.0	+ 2.4	$-0^{s}.425$	$-0^{s}.421$	— 60
Febr.	0.210	59.5	1.1	0.358	374	— 5
March	0.264	57.9	2.7	0.362	389	— 17
April	0.278	65.2	8.6	0.375	409	— 31
May	0.390	61.1	12.3	0.365	396	— 12
June	0.352	65.3	12.6	0.381	401	— 11
July	0.464	61.2	15.4	0.387	391	+ 5
Aug.	0.487	59.0	14.0	0.403	390	+ 11
Sept.	0.389	68.2	14.1	0.433	406	+ 1
Oct.	0.485	53.3	9.5	0.400	366	+ 46
Nov.	0.376	60.1	6.5	0.438	407	+ 11
Dec.	0.237	68.6	4.1	0.460	440	— 17
1866 Jan.	0.366	58.7	5.1	0.433	429	— 2
Febr.	0.473	54.4	4.7	0.487	500	— 69
March	0.425	54.3	4.8	0.435	462	— 27
April	0.394	60.2	8.4	0.425	459	— 21
May	0.347	61.7	9.2	0.385	416	+ 25
June	0.479	60.2	14.9	0.397	417	+ 26
July	0.477	59.9	14.1	0.405	409	+ 35
Aug.	0.536	56.6	13.3	0.431	418	+ 27
Sept.	0.599	56.7	12.5	0.509	482	— 36
Oct.	0.392	64.9	9.1	0.477	443	+ 3
Nov.	0.421	58.6	7.1	0.451	420	+ 26
Dec.	0.351	60.6	5.2	0.443	423	+ 23
1867 Jan.	0.376	52.9	2.2	0.413	409	+ 36
Febr.	0.285	64.4	5.5	0.425	438	+ 7
March	0.407	56.2	3.8	0.462	489	— 45
April	0.457	55.9	7.8	0.438	472	— 29
May	0.396	59.8	10.4	0.386	417	+ 25
June	0.413	63.4	13.0	0.409	429	+ 11
July	0.497	59.1	13.3	0.427	431	+ 7
Aug.	0.505	62.2	14.4	0.459	446	— 10

	Obs^d D. R.	Bar.	Temp.	Red^d D. R. I	Red^d D. R. II	O.—C.
1867 Sept.	— $0^{s}.484$	763.7	+ 13.2	— $0^{s}.480$	— $0^{s}.453$	— 19
Oct.	0.455	59.4	8.9	0.466	432	0
Nov.	0.312	65.9	6.4	0.458	427	+ 2
Dec.	0.266	62.2	3.1	0.417	397	+ 30
1868 Jan.	0.288	58.9	2.1	0.410	406	+ 19
Febr.	0.298	64.6	4.9	0.451	464	— 41
March	0.302	60.6	5.8	0.383	410	+ 11
April	0.344	60.4	7.4	0.395	429	— 10
May	0.359	62.6	12.5	0.351	382	+ 35
June	0.396	65.6	14.0	0.404	424	— 9
July	0.493	62.4	16.5	0.414	418	— 5
Aug.	0.592	60.0	16.1	0.486	473	— 62
Sept.	0.510	59.3	13.2	0.444	417	— 8
Oct.	0.381	60.3	8.4	0.413	379	+ 28
Nov.	0.263	61.7	5.6	0.364	333	+ 71
Dec.	0.421	52.4	5.9	0.386	366	+ 36
1869 Jan.	0.237	63.7	2.9	0.413	409	— 9
Febr.	0.269	60.9	5.7	0.357	370	+ 28
March	0.318	56.4	3.7	0.378	405	— 9
April	0.336	62.4	8.8	0.391	425	— 31
May	0.383	57.2	9.9	0.346	377	+ 14
June	0.358	63.0	11.0	0.383	403	— 14
July	0.415	64.2	14.4	0.397	401	— 14
Aug.	0.420	64.2	13.6	0.416	403	— 18
Sept.	0.456	58.0	12.8	0.379	352	+ 31
Oct.	0.409	61.3	9.2	0.441	407	— 26
Nov.	0.340	58.6	6.0	0.390	359	+ 20
Dec.	0.349	56.5	2.9	0.424	404	— 27
1870 Jan.	0.202	62.7	3.1	0.360	356	+ 19
Febr.	0.132	60.0	0.9	[0.290]	344	+ 29
March	0.280	61.6	3.9	0.408	435	— 63
April	0.226	65.1	7.7	0.337	371	0

	Obs^d D. R.	Bar.	Temp.	Red^d D. R. I	Red^d D. R. II	O.—C.
1870 May	— 0^s.299	763.4	+ 9.9	— 0^s.349	— 0^s.380	— 10
June	0.352	63.9	12.5	0.363	383	— 14
July	0.457	61.1	14.9	0.387	391	— 23
Aug.	0.536	58.5	14.4	0.438	425	— 58
Sept.	0.341	64 4	11.4	0.379	352	+ 14
Oct.	0 475	54.7	8.9	0.420	386	— 21
Nov.	0.388	56.3	5.9	0.407	376	— 12
Dec.	0.217	59.5	1.8	[0.353]	366	— 3
1871 Jan.	0.167	58.9	0.1	0.324	320	+ 42
Febr.	0.114	63.5	2.5	0.293	306	+ 55
March	0.198	62.7	6.0	0.306	333	+ 28
April	0.348	57.6	7.2	0.363	397	— 36
May	0.250	63.2	9.1	0.311	342	+ 18
June	0.391	58.9	11.6	0.348	368	— 8
July	0.458	58.7	14.0	0.370	374	— 14
Aug.	0.427	62.9	15.0	0.381	368	— 8
Sept.	0.475	59.3	12.8	0.416	389	— 29
Oct.	0.357	61 7	7.6	0.423	389	— 29
Nov.	0.309	60.9	3.7	0.432	401	— 41
Dec.	0.178	64.5	2.1	0.378	358	+ 2
1872 Jan.	0.285	54.6	3.6	0.320	316	+ 44
Febr.	0.273	59.8	4.5	0.366	379	— 19
March	0.294	57.4	5.9	0.329	356	+ 4
April	0.317	58.7	8.2	0.330	364	— 4
May	0.344	59.5	9.6	0.344	375	— 15
June	0.385	60.4	13.1	0.337	357	+ 3
July	0.400	60 7	15.5	0.314	318	+ 42
Aug.	0.430	60.4	14.6	0.356	343	+ 17
Sept.	0.464	57.6	13.1	0.376	349	+ 11
Oct.	0.430	55.8	8.8	0.392	358	+ 2
Nov.	0.417	55.3	6.9	0.405	374	— 14
Dec.	0.377	52.3	5.1	0.354	334	+ 26

	Obs^{d} D. R.	Bar.	Temp.	Red^{d} D. R. I	Red^{d} D. R. II	O.—C.
1873 Jan.	$-0^{s}.301$	757.6	+ 4.5	$-0^{s}.363$	$-0^{s}.359$	+ 1
Febr.	0.208	63.6	2.3	0.392	405	— 45
March	0.249	57.5	4.8	0.304	331	+ 29
April	0.263	59.8	7.5	0.304	338	+ 22
May	0.310	60.1	8.7	0.334	365	— 5
June	0.337	60.9	12.7	0.303	323	+ 37
July	0.405	61.2	14.8	0.338	342	+ 18
Aug.	0.429	60.7	14.6	0.359	346	+ 14
Sept.	0.406	60.5	11.5	0.387	360	0
Oct.	0.426	58.0	9.7	0.403	369	— 9
Nov.	0.352	59.2	5.9	0.412	381	— 21
Dec.	0.193	69.2	5.0	0.409	389	— 29
1874 Jan.	0.253	63.0	4.3	0.394	390	— 30
Febr.	0.180	63.8	3.6	0.344	357	+ 3
March	0.168	65.8	5.5	0.327	354	+ 6
April	0.275	59.0	8.5	0.287	321	+ 39

Before I undertook the further investigation of the reduced rates I [1]) I tried to find out the relation of the rates below 0° to those above that temperature. It appeared that a systematic deviation of the former is far less evident than it was in the period 1877—98. In fact such a deviation shows itself clearly only in the two months 1870 February and December. Finally I excluded the days with temperatures below 0° only for these months and for 1864 December [2]).

The modified reduced rates I, together with the corresponding temperatures, are as follows:

	Temp.	Red. D. R. I.
1864 December	+ 2.4	$-0^{s}.390$
1870 February	+ 1.9	— 0.331
December	+ 3.6	— 0.386

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[1]) In comparing my values of the reduced rates I for the two first years with those occurring in KAISER's papers, allowance must be made for the fact that my values apply for a pressure of 760 Mm. at 0°, whereas those of KAISER may be assumed to apply for a barometer-height of 760 Mm. at + 10°.

[2]) During 8 other months the deviations were small and variable in sign.

13. In the first place I have investigated in how far the non-periodic part of the rate, the constant *a*, has varied during the period under consideration.

For this purpose I have combined the monthly means to yearly means. They are as follows, the years beginning with May.

1862	— $0^s.316$	1868	— $0^s.400$
1863	.309	1869	.384
1864	.350	1870	.368
1865	.421	1871	.367
1866	.436	1872	.353
1867	.428	1873	.358

It is seen that the negative rate has somewhat increased in the beginning and somewhat decreased afterwards and that it remained nearly constant during the last four years.

With these values and the corresponding ones for years beginning with August, November and February, I drew, in the same way as was done for the period formerly considered, a curve representing in a first approximation the change of *a* with the time.

14. In the second place the influence of the temperature was investigated. I tried to find out:

1st. In how far, if we assume a linear influence of the temperature, the adopted temperature-coefficient applies for the whole of the period;

2nd. whether there is any term varying as the square of the temperature.

For the first investigation the several years were kept separate. They were assumed to begin with February.

I used 1st. the deviations of the monthly means from their yearly mean, 2nd. the deviations of these same monthly means from the values of *a* taken from the curve. In the third and fourth place the computations were repeated using, not the monthly means themselves, but the mean value for the first month combined with the last, that for the second combined with the last but one, etc. By this device the influence of the "supplementary term" must be nearly completely eliminated at the outset.

In this way I found for the correction of the adopted coefficient — $0^s.0174$, the following four series of values; they are expressed in tenthousandth parts of a second.

	I	II	III	IV
1863	+ 5	+ 4	+ 9	+ 9
1864	+ 28	+ 10	+ 13	0
1865	+ 1	+ 4	+ 6	+ 7
1866	+ 14	+ 17	+ 10	+ 14
1867	— 11	— 6	— 11	— 10
1868	— 26	— 23	— 31	— 32
1869	— 11	— 11	— 15	— 17
1870	— 33	— 28	— 38	— 35
1871	— 26	— 27	— 41	— 41
1872	+ 20	+ 18	+ 15	+ 12
1873	+ 33	+ 35	+ 29	+ 31

The results of the four computations are nearly accordant. The value of the temperature coefficient appears to have varied far less than it did subsequently. A small fluctuation however, of the same nature as that which existed afterwards, appears to have occurred. It might be allowable to assume, in accordance with the second computation, which in my opinion is to be preferred:

1863—66	$\Delta c = + 9$	$c = - 0^s.0165$
1867—71	$- 19$	$- 0.0193$
1872—73	$+ 26$	$- 0.0148$

From all the years together we should find

$$1863\text{—}73 \quad \Delta c = - 1 \quad c = - 0^s.0175$$

The investigation about the existence of a quadratic term I only executed for the mean of the 11 years.

For this purpose I used the deviations according to the second and fourth computation.

If Δc_1 and c_2 represent the correction of the coefficient of $t-t_0$ and the coefficient of $(t-t_0)^2$, t_0 being the mean temperature ($= + 8^\circ.6$ R.), we have, expressing both in tenthousandth parts of the second as unit,

	Δc_1	c_2
2nd Comp.	+ 0.5	— 0.92
4th "	— 6.2	— 0.43

At least for the mean of the 11 years, therefore, a quadratic term must be quite insensible.

15. It seemed unnecessary to apply corrections to the reduced rates I on account of the temperature coefficient, before proceeding to the investigation of the supplementary term. For the mean value of

this coefficient agrees all but absolutely with the value originally adopted and its fluctuations are certainly inconsiderable.

I made use of the deviations of the monthly means from the values of a taken from the curve and I made the years begin with May.

For the sake of brevity I will only give the mean results for 4 groups, each of three years. In the last column the general means are set down.

	62—64	65—67	68—70	71—73	1862—1873
May......	+ 76	+ 44	+ 46	+ 29	+ 48
June	+ 4	+ 29	+ 9	+ 30	+ 18
July......	+ 12	+ 20	— 9	+ 19	+ 10
August ...	— 20	— 3	— 58	— 5	— 22
September.	— 26	— 45	— 14	— 32	— 29
October...	— 52	— 17	— 40	— 45	— 38
November.	— 10	— 18	— 4	— 55	— 22
December.	— 30	— 8	— 17	— 20	— 19
January...	— 9	+ 14	+ 14	+ 1	+ 5
February .	— 2	— 22	+ 51	— 8	+ 5
March....	+ 18	+ 6	+ 13	+ 39	+ 19
April.....	+ 46	+ 13	+ 13	+ 52	+ 31

In each of the 4 partial results the supplementary inequality is quite evident. Its amplitude is of the same order of magnitude as in the period 1877—98. There appears to be no reason for assuming any change in this amplitude during the 12 years 1862—74. I therefore tried to represent the general means by a formula and it appeared that a pretty satisfactory representation may be obtained by a simple sine:

$$\Delta g = + 0^{s}.0341 \cos 2\pi \frac{T - Apr.\ 23}{365}.$$

The sinusoïd corresponding to this formula, together with the points given by the observation is represented in Fig. 4.

The differences between the observation and the curve, in thousandth parts of the second, are as follows:

May	+ 17	Sept.	— 2	Jan.	+ 9
June	— 2	Oct.	— 4	Febr.	— 8
July	+ 6	Nov.	+ 9	March	— 8
Aug.	— 9	Dec.	+ 1	April	— 3

The fact that the supplementary term can be represented by a simple sinusoid and that a half-yearly inequality is not shown, agrees with the result found a moment ago, that no term varying as the square of the temperature is indicated [1]). Properly speaking the two results are equivalent.

16. Finally I have again tried to clear the monthly means of the rates, as well as possible, of all periodic terms. In doing this I have applied no further corrections for the influence of the temperature because the variation of its coefficient — the results of the years 1871 and 1873 are just those differing most considerably — did not seem as yet sufficiently demonstrated.

No other reductions were applied, therefore, but those for the supplementary term according to the formula found above.

The rates corrected in this way (= term *a*) have been inserted, in the table already given, in the column Red. D. R. II.

These values of the term *a* have been represented as well as possible by a simple curve reproduced in Fig. 5.

In this figure the results of the observation are also shown, not for every month separately, but for the mean of any three consecutive months [2]).

I have tried to draw this curve about as simply as that for the period 1878—98. The outstanding differences $O—C$ ($C =$ curve) are contained in the last column of the table.

These differences lead to the following mean amounts, which we might consider as the mean errors of a monthly mean:

1862—1867 M. E. $= \pm\ 0^s.0309$
1868—1874 $.0273$

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[1]) The remark made at the end of § 7, p. 23 (90) does not make sufficient allowance for the fact that, as long as no physical explanation has been given for the "supplementary term", a variability of this term might be deemed no more probable than the variability in the course of time of a term varying as the square of the temperature.

[2]) On page 24 (91) I forgot to remark that the same was done in Fig. 3, which represents the period 1878—1898.

whereas, if we had neglected the consideration of the supplementary term, we should have found:

1862—1867	M. E. = ±	$0^s.0382$
1868—1874		.0377

which values are considerably greater.

IV. *The period* 1899—1902.

17. Since the time, 1898 December, that the clock Hohwü 17 has been mounted in the niche of the pier of the 10-inch-refractor, its rates are kept under constant control by computations which are made, immediately after the time-determinations, by Mr. Hamersma, computer at the observatory. He computes moreover mean values of the rate at the end of every month, which are at once inserted in graphical representations. The following investigation was founded on these results only slightly modified.

The modification is the consequence of a small correction of the barometer-readings caused by the fact that the temperature of the clock is no longer the same as that of the barometer in the transit-room. The barometer-readings were reduced therefore to what they would have been at the former temperature [1]). As my investigation, which includes no more than three years, must be considered as a preliminary one, it seemed useless to replace the original mean readings by the mean values according to the barograph-diagrams. Moreover the constant correction of the barometer used was neglected.

As before the temperatures were determined from the readings of the upper one of the two thermometers suspended in the clock case. The former thermometers had been replaced however by two other ones having centigrade scales.

Besides the temperature in the niche below the clockcase has been determined for the period of a year by means of a thermograph of Richard. It appeared that, even there, no trace of a daily period in the temperature is noticeable.

In general the changes in the temperature have now become much slower and much more regular. At the same time the temperature in winter time does not nearly sink to so low a point as formerly; this is shown even in the monthly means. In the years now under consideration the temperature in the clock case never sunk below + 2° C.

As was done for the other periods, I have computed the differences

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[1]) The reduction amounted to 0.4 Mm. in maximo.

between the upper and lower thermometer for this period after the clock had been mounted in the niche. The monthly means of these differences, resulting from the five hours of observation and from the three years 1899—1901, are as follows:

January	$+0^{\circ}.02$	July	$+0^{\circ}.21$
February	$+0.01$	August	$+0.17$
March	$+0.01$	September	$+0.06$
April	$+0.02$	October	$+0.02$
May	$+0.05$	November	$+0.01$
June	$+0.15$	December	$+0.02$

The differences are now expressed in degrees Celsius. The index-errors of these thermometers are insensible.

18. The observed daily rates were originally reduced to 760 Mm. and + 10° C. by means of the coefficients:

$$b = +0^{s}.0140$$
$$c = -0\ .0170$$

In the following table, however, the Red. D. R. I. have been computed, not with this value of the temperature coefficient, which had originally been derived from only the first months, but with the value

$$c = -0^{s}.0220$$

which accords better with the observations. The meaning of the two last columns of the table will be explained hereafter.

The four months immediately following the mounting and the regulation of the clock, during which the rate proved to be still somewhat variable, have been left out of consideration and have not been inserted in the table.

	Obs^{d} D. R.	Bar.	Temp.	Red^{d} D. R. I	Red^{d} D. R. II	Red^{d} D. R. III
					$-0^{s}.157$	$-0^{s}.169$
1899 May	$-0^{s}.116$	763.2	$+11.8$	$-0^{s}.121$	$-$ 4	$+$ 6
June	0.132	65.7	15.0	0.102	$+$ 17	$+$ 30
July	0.192	65.4	18.1	0.090	$+$ 42	$+$ 43
Aug.	0.228	66.0	18.7	0.120	$+$ 36	$+$ 31
Sept.	0.353	59.1	16.0	0.208	$-$ 11	$-$ 14

	Obs$^{\mathrm{d}}$ D. R.	Bar.	Temp.	Red$^{\mathrm{d}}$ D. R. I	Red$^{\mathrm{d}}$ D. R. II	Red$^{\mathrm{d}}$ D. R. III
					$-0\overset{s}{.}157$	$-0\overset{s}{.}169$
1899 Oct.	$-0\overset{s}{.}160$	767.0	+ 11.7	$-0\overset{s}{.}221$	+ 1	− 4
Nov.	0.156	67.4	11.6	0.225	− 13	− 6
Dec.	0.048	61.7	5.7	0.167	+ 13	+ 10
1900 Jan.	0.097	59.6	5.7	0.186	− 30	− 29
Febr.	0.158	52.8	5.4	0.158	− 18	− 29
March	0.058	61.1	6.5	0.151	− 22	− 33
April	0.065	62.2	8.4	0.131	− 10	− 13
May	0.153	62.2	11.7	0.147	− 30	− 20
June	0.247	61.7	16.4	0.130	− 11	− 5
July	0.258	63.8	18.3	0.128	+ 4	+ 2
Aug.	0.328	62.8	18.2	0.187	− 31	− 31
Sept.	0.252	67.4	16.5	0.214	− 17	− 23
Oct.	0.278	61.9	13.6	0.226	− 4	− 10
Nov.	0.255	58.4	10.2	0.229	− 17	− 13
Dec.	− 0.129	61.2	8.8	0.172	+ 8	+ 27
1901 Jan.	+ 0.052	63.2	5.2	0.099	+ 57	+ 52
Febr.	+ 0.023	61.1	5.1	0.099	+ 41	+ 27
March	− 0.098	57.7	6.7	0.134	− 5	− 16
April	0.105	59.7	9.6	0.110	+ 11	+ 14
May	0.104	65.1	12.6	0.118	− 1	+ 9
June	0.216	64.3	16.0	0.144	− 25	− 16
July	0.266	64.5	19.3	0.125	+ 7	− 3
Aug.	0.286	65.5	19.2	0.161	− 5	− 15
Sept.	0.315	61.7	16.2	0.203	− 6	− 11
Oct.	0.266	61.7	13.5	0.212	+ 10	+ 3
Nov.	0.120	64.0	9.7	0.183	+ 29	+ 32
Dec.	0.185	56.5	7.3	0.196	− 16	− 6
1902 Jan.	0.070	62.8	7.5	0.163	− 7	+ 8
Febr.	0.034	59.6	4.6	0.147	− 7	− 26
March	0.107	57.9	7.8	0.126	+ 3	+ 1
April	0.085	61.6	10.0	0.107	+ 14	+ 18

19. The reduced daily rates I of this table show at once and with evidence the presence of the supplementary term; for the rest the rate of the clock in the present period appears to be a very regular one. If, first of all, we combine the monthly means into 3 yearly means, from May to April, we find:

1899	$-\ 0.^{s}158$
1900	.156
1901	.157

There is no trace of a progressive change in the rate and for the further investigation of the influence of the temperature we may simply use the deviations from the general mean $= -\ 0.^{s}157$.

If in the first place we assume that the influence of the temperature is a linear one, we find

1st from the monthly means,

2nd from the means for two months combined in such a way that the supplementary term is nearly completely eliminated, respectively:

$$c = -\ 0.^{s}0224$$

and

$$= -\ 0.0220$$

which values are practically identical with that used for the determination of the reduced daily rates I.

In the second place let us assume the existence of a term varying as the square of the temperature. In this assumption we find, proceeding in the same way as before, for the total influence of the temperature: [1]

$$-\ 0.^{s}0253\,(t-10^{\circ}) + 0.^{s}00074\,(t-10^{\circ})^{2}$$

and

$$-\ 0.0247\,(t-10^{\circ}) + 0.00069\,(t-10^{\circ})^{2}$$

respectively. We thus find for this period a quadratic term of appreciable value. The difference between the two formulae is small; I will definitively adopt the former.

20. It thus becomes necessary to use a quadratic formula in order to clear the rates completely from the direct influence of the temperature, as is required for the determination of the supplementary inequality. We may, however, as well *take* the influence of the temperature *to be proportional to its first power* and then *consider* the remaining periodic part of the rate as "supplementary inequality".

I have followed both ways. In the following table I have inserted, first, the values found for the supplementary term in the first way, giving the results of the three years separately, as well as in the mean. These mean values are pretty well represented by the following simple sine-formula:

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[1] The mean temperature of the 3 years was + 11°.6 C.

$$\Delta g = + 0.^{s}0465 \cos 2\pi \frac{T - May\ 3}{365}$$

The last column of the table contains the differences between the observation and the computation. Everything has been expressed in thousandth parts of the second.

	1899	1900	1901	Mean	O.—C.
May........	+ 52	+ 26	+ 55	+ 44	— 2
June........	+ 65	+ 30	+ 19	+ 38	+ 3
July........	+ 58	+ 17	+ 12	+ 29	+ 14
August	+ 22	— 40	— 24	— 14	— 5
September ..	— 45	— 54	— 42	— 47	— 16
October.....	— 48	— 54	— 41	— 48	— 4
November...	— 52	— 59	— 14	— 42	+ 4
December ...	— 25	— 8	— 41	— 25	+ 10
January	— 44	+ 37	— 7	— 5	+ 10
February ...	— 20	+ 36	— 17	0	— 9
March	— 2	+ 15	+ 32	+ 15	— 16
April	+ 31	+ 58	+ 62	+ 50	+ 6

The mean monthly results of the observations, together with the sinusoid by which they are represented, have been reproduced in fig. 6.

In the second place we give, in the column *O* of the following table, the values of the supplementary inequality which we find in the mean, if we assume — $0^{s}.0220$ $(t - 10°)$ for the influence of the temperature. These values are represented by a curve reproduced in fig. 7. The column *O.—C.* of the table contains the deviations from this curve.

	O.	*O.—C.*		*O.*	*O.—C.*
May	+ 28	— 12	Nov.	— 55	0
June	+ 32	— 6	Dec.	— 21	+ 2
July	+ 43	+ 18	Jan.	+ 8	+ 7
Aug.	+ 1	0	Febr.	+ 22	+ 5
Sept.	— 51	— 11	March	+ 20	— 8
Oct.	— 63	+ 2	April	+ 41	+ 5

As might have been expected, the curve shows clearly a half-yearly inequality.

21. Finally I have reduced the monthly means of the rates both, by the linear temperatureformula with the curve of fig. 7, and by the quadratic formula with the sinusoid of fig. 6. The rates, thus reduced, have been inserted in the columns Red. D. R. II and Red. D. R. III of the general table.

These columns do not contain the reduced rates themselves, but their mean values, together with the deviations from the latter.

These deviations lead to a mean error of a monthly mean

$$M.\ E. = \pm\ 0^s0211$$

if we adopt the linear formula (Red. D. R. II), and

$$M.\ E. = \pm\ 0.^s0218.$$

if we adopt the quadratic formula (Red. D. R. III).

The two methods of reduction thus lead to nearly the same degree of agreement and a decision about the preference to be given to one of the two cannot, therefore, be derived from the monthly rates.

If no reduction for the supplementary inequality had been applied, we should have found in the two cases:

$$M.\ E. = \pm\ 0^s.0422$$
$$\text{''} \quad = \pm\ 0\ .0398.$$

The increase of the *M. E.* is still considerably greater than it is for the other periods. The quadratic formula now leads to slightly better results than the linear one; the difference is small, however.

V. *Amplitude of the oscillations of the pendulum in the period* 1878—1888.

22. As has been mentioned before, H. G. VAN DE SANDE BAKHUYZEN caused a small mirror to be attached to the pendulum in 1877 [1]), for the purpose of determining accurately the amplitude of the oscillation by the aid of the reflected image of a metallic wire placed before a flame of petroleum. The image was projected on a divided scale by means of a lens. 1 Mm. in the scale nearly corresponds to 0.'5 in the total amplitude; the reading could be made accurate to tenths of the millimeter. In this way a determination of the amplitude was made, generally 4 times a day, from 1878 April to 1899.

The determinations of the years 1878, 79 and 80 were elaborately studied by H. G. VAN DE SANDE BAKHUYZEN. The influence of the temperature, of the atmospheric pressure and also that of the position of the driving weight were thoroughly investigated. Having the inten-

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[1]) See: Verslag van den staat der sterrenwacht te Leiden 1876—77 pag. 12.

tion of prosecuting this investigation he did not yet publish his results.

23. It seemed possible that the investigation of these amplitude-observations might contribute to the discovery of an explanation of the supplementary term found in the rates. I intended therefore to inquire whether the corrected amplitudes too would still show a yearly inequality.

As H. G. VAN DE SANDE BAKHUYZEN gave leave to take advantage of his results for the present paper, his corrected amplitudes could be compared at once with each other for the period 1878—80. Furthermore I tried to execute a somewhat provisional investigation for the eight following years. For these years the monthly means of the amplitude found in a first approximation [1]) were corrected for the influence of the atmospheric-pressure, as found by H. G. VAN DE SANDE BAKHUYZEN. A correction for the temperature was not so easily applied, because it appeared that its influence has considerably increased in the course of the years. Finally I proceeded simply in this way, that I derived the value of the amplitude for + 8° R. for every spring and every autumn by interpolations between monthly means corrected for the barometer-reading.

The results have been brought together in the following table:

	Spring.	Spring red.	Autumn.	A.—S.
1878	37.77	38.22	39.71	+ 1.49
1879	38.68	38.76	37.66	— 1.10
1880	38.84	40.06	39.50	— 0.56
1881	41.27	40.48	40.47	— 0.01
1882	39.70	39.18	39.19	+ 0.01
1883	38.66	35.42	35.67	+ 0.25
1884	32.19	30.70	29.22	— 1.48
1885	29.20	30.55	28.35	— 2.20
1886	31.90	32.30	32.33	+ 0.03
1887	32.71	31.86	31.68	— 0.18
1888	31.01			

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[1]) As many observations are wanting the corresponding values had to be assumed.

These results are expressed in millimeters of the scale and they represent the total amplitude on that scale diminished by 320 Mm.

The 2nd and the 4th column contain the results obtained for the spring and the autumn; the 3rd contains the means of two consecutive results for the spring; the 5th the differences autumn — spring obtained by substracting the numbers of the 3rd column from those in the 4th. The differences prove to be very small; their mean amounts only to — 0,38 Mm. or, if we exclude 1878 on account of a possible displacement of the lens, — 0.58 Mm., *i. e.* —0′2 or —0.′3 respectively, whereas the effect of 1° R. is 0.′6 in the beginning and about 1′ afterwards. Besides, the sign of the mean difference is the reverse of what we should have found, when the amplitude of the pendulum lags behind the temperature. Thus already this superficial investigation seems to show, that there is no term in the amplitude analogous to the supplementary term in the rates.

VI. *Comparison of the results.*

24. If we consider the results obtained in the preceding pages in their mutual relation, we are struck in the first place by the fact that the clock Hohwü 17, which at present has been going for more than forty years, far from showing the defects of old age, has increased on the contrary in regularity of rate in the course of the years. We have seen that both in the period 1862—1874 and in that of 1878—1898 the greatest regularity was only reached after some years. It may be pointed out now that this regularity has also increased from period to period.

For we found for the mean deviation of the monthly means from a simple curve (1st and 2nd period) or from a constant value (3rd period) the numbers:

1862—1874	± 0s.0291
1879—1896	.0237
1899—1902	.0215

The diminution of the mean deviation is considerable and whereas in the 3rd period the amelioration in the clock's position may have contributed towards this diminution, the difference between the first and the second is very striking. We have to consider in this connection that, for the two former periods, a whole year at the beginning has been left out of consideration, whereas for the third the 5th month has already been taken into account.

The only point in which the second period is at a disadvantage as compared to the first is that the influence of the temperature has been more variable.

This however is mainly the case only for the last years, when, evidently, the cleaning of the clock had been already too long deferred.

If we reduce the temperature-coefficient found for the third period to what it becomes for 1° R. instead of for 1° C., if further we reduce the mean coefficient of the first period to the value which would have been found, had not the barometer-reading been reduced to 0°, and if, lastly, we add the value found for the middle part of the second period [1]), leaving the quadratic terms out of consideration throughout, we find:

1862—1874	$c = -\ 0^s.0196$
1885—1891	$-\ 0\ .0269$
1899—1902	$-\ 0\ .0275$

Between the 2nd and the 3rd period the pendulum has not been taken to pieces and only a small stain of rust has been removed from the suspension-spring.

25. Let us now consider the results obtained for the supplementary inequality. Setting aside a half-yearly inequality, sometimes shown, which is connected with the precise form of the influence of the temperature, we find in all the periods a supplementary yearly inequality in the rates which can be nearly represented by a simple sinusoid having its maxima about May 1 and November I, the semi-amplitude of which amounts to:

1862—1874	$+\ 0^s.0341$
1878—1886	$.0455$
1887—1896	$.0254$
1899—1902	$.0465$

In the latter part of the period 1878—1898 the amplitude of the supplementary inequality seems to have appreciably diminished so that in the years 1897—1898 it is hardly sensible. For the rest the amplitude of the inequality appears to have had nearly the same amount under any circumstances.

The question now arises:

What explanation can be offered of this inequality? If we consider only the monthly rates, we may mathematically represent it as a lagging behind of about half a month of the influence of the temperature. This cannot be the true physical explanation, however,

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[1]) See also the values of c for the 2nd period on p. 20 (87).

because it appears from the rates during short periods, that abrupt changes in the temperature are reflected almost immediately. Notwithstanding this, I deemed it possible, at first, that the true explanation might be found in such a cause, by assuming that *part* of the effect of the temperature on the rate — perhaps by the intervention of the elasticity of the suspension-spring, — is only felt after a long time. In this case however, we ought to find another and smaller temperature-coefficient from swift changes in temperature than from the comparison of summer- and winterrates. In reality, however, it seems, that the coefficients obtained in the two ways agree in the main, at least as far as can be judged now, before the completion of a more elaborate investigation by Mr. WEEDER.

Besides a change in the elasticity of the suspension-spring, lagging behind the yearly change of temperature, has become improbable since we found no trace of it in the amplitudes of the oscillations.

Another possible explanation might be found in the hypothesis that the temperature of the different parts of the pendulum is permanently unequal and that the distribution of temperature varies systematically with the season, in such a way that it is not identical in the spring and the autumn. The influence of a small inequality of the temperature is considerable. For if the temperature of the pendulum-rod changes only by so much as 0°.1 R., whereas that of the mercury remains constant, the daily rate changes by $0^s.065$.

The differences between the readings of the upper and lower thermometer in the clock-case must throw light on this distribution of the temperature. The information however must be defective 1st. on account of the small accuracy of the thermometers, 2nd because we do not know the relation existing between the temperature of the steel and the mercury of the pendulum and that of the surrounding air. If we consult the mean values of these differences of temperature for the three periods, we see that in the two former the difference: Upper temperature—Lower temperature has been really found + 0°.1 R. greater in April and May than in October and November. This would produce a difference in the rate agreeing in sign with that which is really found. In the 3rd period, however, spring and autumn agree nearly perfectly.

It seems to me still very uncertain, therefore, whether the cause of the phenomenon in question may be found in this distribution of the temperature. The fact that, whereas the clock was in very different circumstances, the inequality of the rate was very nearly constant and also the fact that it seems to have diminished in the second period, seem, even *a priori,* contrary to such a hypothesis.

E. F

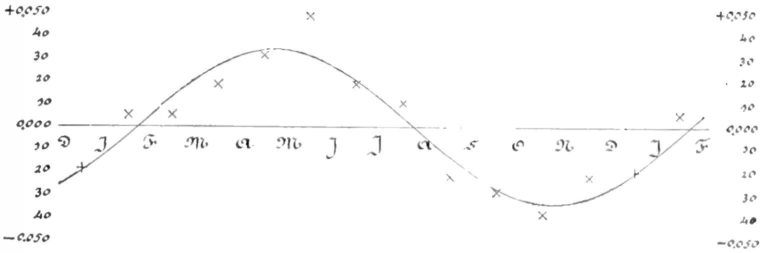
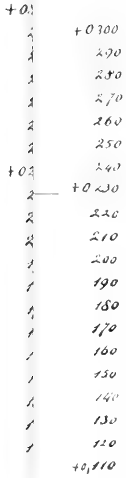


Fig. 4.



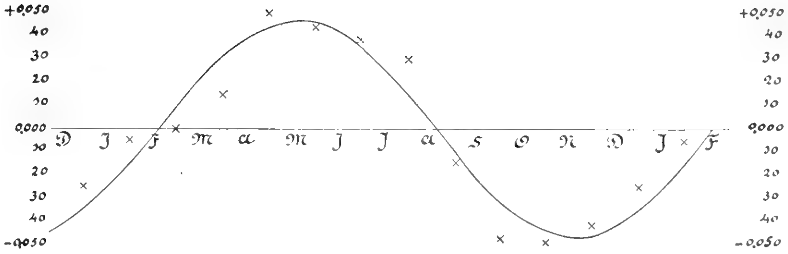


Fig. 6.

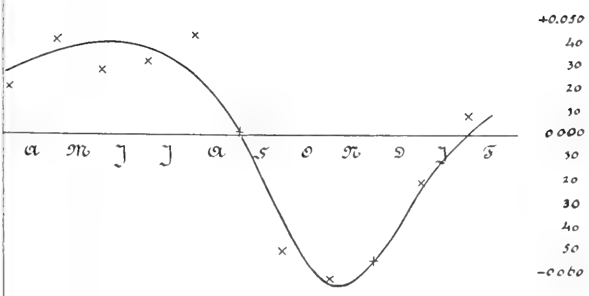


Fig. 7.

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E. F. VAN DE SANDE BAKHUYZEN: „On the yearly periodicity of the rates of the standardclock of the observatory at Leyden Hohwü Nr. 17".

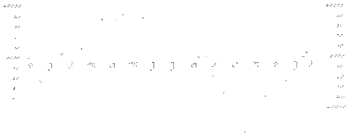

Fig. 1.

Fig. 2.

Fig. 4.

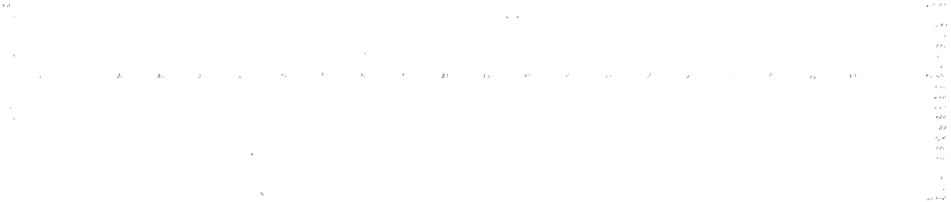

Fig. 3.

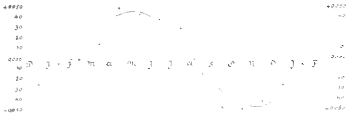

Fig. 6.

Fig. 5.

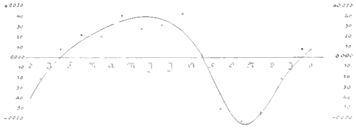

Fig. 7.

And so as yet I feel unable to give a sufficient explanation of the inequality which has been found.

EXPLANATION OF THE FIGURES.

Fig. 1. Supplementary inequality 1878—1886.
„ 2. „ „ 1887—1896.
„ 3. Non-periodic part of the daily rate for + 8°.7 R. 1878—1898.
„ 4. Supplementary inequality 1862—1874.
„ 5. Non-periodic part of the daily rate for + 10° R. 1862—1874.
„ 6. Supplementary inequality 1899—1902.
„ 7. The same inequality if the influence of the temperature is assumed to be linear.

In the Fig. 1, 2, 4, 6, 7 the letters D., J. etc. stand for: December 1, January 1, etc.

In the Fig. 3 and 5 the numbers: 78, 62 etc. stand for: 1878 June 15, 1862 June 15 etc.

In Fig. 5 for 79 read 69.

ERRATUM:

p. 47. Behind the title of the communication of Prof. J. W. van Wijhe is omitted:

(Communicated in the meeting of April 19, 1902).

(August 8, 1902).

KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN TE AMSTERDAM.

PROCEEDINGS OF THE MEETING

of Saturday September 27, 1902.

(Translated from: Verslag van de gewone vergadering der Wis- en Natuurkundige Afdeeling van Zaterdag 27 September 1902, Dl. XI).

CONTENTS.

The following papers were read:

Physics. — "*On the advantage of metal-etching by means of the electric current*". By Mr. A. H. Sirks. (Communicated by Prof. J. L. C. Schroeder van der Kolk).

(Communicated in the meeting of June 28, 1902).

Side by side with the tension- and bending-tests to which metals and their alloys are submitted, with the object to find out, whether the material answers to the requirements, Prof. Behrens gives, as a new method: a microscopic examination, which is deservedly made use of on a large scale. In a special work on the subject: "Das mikroskopische Gefüge der Metalle und Legierungen," this method and the practical use made of it, is treated exhaustively. The main substance of it is this:

A piece of the material, which is to be submitted to microscopic examination is filed, till it is perfectly smooth, different numbers of carborundum-powder being used for the grinding, after which it is polished with tin-oxide or chrome-oxide, if a perfectly smooth slide is required; then, by means of the annealing colours, the ground plane will show a design, sharp-outlined. Since most metals and alloys have crystal-formations at their fractures, the annealing colours will produce a very strongly marked outline between the crystals and the ground-mass, because it is a known fact, that two substances, submitted to the same temperature, but of different formation (the crystals- and the surrounding mother-water) will not take the same tempering-colours. Next by making scratches on the surface, with needles of known hardness (analogous with the known hardness-scale of Mohs) the hardness of the material may be fixed.

A similar design, not so minutely detailed however, may be called forth by the corroding influence of acids, bases or salt-solutions, which the crystals and the encompassing matter are not equally proof against. For this purpose the rubbing and polishing need not be done so carefully.

This method however has also its difficulties, which may often be very troublesome. As is always the case, when an acid operates upon a metal, also in this etching-process gas will be developed. The microscopically small gas-bubbles which are formed on the slide will locally prevent the corroding process of the acid and be the cause of little holes and dots that have nothing to do with the design and may easily lead to faulty conclusions. The very long time the grinding and polishing sometimes takes (I state here the grinding of different species of iron and babbits) will keep many from applying this method.

No satisfactory results, in some cases, being obtained by this method, although the material showed distinct crystals at its fracture. Prof. Schroeder van der Kolk was struck by the idea, whether it would not be possible to etch metal-planes in another way than by corroding through acids. It is a known fact that a metal in a galvanic cell will corrode at its negative pole. I need only state the equally known fact, that the zinc of a bichromate cell, after the electric current is set working, shows a magnificent structure. To forestall the objection, that the chromic-acid of the cell has been predominating here in the etching-process, I will just remark that a slight experiment, i. e., by putting the zinc into the fluid, without letting the cell give a current, was sufficient to prove that the etch-design obtained in the first case, stood out in much stronger relief than had been the case, when exclusively applying acids.

As in any electrolytical process anions are formed which together with the metal of the electrode may produce dissoluble salts, it was important to find out what disturbing influence this would have, and combine with it an examination into the practicability of this etching method and see whether it could replace the one of Prof. BEHRENS, in case the results might be unsatisfactory. The corroding influence of acids having to be avoided as much as possible, preference has been given to use the electric current of a battery instead of producing it within the apparatus itself, as happens in any cell. The apparatus was constructed as simply as possible and is exactly the same as that used for ordinary electrolytical experiments.

The object that was to be etched was used as anode (the place where the electric current enters), whereas a piece of copper-plate serves as cathode. The electric current was furnished by an accumulator-battery, having a terminal voltage of 4 volts. In etching alloys of copper, it proved recommendable, every time to connect two apparatuses in series or in some other way to diminish the potential difference, on account of the highly fleecy deposit on the cathode. As electrolyte, water was used to which for every 100 cm^3 ± 6 drops of diluted sulphuric-acid had been added, in the first place better to conduct the electric current; in the second place, as much as possible, to prevent the formation of base metal-deposits [1]). Of course a controlling experiment was taken by hanging a second piece of the alloy, perfectly alike, in a fluid of which the percentage of acid was the same, in order to be able to eliminate etching by the acid. I have preferred to begin experimenting with copper-tin- and copper-zinc-alloys on account of the sometimes beautiful results obtained by the rubbing and polishing method.

In most cases I melted myself the alloys to be sure of the absence of foreign substances, which may cause very great changes in structure.

The metal-slides were hung to a piece of copper-wire, but precautions were taken that there was no contact between the wire and the electrolyte, to be sure that the metal-plate, which had to be etched, did its work as electrode. For half an hour the electrolysis went

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[1]) In alloys containing lead (babbits, type-metal, etc.) the sulphuric-acid on account of the indissolubleness of the sulphate of lead was replaced by nitric-acid.

on so as to produce a sharply outlined design on the brass- and bronze-slides.

That to no other cause any difference might be attributed, all slides were finished off in exactly the same way as had been done for the acid-etchings of Prof **Behrens**; the etching standing out much stronger, this soon proved to be entirely superfluous and so the slides were filed only with a smooth-file. The first experiment was taken with a small piece of cast-brass, which proved to be composed of 58.5 °/₀ of copper, 40.5 °/₀ of zinc, also traces of lead and of tin being found. For half an hour it was submitted to electrolysis, the density of the current being ± 2 amp. p. dM^2. The result of this experiment is reproduced in fig. 1. The indented structure is very distinctly visible, there being in the slide besides a marked difference in colour between the crystal-formation and the encompassing ground-mass. Bright yellow, the crystals stand out from the enclosing mother-water.

When a second experiment was taken the same alloy was submitted to electrolysis for 12 hours. Under the anode a glass-cup filled with glycerine and with oxide of magnesium was placed to catch up the crystals that might be hollowed out by electrolysis and which will be caused to sink by their weight, for as was to be expected (a thing which was proved by the experiment) the crystals having a higher percentage of copper than the mother-water (in which zinc prevails) will be better proof against electrochemical influence and so in the end get isolated and detached. The residue left in the glass-cup was washed out with alcohol it being found that without this precaution the crystals, that had got detached, easily corroded, leaving nothing behind but a green powder; they were then dried in ether; the residue proved to contain 1.78 mG. metal-crystals. Although these crystals had not got loose entirely intact, they were distinctly angular in form and showed facets. Being submitted to electrolysis (I wish to thank Mr. **Vermaes** for his assistance in this) these crystals were found to contain 1.19 mG. of copper, equal to a copper-percentage of 66.8°/₀. Traces of lead were found on the anode and proved to be PbO_2 but the quantity was too small to permit weighing.

The second design is of a piece of plate-brass, of which the ground slide is in my possession. Etching and colouring after perfect grinding and polishing, had yielded no result. The result of half an hour's electrolysis with a current of the same density as with the first experiment, and the same fluid as electrolyte, is shown in the adjoined photogram. Also the effect of the mechanic treatment can be distinctly noticed. Everywhere in the slide twin-crystals are to be found, which as Prof. **Behrens** explains in his work, are apt to be formed in conse-

A. H. SIRKS. „On the advantage of metal-etching by means of the electric current.”

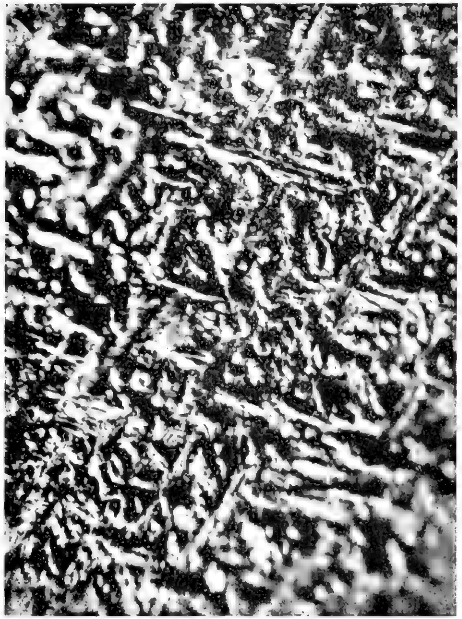

Fig. 1. Cast-brass.

Fig. 2. Plate-brass.

Fig. 3. Bronze for coining.

quence of the mechanic treatment to which the material has been submitted. This slide was the first which was no longer ground with carborundum-powder, but only filed.

The ordinary bronze for coining (see fig. 3) equally shows a structure in which the mechanic operation is visible, both in its crystal-formation and in the position and direction of the crystals, where the more or less flattened parts meet.

From a piece of cast-bronze of a connecting rod a thinnest possible sheet was filed and polished; after heating, stuck on a slide-glass and submitted to etching by electrolysis. A beautifully executed, right-angled lace-work remained, very typical for bronze structures. The encompassing matter of high tin-percentage had been etched away; the crystals, rich in copper, had remained. From a piece of heavily wrought phosphor-bronze, which had remained unaffected by colouring, I have obtained a slide with such a strong relief, that I have not succeeded in taking a photography of it. Also here even the bare eye could see the right-angled structure. The arrangement of the crystals was like that of tiles on a roof.

On account of the great practical use made of white-metal in the technical branches, I have experimented also with that. After half an hour also here, intact cubes of alloy of tin and antimony outlined themselves; also here it was possible to go on etching very deep and without much difficulty to detach the cubes, entirely intact from the alloy. The little time left to me for the moment, necessitates my putting off the analysis of those cubes till later.

Whereas at the beginning only copper-tin and copper-zinc alloys were etched, now also iron has been experimented with. The fact, that it is fine-grained, that the etched facets easily oxidize, that base-metal-deposits [1]) are apt to be formed, all that naturally causes difficulties. The use made of salt-solutions, as electrolyte, to diminish the internal resistance, has yielded no result worth mentioning I have submitted to etching a piece of an iron-bar rolled square. After a few hours the fibrous structure was distinctly visible with the bare eye, both lengthways along the fibres and crosswise, vertically on them. With some difficulty I succeeded in isolating iron-slivers, which, if only collected in sufficient quantity, might be analysed quantitatively. A socle of a gaspipe sawed through, showed cubes in the profile: all the crystals having grouped themselves in the rolling-direction. A piece of a steel angle-iron having been submitted to the bending-test, yielded no other result as

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[1]) For on account of the corroding influence of acids on iron and steel a very small quantity of sulphuric-acid can be experimented with.

yet, but the one that also here, just as with the piece of bar-iron, the direction of the fibres could be seen with the bare eye, as well as a very distinct difference between the drawn and the compressed fibre.

As to the structure and formation of the carbide crystals nothing could be fixed at this first experiment, I do not doubt however, but also here the results will be satisfactory.

Worth mentioning still is the etching of a cylinder-shaped piece of cast-steel, which was submitted to electrolysis for 36 hours. Although outwardly no etched design could be seen, a porous coat of ± $^1/_8$ inch of some iron-carbide appeared to be have been formed, which, coming in contact with the air, was apt to oxidize, could be cut with a knife, and in the incision glittered like metal. When analysed the iron-percentage proved to be $91^1/_2\ ^0/_0$.

The great results, obtained also here, are a stimulus to me, to investigate this matter later more thoroughly.

Those experiments suggested to Prof. SCHROEDER VAN DER KOLK the idea, whether crystals of minerals treated in this way, would show a design. Considering the results, obtained with copper-alloys, a piece of a copper-ore was used for the first experiment. After an hour, also this material showed a distinct etch-design, which is probably connected with a crystal formation. Not to be led away from my subject, I will only just mention the phenomenon.

Before concluding, I will resume the advantages, gained by the way indicated.

1$^{\text{stly}}$. Results having been obtained, where the ordinary grinding-polishing- and etch-methods had failed.

2$^{\text{ndly}}$. The obtained preparations show a far more detailed design, which stands out in much stronger relief than the ordinary etch-slide.

3$^{\text{rdly}}$. It is not necessary to finish off the slides half so carefully, as the tempering-method requires.

4$^{\text{thly}}$. From different alloys crystals or fragmentary crystals have been detached which permit of analysis and show remarkable differences with the average percentage of the alloys.

The good results are a sufficient recommendation for practical purposes, time may still be saved by connecting many apparatuses in series, so as to be able to etch different slides at the same time.

To my opinion it will be possible with careful treatment (regulating the power of the current and using different acids) in this way, from all cast-metals and alloys, to detach the crystals, thus making it possible to find out the quality and formation of the materials.

After I had concluded these preliminary experiments, it came to my knowledge that the electric current had already been used as an etching medium in the work called "Contribution à l'étude des Alliages" edited by the Société d'Encouragement de l'Industrie Nationale, Mr. CHARPY describes a method, successfully made use of by him and which according to the added photograms, shows great resemblance with our method. He namely used an ordinary DANIELL-cell to furnish the electric current and in it replaced zinc by the alloy, that has to be etched, made a short circuit of the cell and obtained an etched design after having submitted the previously polished plane for half an hour to electrolysis.

To my opinion however there are great objections here. For to obtain a somewhat powerful current it is necessary to reduce the inward resistance to a minimum, either by using larger electrodes or by considerably increasing the acid-percentage of the electrolyte. Especially with the etching of iron and steel the high percentage of acid will be an unsurmountable obstacle. A second objection is the impossibility, on account of that acid, to go on etching deep enough to detach crystals, for the angles and ribs which will be laid open by the etching-process will very soon dissolve again.

Before I conclude, I will here openly thank Prof. SCHROEDER VAN DER KOLK for his readiness in furnishing me all I wanted, to render this investigation possible.

The Hague, June 1902.

Physics. — "*On the conditions for the occurrence of a minimum critical temperature for a ternary system.*" By Prof. J. D. VAN DER WAALS.

Already in my "Molecular theory" I have derived the condition on which a binary system presents a minimum critical temperature (Cont. II, p. 20). Starting from the form of the equation of state I have assumed there, we namely find:

$$RT_{cr} = \frac{8}{27} \frac{a_x}{b_x}$$

where T_{cr} represents the temperature, for which the maximum and the minimum of the isothermal coincide. Discussing the conditions of coexistence we have pointed out that the critical phenomena for a binary system, though they are different from those which occur for a simple substance, yet in the case that the value of T_{cr} defined by the above equation is a minimum, differ so slightly from those for a simple substance that this equation has a sufficient degree of approximation for the determination of the critical phenomena as we may realize them experimentally. Also for a ternary system the critical phenomena will differ from those for a simple substance, and we may expect that the difference will even be more considerable than in the case of a binary system. Yet also for a ternary system this difference will not be so great, that the conditions for the existence of a minimum value of $\frac{a_{xy}}{b_{xy}}$ will differ sensibly from the conditions for the existence of the minimum critical temperature as it may be realized experimentally.

In order to find this condition for a binary system I have investigated in what circumstances $\frac{a_x}{b_x}$ taken as a function of x, can assume a minimum value, and so I have discussed the equation:

$$\frac{d\frac{a_x}{b_y}}{dx} = 0.$$

Analogous to this we should have to discuss the following equations in order to find this condition for a ternary system:

$$\frac{d\frac{a_{xy}}{b_{xy}}}{dx} = 0,$$

and

$$\frac{d\frac{a_{xy}}{b_{xy}}}{dy} = 0.$$

At present however I will follow another way, which leads us more easily to our aim and which yields the results in such a manner that they may be better surveyed.

If we write for a binary system:

$$\frac{a_1\,(1-x)^2 + 2\,a_{12}\,x\,(1-x) + a_2\,x^2}{b_1\,(1-x)^2 + 2\,b_{12}\,x\,(1-x) + b_2\,x^2} = \lambda,$$

then the solution of the equation:

$$(a_1-\lambda\,b_1)\,(1-x)^2 + 2\,(a_{12}-\lambda\,b_{12})\,x\,(1-x) + (a_2-\lambda\,b_2)\,x^2 = 0$$

yields that value of x, for which $\frac{a_x}{b_x}$ assumes the given value λ. So we find:

$$\frac{x}{1-x} = -\frac{a_{12}-\lambda b_{12}}{a_2-\lambda b_2} \pm \sqrt{\left\{\frac{(a_{12}-\lambda b_{12})^2-(a_1-\lambda b_1)(a_2-\lambda b_2)}{(a_2-\lambda b_2)^2}\right\}}.$$

If:

$$(a_{12}-\lambda b_{12})^2-(a_1-\lambda b_1)(a_2-\lambda b_2) < 0,$$

the quantity $\frac{x}{1-x}$ is complex. This cannot be the case if the value of λ lies between $\frac{a_1}{b_1}$ and $\frac{a_2}{b_2}$. It can only occur if λ is chosen either smaller than $\frac{a_1}{b_1}$ and $\frac{a_2}{b_2}$ or greater than both these values.

If λ is chosen such that

$$(a_1-\lambda b_1)(a_2-\lambda b_2)-(a_{12}-\lambda b_{12})^2 = 0 \quad . \quad . \quad . \quad . \quad . \quad (1)$$

then this equation will yield the minimum value of λ. If we put in this equation either:

$$\lambda = \frac{a_1}{b_1} \text{ or } \lambda = \frac{a_2}{b_2}$$

then the first member will be negative. If we put:

$$\lambda = \frac{a_{12}}{b_{12}}$$

then the sign of the first member will be the same as that of $(a_1 \quad \lambda b_1)(a_2-\lambda b_2)$. The second member is positive, if $\frac{a_{12}}{b_{12}}$ is smaller than $\frac{a_1}{b_1}$ and also smaller than $\frac{a_2}{b_2}$. Consequently a value of λ must exist for which $(1) = 0$ and for which therefore $\frac{a_x}{b_x}$ assumes a minimum value. This value lies between $\frac{a_{12}}{b_{12}}$ and $\frac{a_1}{b_1}$; or if $\frac{a_2}{b_2} < \frac{a_1}{b_1}$ between $\frac{a_{12}}{b_{12}}$ and $\frac{a_2}{b_2}$.

In the case that $\frac{a_{12}}{b_{12}}$ is both greater than $\frac{a_1}{b_1}$ and than $\frac{a_2}{b_2}$, the first member of equation (1) changes its sign in the same way, and the value of λ for which the first member vanishes, lies also between $\frac{a_1}{b_1}$ and $\frac{a_{12}}{b_{12}}$ or if $\frac{a_2}{b_2} > \frac{a_1}{b_1}$ between $\frac{a_2}{b_2}$ and $\frac{a_{12}}{b_{12}}$. So for a minimum value of λ we have $\lambda_m > \frac{a_{12}}{b_{12}}$ and for a maximum value $\lambda_m < \frac{a_{12}}{b_{12}}$. If λ has the value of λ_m also the following two equations hold:

$$\frac{x}{1-x} = -\frac{a_{12}-\lambda_m b_{12}}{a_2-\lambda_m b_2},$$

and

$$\frac{1-x}{x} = -\frac{a_{12}-\lambda_m b_{12}}{a_1-\lambda_m b_1}.$$

As $\frac{x}{1-x}$ must be positive because x must lie between 0 and 1, the sign of $a_{12}-\lambda_m b_{12}$ is opposite to that of $a_1-\lambda_m b_1$ and $a_2-\lambda_m b_2$. This agrees with what we have deduced concerning the relative value of λ_m and $\frac{a_{12}}{b_{12}}$.

We should have obtained the same results, if we had written the relation $a_x = \lambda b_x$ in the following form:

$$\frac{\{(a_1-\lambda b_1)(1-x)+(a_{12}-\lambda b_{12})x\}^2}{a_1-\lambda b_1} + x^2 \left\{ (a_2-\lambda b_2) - \frac{(a_{12}-\lambda b_{12})^2}{(a_1-\lambda b_1)} \right\} = 0.$$

In the case that $a_1-\lambda b_1$ is positive namely this equation cannot be satisfied if the coefficient of x^2 is positive; so if

$$(a_1-\lambda b_1)(a_2-\lambda b_2) - (a_{12}-\lambda b_{12})^2 > 0.$$

If the coefficient of x^2 is zero, then this equation can only be satisfied if we put:

$$(a_1-\lambda b_1)(1-x) + (a_{12}-\lambda b_{12})x = 0.$$

On the other hand in the case that $a_1-\lambda b_1$ is negative this equation cannot be satisfied if the coefficient of x^2 is negative. This however also yields:

$$(a_1-\lambda b_1)(a_2-\lambda b_2) - (a_{12}-\lambda b_{12})^2 > 0.$$

If therefore we have the equation:

$$(a_1-\lambda b_1)(a_2-\lambda b_2) - (a_{12}-\lambda b_{12})^2 > 0$$

then the value of λ must be either less than the minimum value of $\frac{a_x}{b_x}$ or more than the maximum value.

We must however distinguish between a minimum value of λ which occurs at positive value of $\frac{x}{1-x}$ and a minimum value of λ corresponding to a negative value of $\frac{x}{1-x}$. The former, which really exists, requires that $\frac{a_{12}}{b_{12}}$ is both smaller than $\frac{a_1}{b_1}$ and than $\frac{a_2}{b_2}$. The latter cannot of course be realized. Solving the equation

$$(a_1-\lambda b_1)\,(a_2-\lambda b_2)-(a_{12}-\lambda b_{12})^2=0$$

we find:

$$\lambda=\frac{-(a_1b_2+a_2b_1-2a_{12}b_{12})\pm\sqrt{\{(a_2b_1-a_1b_2)^2+4(a_1b_{12}-a_{12}b_1)(a_2b_{12}-b_2a_{12})\}}}{2(b_1b_2-b_{12}{}^2)}.$$

This equation can be satisfied by a real value of λ if:

$$\frac{b_1b_2}{4b_{12}{}^2}\left(\frac{a_1}{b_1}-\frac{a_2}{b_2}\right)^2+\left(\frac{a_1}{b_1}-\frac{a_{12}}{b_{12}}\right)\left(\frac{a_2}{b_2}-\frac{a_{12}}{b_{12}}\right)>0.$$

This equation is certainly satisfied if $\frac{a_{12}}{b_{12}}$ is both smaller than $\frac{a_1}{b_1}$ and than $\frac{a_2}{b_2}$, but it may also be satisfied in other cases. Let us assume that $\frac{a_1}{b_1}>\frac{a_{12}}{b_{12}}$ and $\frac{a_{12}}{b_{12}}>\frac{a_2}{b_2}$. If we then have:

$$\left(\frac{a_{12}}{b_{12}}-\frac{a_2}{b_2}\right)\left(\frac{a_1}{b_1}-\frac{a_{12}}{b_{12}}\right)<\frac{b_1b_2}{4b_{12}{}^2}\left(\frac{a_1}{b_1}-\frac{a_2}{b_2}\right)^2$$

a minimum value of λ occurs indeed, but in this case it corresponds, according to our previous observations, to a negative value of $\frac{x}{1-x}$. We arrive at the same result starting from the equation of Cont. II p. 20.

For a ternary system we have, putting $\frac{a_{xy}}{b_{xy}}=\lambda$:

$$(a_1-\lambda b_1)(1-x-y)^2+(a_2-\lambda b_2)x^2+(a_3-\lambda b_3)y^2+2(a_{12}-\lambda b_{12})x(1-x-y)+$$
$$+2(a_{13}-\lambda b_{13})x(1-x-y)+2(a_{23}-\lambda b_{23})xy=0.$$

We may represent this by the sum of three squares:

$$\frac{[(a_1-\lambda b_1)(1-x-y)+(a_{12}-\lambda b_{12})x+(a_{13}-\lambda b_{13})y]^2}{(a_1-\lambda b_1)}+$$

$$+\frac{\left[x\left\{(a_2-\lambda b_2)-\frac{(a_{12}-\lambda b_{12})^2}{a_1-\lambda b_1}\right\}+y\left\{(a_{23}-\lambda b_{23})-\frac{(a_{12}-\lambda b_{12})(a_{13}-\lambda b_{13})}{a_1-\lambda b_1}\right\}\right]^2}{(a_2-\lambda b_2)-\frac{(a_{12}-\lambda b_{12})^2}{a_1-\lambda b_1}}+$$

$$+y^2\left\{(a_3-\lambda b_3)-\frac{(a_{13}-\lambda b_{13})^2}{a_1-\lambda b_1}-\frac{\left[(a_{23}-\lambda b_{23}-\frac{(a_{12}-\lambda b_{12})(a_{13}-\lambda b_{13})}{a_1-\lambda b_1}\right]^2}{(a_2-\lambda b_2)-\frac{(a_{12}-\lambda b_{12})^2}{a_1-\lambda b_1}}\right\}=0.$$

In the case that $a_1-\lambda b_1>0$ and $(a_1-\lambda b_1)\,(a_2-\lambda b_2)>(a_{12}-\lambda b_{12})^2$, this equation cannot be satisfied if the coefficient of y^2 is positive. If this coefficient decreases to zero, then the equation is satisfied by only one set of values for x and y, namely by those values for which both the other squares are equal to zero. If the coefficient of y^2 is negative, then a locus exists (a conic section) which indicates all mixtures for which $\lambda = \dfrac{a_{xy}}{b_{xy}}$ has the same value. If this locus is reduced to one point, as is the case if the coefficient of y^2 vanishes, then λ is for that point a minimum, respectively a maximum. The minimum value of λ satisfies therefore the equation:

$$\{(a_1-\lambda b_1)(a_2-\lambda b_2)-(a_{12}-\lambda b_{12})^2\}\{(a_1-\lambda b_1)(a_3-\lambda b_2)-(a_{13}-\lambda b_{13})^2\}-$$
$$-\{(a_1-\lambda b_1)(a_{23}-\lambda b_{23})-(a_{12}-\lambda b_{12})(a_{13}-\lambda b_{13})\}^2=0,$$

or

$$\begin{vmatrix} a_1-\lambda b_1\,, & a_{12}-\lambda b_{12}\,, & a_{13}-\lambda b_{13} \\ a_{12}-\lambda b_{12}\,, & a_2-\lambda b_2\,, & a_{23}-\lambda b_{23} \\ a_{13}-\lambda b_{13}\,, & a_{23}-\lambda b_{23}\,, & a_3-\lambda b_3 \end{vmatrix} = 0. \quad . \quad . \quad . \quad (2)$$

For the determination of x and y we have moreover the equation:

$$(a_1-\lambda b_1)(1-x-y)+(a_{12}-\lambda b_{12})x+(a_{13}-\lambda b_{13})y=0$$

and the equation, which follows from the other square when it is equated to zero.

Another way in which we might have reduced the equation $a_{xy}-\lambda b_{xy}=0$ to the sum of three squares, would have yielded the following two equations for the determination of x and y.

$$(a_{12}-\lambda b_{12})(1-x-y)+(a_2-\lambda b_2)x+(a_{23}-\lambda b_{23})y=0$$

and

$$(a_{13}-\lambda b_{13})(1-x-y)+(a_{23}-\lambda b_{23})x+(a_3-\lambda b_3)y=0.$$

Eliminating $1-x-y$, x and y from these three equations in which they occur linearly, we find again equation (2).

In order to calculate x and y we may derive the following relations from these three equations.

$$\frac{1-x-y}{\begin{vmatrix} a_{12}-\lambda b_{12}\,, & a_{13}-\lambda b_{12} \\ a_2-\lambda b_2\,, & a_{23}-\lambda b_{23} \end{vmatrix}} = \frac{x}{\begin{vmatrix} a_{13}-\lambda b_{13}\,, & a_1-\lambda b_1 \\ a_{23}-\lambda b_{23}\,, & a_{12}-\lambda b_{12} \end{vmatrix}} = \frac{y}{\begin{vmatrix} a_1-\lambda b_1\,, & a_{12}-\lambda b_{12} \\ a_{12}-\lambda b_{12}\,, & a_2-\lambda b_2 \end{vmatrix}}.$$

or

$$\frac{1-x-y}{\begin{vmatrix} a_2-\lambda b_2\,, & a_{23}-\lambda b_{23} \\ a_{23}-\lambda b_{23}\,, & a_3-\lambda b_3 \end{vmatrix}} = \frac{x}{\begin{vmatrix} a_{23}-\lambda b_{23}\,, & a_{12}-\lambda b_{12} \\ a_3-\lambda b_3\,, & a_{13}-\lambda b_{13} \end{vmatrix}} = \frac{y}{\begin{vmatrix} a_{12}-\lambda b_{12}\,, & a_2-\lambda b_2 \\ a_{13}-\lambda b_{13}\,, & a_{23}-\lambda b_{23} \end{vmatrix}}$$

and

$$\frac{1-x-y}{\begin{vmatrix} a_{23}-\lambda b_{23}\,, & a_3-\lambda b_3 \\ a_{12}-\lambda b_{12}\,, & a_{13}-\lambda b_{13} \end{vmatrix}} = \frac{x}{\begin{vmatrix} a_3-\lambda b_3\,, & a_{13}-\lambda b_{13} \\ a_{13}-\lambda b_{13}\,, & a_1-\lambda b_1 \end{vmatrix}} = \frac{y}{\begin{vmatrix} a_{13}-\lambda b_{13}\,, & a_{23}-\lambda b_{23} \\ a_1-\lambda b_1\,, & a_{12}-\lambda b_{12} \end{vmatrix}}$$

In order that λ have a minimum value for positive values of x, y and $1-x-y$ the following relations must hold:

$$\begin{gathered}
a_1 - \lambda b_1 > 0 \\
a_2 - \lambda b_2 > 0 \\
a_3 - \lambda b_3 > 0 \\
(a_1 - \lambda b_1)(a_2 - \lambda b_2) - (a_{12} - \lambda b_{12})^2 > 0 \\
(a_1 - \lambda b_1)(a_3 - \lambda b_3) - (a_{13} - \lambda b_{13})^2 > 0 \\
(a_2 - \lambda b_2)(a_3 - \lambda b_3) - (a_{23} - \lambda b_{23})^2 > 0 \\
(a_{12} - \lambda b_{12})(a_{13} - \lambda b_{13}) - (a_1 - \lambda b_1)(a_{23} - \lambda b_{23}) > 0 \\
(a_{12} - \lambda b_{12})(a_{23} - \lambda b_{23}) - (a_2 - \lambda b_2)(a_{13} - \lambda b_{13}) > 0 \\
(a_{13} - \lambda b_{13})(a_{23} - \lambda b_{23}) - (a_3 - \lambda b_3)(a_{12} - \lambda b_{12}) > 0,
\end{gathered}$$

and λ, must satisfy equation (2).

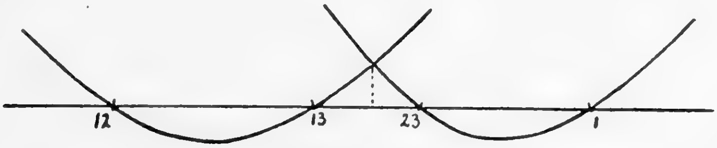
The first set of three inequalities indicates, that this value of λ must be lower than that of the components. The second set indicates that it must be lower than the minimum value of λ for each of the pairs of components of which the ternary system consists. The third set must be fulfilled in order that x, y and $1-x-y$ be positive.

Let us assume $\frac{a_{12}}{b_{12}} < \frac{a_{13}}{b_{13}} < \frac{a_{23}}{b_{23}}$ and suppose that the values of $\frac{a_1}{b_1}$, $\frac{a_2}{b_2}$ and $\frac{a_3}{b_3}$ are higher than that of $\frac{a_{23}}{b_{23}}$ without deciding anything about the relation between the values of the quantities $\frac{a_1}{b_1}$, $\frac{a_2}{b_2}$ and $\frac{a_3}{b_3}$.

According to our assumption the expression

$$(a_{12} - \lambda\, b_{12})(a_{13} - \lambda\, b_{13}) - (a_1 - \lambda\, b_1)(a_{23} - \lambda\, b_{23})$$

is negative for $\lambda = \frac{a_{12}}{b_{12}}$ and also for $\lambda = \frac{a_{13}}{b_{13}}$ and it is positive for $\lambda = \frac{a_{23}}{b_{23}}$ and for $\lambda = \frac{a_1}{b_1}$. This is perhaps best illustrated by a graphical representation.



Here the points 12 and 13 represent the values of $\frac{a_{12}}{b_{12}}$ and $\frac{a_{13}}{b_{13}}$ and the parabolic curve passing through these points the value of

$$(a_{12} - \lambda\, b_{12})(a_{13} - \lambda\, b_{13}).$$

In the same way the points 23 and 1 represent the value of $\frac{a_{23}}{b_{23}}$ and of $\frac{a_1}{b_1}$ and the parabolic curve passing through these points the value of

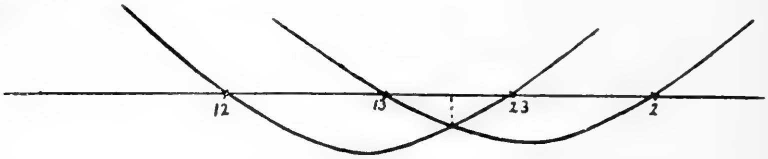
$$(a_1-\lambda\, b_1)\,(a_{23}-\lambda\, b_{23}).$$

These parabolae intersect between the points 13 and 23 and on the right side of the point of intersection the first mentioned parabola lies higher than the second mentioned; the expression under consideration is there therefore positive.

The graphical representation of the expression

$$(a_{12}-\lambda\, b_{12})\,(a_{23}-b_{23}) - (a_2-\lambda\, b_2)\,(a_{13}-\lambda\, b_{13})$$

has the following shape:



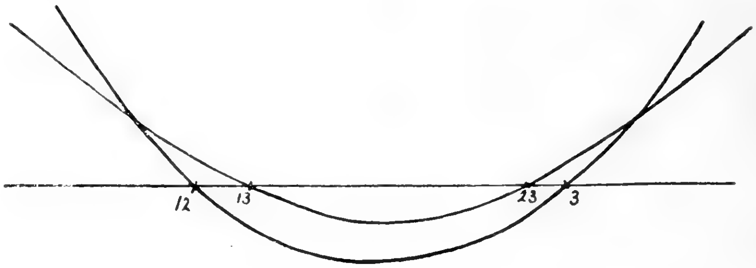
from which we see in the same way that these parabolae intersect between the points 13 and 23 and that this expression is positive for higher values of λ.

The third expression:

$$(a_{13}-\lambda\, b_{13})\,(a_{23}-\lambda\, b_{23}) - (a_3-\lambda\, b_3)\,(a_{12}-\lambda\, b_{12})$$

is positive for λ equal to $\frac{a_{12}}{b_{12}}, \frac{a_{13}}{b_{13}}, \frac{a_{23}}{b_{23}}$ and $\frac{a_3}{b_3}$ and, when equated to zero, it will in general not yield a real root; at least not between 12 and 3.

The graphical representation of this third expression has the following form:



where the parabola passing through the points 13 and 23 lies everywhere higher than the other one. The first mentioned parabola would, if there should exist roots, descend below the second one between the points 13 and 23, and so the two roots would lie between those points. But in this case also the third expression is positive above a certain value of λ below $\frac{a_{23}}{b_{23}}$. Or both parabolae might also intersect on the left side of 12 and on the right side of 1. Also in this case this expression is positive and even within broader limits.

In the case that a value of λ for which the left hand member of equation (2) vanishes, is higher than the value discussed for these three expressions, a minimum value of λ will exist, which represents a really occurring minimum critical temperature. Let us write equation (2) in the following form:

$$\{(a_1-\lambda b_1)(a_2-\lambda b_2)-(a_{12}-\lambda b_{12})^2\}\{(a_1-\lambda b_1)(a_3-\lambda b_3)-(a_{13}-\lambda b_{13})^2\}-$$
$$-\{(a_{12}-\lambda b_{12})(a_{13}-\lambda b_{13})-(a_1-\lambda b_1)(a_{23}-\lambda b_{23})\}^2=0.$$

The first member is negative if we choose for the value of λ either the minimum value of λ for the pair 1 and 2, or for the pair 1 and 3. We will denote these minimum values by $(\lambda_m)_{12}$ and $(\lambda_m)_{13}$.

On the other hand the first member is positive if we choose for λ a value for which the expression, the square of which must be taken, vanishes, — this holds however only in the case that the value of this last root is lower than that of the quantities $(\lambda_m)_{12}$ and $(\lambda_m)_{13}$. In this case the equation (2) has a root which satisfies all the requirements for a minimum value of λ at positive values of $1-x-y$, x and y.

As an instance we choose the following numeric values:

$$b_1=1.6,\quad b_2=1.4\ ,\quad b_3=1\quad ,\quad b_{12}=1.5,\quad b_{13}=1.3\quad ,\quad b_{23}=1.2$$

$$\frac{a_1}{b_1}=3\quad ,\quad \frac{a_2}{b_2}=3.2\ ,\quad \frac{a_3}{b_3}=3.372,\quad \frac{a_{12}}{b_{12}}=2.8,\quad \frac{a_{13}}{b_{13}}=2.846,\quad \frac{a_{23}}{b_{23}}=2.9103$$

$$a_1=4.8,\quad a_2=4.48,\quad a_3=3.372,\quad a_{12}=4.2,\quad a_{13}=3.7\quad ,\quad a_{23}=3.4924$$

From this we find:

$$(\lambda_m)_{12}=2.933\ \ldots\ldots$$
$$(\lambda_m)_{13}=2.962\ \ldots\ldots$$
$$(\lambda_m)_{23}=3.15\ \ \ldots\ldots$$

A value for $\lambda < 2.933\ldots.$ makes therefore the three following expressions positive:

$$(a_1-\lambda b_1)(a_2-\lambda b_2)-(a_{12}-\lambda b_{12})^2$$
$$(a_1-\lambda b_2)(a_3-\lambda b_3)-(a_{23}-\lambda b_{23})^2$$

and

$$(a_3-\lambda b_3)(a_1-\lambda b_1)-(a_{31}-\lambda b_{31})^2$$

For the value of λ for which the quantity:

$$(a_{12}-\lambda b_{12})(a_{13}-\lambda b_{13})-(a_1-\lambda b_1)(a_{23}-\lambda b_{23})$$

is positive we find: $\lambda > 2.884\ldots.$

For the value for which the expression

$$(a_{23}-\lambda b_{23})(a_{21}-\lambda b_{21})-(a_2-\lambda b_2)(a_{31}-\lambda b_{31})$$

is positive we find: $\lambda > 2.855$ and the last of the given expressions is positive within the limits $\frac{a_{12}}{b_{12}} < \lambda < \frac{a_3}{b_3}$.

The value of λ for which the equation (2) vanishes, lies therefore between 2.884 . . . and 2.933, and the shape of this equation shows that it must lie nearer to 2.933 than to 2.884. We find in fact $\lambda_m = 2.9252 \ldots$.

With the aid of this value of λ_m we may calculate the values of $\frac{x}{1-x-y}$ and $\frac{y}{1-x-y}$ from the equations of p. 230. But if the degree of approximation with which λ_m is determined is not high, the coordinates of the point to which λ_m relates, are only known inaccurately.

These coordinates however may be calculated directly by means of the following equations:

$$\frac{a_1(1-x-y)+a_{12}x+a_{13}y}{b_1(1-x-y)+b_{12}x+b_{13}y}=\frac{a_{12}(1-x-y)+a_2x+a_{23}y}{b_{12}(1-x-y)+b_2x+b_{23}y}=\frac{a_{13}(1-x-y)+a_{23}x+a_3y}{b_{13}(1-x-y)+b_{23}x+b_3y}=\lambda$$

We obtain these equations when we determine the centre of the ellipse

$$a_{xy} = \lambda\, b_{xy}$$

and when we eliminate the quantity λ from the equations $f''_x = 0$ and $f''_y = 0$. So we find:

$$\lambda=\frac{(a_1-a_{12})\,(1-x-y)+(a_{12}-a_2)\,y+(a_{13}-a_{23})\,y}{(b_1-b_{12})\,(1-x-y)+(b_{12}-b_2)\,y+(b_{13}-b_{23})\,y}=$$

$$=\frac{(a_1-a_{13})\,(1-x-y)+(a_{12}-a_{23})\,y+(a_{13}-a_3)\,y}{(b_1-b_{13})\,(1-x-y)+(b_{12}-b_{23})\,y+(b_{13}-b_3)\,y}.$$

Introducing the condition, that the centre lies on the ellipse itself we get the given equations.

In the case that $b_{12}=\frac{b_1+b_2}{2}$, $b_{13}=\frac{b_1+b_3}{2}$ and $b_{23}=\frac{b_2+b_3}{2}$ which equations may be satisfied approximately, then the locus of the centres is greatly simplified and may be written as follows:

$$\frac{(a_1-a_{12})(1-x-y)+(a_{12}-a_2)x+(a_{13}-a_{23})y}{b_1-b_2}=$$

$$=\frac{(a_1-a_{13})(1-x-y)+(a_{12}-a_{23})x+(a_{13}-a_3)y}{b_1-b_3}.$$

It is therefore a straight line, at least in approximation. With the given numeric values we find:

$$\frac{0,6(1-x-y)-0,28x+0,2076y}{0,2}=\frac{1,1(1-x-y)+0,7076x+0,328y}{0,6}$$

or

$$0{,}7\,(1-x-y)\;-\;1{,}5476\,x+0{,}2948\,y=0.$$

With this simplification the determination of the coordinates comes therefore to the same as the determination of the point of intersection of a conic section, e.g.

$$\frac{a_1(1-x-y)+a_{12}x+a_{13}y}{b_1(1-x-y)+b_{12}x+b_{13}y}=\frac{a_{12}(1-x-y)+a_2x+a_{23}y}{b_{12}(1-x-y)+b_2x+b_{23}y}$$

with a given straight line.

In this case we find:

$$\frac{x}{1-x-y}=\frac{1}{2}$$

and

$$\frac{y}{1-x-y}=\frac{1}{4}.$$

In fact the given numeric values for a_{23} and a_3 were chosen such that we might find simple values for the coordinates.

Because of the asymmetry round the mixture with minimum critical temperature we might of course have expected that the centre of the ellipses which vary with the temperature, would change its place.

For the theory of binary systems it was necessary to introduce the quantity a_{12}, whose value we are not yet able to deduce from the properties of the components. From the calculation of $(\lambda_m)_{12}$ by means of the equation

$$(a_1-\lambda b_1)\,(a_2-\lambda b_2)-(a_{12}-\lambda b_{12})^2=0$$

follows, that for substances with a minimum critical temperature this quantity cannot be equal to $\sqrt{a_1a_2}$ but that it must be less. If it were equal to $\sqrt{a_1a_2}$ the equation would yield a value $\lambda=0$. Moreover it would follow from $a_1a_2=a_{12}^2$ that $\frac{a_1}{b_1}\cdot\frac{a_2}{b_2}$ would be greater than $\frac{a_{12}^2}{b_{12}^2}$, as b_1b_2 in any case will be probably less than b_{12}^2.

For the application of our theory on a ternary system therefore, also knowledge of the quantities a_{12}, a_{13} and a_{23}, is required, which however must be assumed to be known from the knowledge of binary systems.

The theory of the ternary systems therefore does not require any new data, above those of the theory of binary systems.

Physics. — W. H. KEESOM. "*Reduction of observation equations containing more than one measured quantity.*" (Supplement N°. 4 to the Communications of the Physical Laboratory at Leiden by Prof. H. KAMERLINGH ONNES).

(Communicated in the meeting of May 31, 1902).

§ 1. The most widely read text books on the theory of probabilities and the method of least squares treat of the reduction of observation-equations each of them containing one variable.

In physical measurements, however, we obtain equations between different quantities each of which must be considered as liable to an accidental error. This, for instance, occurs when we have measured the pressure of a gas or a liquid at different volumes and temperatures, and we want to deduce from the observations the equation which represents the most probable relation between these quantities investigated. As in the literature on this subject I have not found a general solution for such a case, it may be useful to give it here. [1])

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[1]) Literature on this subject:

CHAS. H. KUMMEL. Reduction of observation equations which contain more than one observed quantity. The Analyst. July, 1879 (Vol. VI, N°. 4).

I have not been able to find this volume of the periodical in Holland.

MERRIMAN. The Determination, by the Method of Least Squares, of the relation between two variables, connected by the equation $Y = AX + B$, both variables being liable to errors of observation. U. S. Coast and Geodetic Survey, Report 1890, p. 687. A Textbook on the Method of Least Squares, § 107.

Here an elegant solution of the problem is given for the case in which a linear relation exists between the two measured quantities.

JULES ANDRADE. Sur la Méthode des moindres carrés. C. R. t. 122, p. 1400, 1896.

The author gives a solution for the case when:

$$F(a, b, c \ldots . ;\ t_i) = N_i ,$$

in which t_i and N_i represent measured quantities, and a, b, $c \ldots .$ are to be determined.

RAVENSHEAR. The use of the Method of Least Squares in Physics. Nature, March 21, 1901, p. 489.

The author, apparently not acquainted with the literature mentioned above, points out that in treating equations between several measured quantities, we must make allowance for the fact that each of these quantities has an error of observation, and he gives a graphic solution for the case in which a linear relation exists between two quantities, some supposition regarding the accuracy of the measurements of each of those quantities being assumed.

K. PEARSON. On Lines and Planes of Closest Fit to Systems of Points in Space. Phil. mag. (6) Vol. 2, p. 559, Nov. 1901.

The author gives an elaborate essay on the lines and planes (if necessary in a higher-dimensional space) which are such that the sum of the squares of the perpendicular distances between a number of points not situated in a straight line or a plane, and those lines or planes becomes as small as possible.

§ 2. Suppose, we have measured some series of the quantities $L, M, N \ldots$, between which the following relation exists:

$$F(L, M, N \ldots ; \quad X, Y, Z \ldots) = 0 \quad . \quad . \quad . \quad . \quad (1)$$

where $X, Y, Z \ldots$ are unknown quantities which we want to calculate. We assume that the number of equations between the observed quantities is larger than the number of unknown quantities, so that we want to calculate the most probable values of $X, Y, Z \ldots$ by means of the method of least squares.

Let $L_1, M_1, N_1 \ldots$ be a set of values belonging together, as yielded by the observations,

$l_1, m_1, n_1 \ldots$ the errors made in these observations,

$m_{l_1}, m_{m_1}, m_{n_1} \ldots$ the mean errors in those measurements $L_1, M_1, N_1 \ldots$, which we assume to be known before hand,

$X_0, Y_0, Z_0 \ldots$ a set of approximate values for $X, Y, Z \ldots$

$x, y, z \ldots$ the corrections to be calculated, which must be applied to those approximate values.

Each measurement gives then according to (1) an equation:

$$\boldsymbol{L}_1 . l_1 + \boldsymbol{M}_1 . m_1 + \boldsymbol{N}_1 . n_1 \ldots = -F_1 - \boldsymbol{X}_1 . x - \boldsymbol{Y}_1 . y - \boldsymbol{Z}_1 . z \ldots \equiv \eta_1 . \quad (2)$$

where:

$$\boldsymbol{L}_1 = \left(\frac{\partial F}{\partial L}\right)_{\substack{L = L_1,\ M = M_1 \ldots \\ X = X_0,\ Y = Y_0 \ldots}}$$

$$\boldsymbol{X}_1 = \left(\frac{\partial F}{\partial X}\right)_{\substack{L = L_1,\ M = M_1 \ldots \\ X = X_0,\ Y = Y_0 \ldots}}$$

$$F_1 = F(L_1, M_1, N_1, \ldots ; X_0, Y_0, Z_0 \ldots).$$

Yet $x, y, z \ldots$ must be chosen so that [1]

$$\Sigma \left(\frac{l_1^2}{m_{l_1}^2} + \frac{m_1^2}{m_{m_1}^2} + \frac{n_1^2}{m_{n_1}^2} + \ldots \right) \text{ is a minimum.} \quad . \quad . \quad (3)$$

If now the coefficients $X, Y, Z \ldots$, are known, what errors, $l_1, m_1, n_1 \ldots$ correspond to the observed quantities $L_1, M_1, N_1 \ldots$? It is evident that various sets of quantities $L, M, N \ldots$ may have given rise to the same sets of quantities $L_1, M_1, N_1 \ldots$, and that those values of L, M, N and hence of l_1, m_1, n_1 are the most probable for which

$$\frac{l_1^2}{m_{l_1}^2} + \frac{m_1^2}{m_{m_1}^2} + \frac{n_1^2}{m_{n_1}^2} \ldots \text{ is a minimum,}$$

---

[1] KOHLRAUSCH, Lehrbuch der praktischen Physik, p. 16 considers the equations:

$$u = f(A, B, C, r, s, t \ldots)$$

"where $r, s \ldots$, and often u are instrumental readings" and yet he determines (see p. 11) A, B, C so that the sum of the squares of errors in u is as small as possible.

while we have the relation:

$$\boldsymbol{L}_1 l_1 + \boldsymbol{M}_1 m_1 + \boldsymbol{N}_1 n_1 + \dots = \eta_1 = \textit{constant.}$$

We then obtain l_1, m_1, $n_1 \dots$, from

$$\frac{l_1}{m_{l_1}{}^2} + K . \boldsymbol{L}_1 = 0$$

$$\frac{m_1}{m_{m_1}{}^2} + K . \boldsymbol{M}_1 = 0$$

$$\frac{n_1}{m_{n_1}{}^2} + K . \boldsymbol{N}_1 = 0$$

$$\dots\dots\dots\dots$$

where:

$$K = -\frac{\eta_1}{\boldsymbol{L}_1{}^2 m_{l_1}{}^2 + \boldsymbol{M}_1{}^2 m_{m_1}{}^2 + \boldsymbol{N}_1{}^2 m_{n_1}{}^2 \dots} .$$

With this (3) becomes

$$\Sigma \frac{\eta_1{}^2}{\boldsymbol{L}_1{}^2 m_{l_1}{}^2 + \boldsymbol{M}_1{}^2 m_{m_1}{}^2 + \boldsymbol{N}_1{}^2 m_{n_1}{}^2 \dots} \text{ is a minimum } . \quad (4)$$

If we define the weight of the observation equation by:

$$g_1 = \frac{1}{\boldsymbol{L}_1{}^2 m_{l_1}{}^2 + \boldsymbol{M}_1{}^2 m_{m_1}{}^2 + \boldsymbol{N}_1{}^2 m_{n_1}{}^2 \dots} \quad . \ . \ . \quad (5)$$

then (4) is reduced to

$$\Sigma g_1 \eta_1{}^2 \text{ is a minimum,}$$

and the equations for the determination of x, y, $z \dots$: become:

$$\Sigma g_1 \boldsymbol{X}_1 \eta_1 = 0$$
$$\Sigma g_1 \boldsymbol{Y}_1 \eta_1 = 0$$
$$\Sigma g_1 \boldsymbol{Z}_1 \eta_1 = 0$$
$$\dots\dots\dots$$

or:

$$\left.\begin{array}{l} [g\boldsymbol{XX}]x + [g\boldsymbol{XY}]y + [g\boldsymbol{XZ}]z \dots + [g\boldsymbol{X}F] = 0 \\ [g\boldsymbol{YX}]x + [g\boldsymbol{YY}]y + [g\boldsymbol{YZ}]z \dots + [g\boldsymbol{Y}F] = 0 \\ [g\boldsymbol{ZX}]x + [g\boldsymbol{ZY}]y + [g\boldsymbol{ZZ}]z \dots + [g\boldsymbol{Z}F] = 0 \end{array}\right\} \quad . \quad (6)$$

$$\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots$$

where, according to the usual notation:

$$[g\boldsymbol{XX}] = g_1 \boldsymbol{X}_1^2 + g_2 \boldsymbol{X}_2^2 + \dots + g_n \boldsymbol{X}_n^2$$
$$[g\boldsymbol{XY}] = g_1 \boldsymbol{X}_1 \boldsymbol{Y}_1 + g_2 \boldsymbol{X}_2 \boldsymbol{Y}_2 + \dots + g_n \boldsymbol{X}_n \boldsymbol{Y}_n$$

if n stands for the number of observations.

We hence arrive at this very simple result, that from the equations

$$\boldsymbol{X}_1 x + \boldsymbol{Y}_1 y + \boldsymbol{Z}_1 z + \dots \quad F_1 = 0$$
$$\boldsymbol{X}_2 x + \boldsymbol{Y}_2 y + \boldsymbol{Z}_2 z + \dots \quad F_2 = 0$$
$$\dots\dots\dots\dots\dots\dots\dots\dots$$

reduced to the linear form, the normal equations are deduced in the same way as when the quantities F_1, $F_2 \dots$ are directly derived from the observations, if we accord the weight determined by equation (5) to each of those observation equations [1]).

This treatment of the equations with several observed quantities agrees with the solution for two measured quantities given by ANDRADE. For the case that a linear relation exists between two measured quantities this one is simpler than MERRIMAN's solution.

§ 3. In the following way it is easily shown that the mean error in the result is also found according to the usual rules, as applied to equations with one measured quantity. From the normal equations (6) we find

$$x = a_1 F_1 + a_2 F_2 + a_3 F_3 \dots \quad + a_n F_n \,.$$

Here x is expressed as a function of the measured quantities $L_1, M_1, N_1 \dots \; L_2, M_2, N_2 \dots$

The mean error in x is obtained from:

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[1]) For the equations, which SCHALKWIJK used (Comm. Nr. 70, Continued, Proceedings June 1901; Thesis for the Doctorate, p. 115) viz.

$$PV_{20} - 1.07323 = B_{S_{20}}(d - 0.93177) + C_{S_{20}}(d^2 - 0.868),$$

where P and $V_{20} = \frac{1}{d}$ have been measured, $B_{S_{20}}$ and $C_{S_{20}}$ are to be calculated according to the method of least squares, we find from (5) the weight of each observation equation:

$$\frac{g_1}{\mu_0^{\,2}} = \frac{1}{P_1^{\,2} V_{1_{20}}^{\,2} \mu_{p_1}^{\,2} + \{P_1 V_{1_{20}} + B_{S_{20}} d + 2 C_{S_{20}} d^2\}^2 \mu_{d_1}^{\,2}}$$

if μ_{p_1} and μ_{d_1} respectively represent the mean relative error in the pressure- and density measurement, and μ_0 the mean relative error for a measurement to which the weight 1 is assigned. If we put $\mu_{p_1} = \mu_{d_1} = \mu_0 \left(= \frac{1}{10000}\right)$, then if:

$$d = 6.2394: \quad g = \frac{1}{2.23},$$

$$d = 53.988: \quad g = \frac{1}{2.56}.$$

The terms with d will have little influence in the value for g, as long as d does not become very large, as appears a priori from the fact that the coefficients $B_{S_{20}}$ and $C_{S_{20}}$ are small. (Comp. SCHALKWIJK's Thesis for the Doctorate p. 115, where he gives: $B_{S_{20}} = 0.000667^1$, $C_{S_{20}} = 0.00000099^3$). In this case errors of observation in d will have little influence on the second member, and this second member may be considered as precisely known. As the values of PV_{20} differ comparatively little for the different densities at which the observations are made, an equal weight has been assigned to each observation equation. This is the more justified if we consider that he was able to measure the higher pressures with greater precision than the lower, as in the former in adding the measured lengths of each column of mercury the accidental errors partly neutralise each other.

$$m_x^2 = a_1^2 \mathbf{L}_1^2 m_{l_1}^2 + a_1^2 \mathbf{M}_1^2 m_{m_1}^2 + a_1^2 \mathbf{N}_1^2 m_{n_1}^2 + \ldots . a_2^2 \mathbf{L}_2^2 m_{l_2}^2 + \ldots .$$

. . . .

or
$$m_x^2 = \frac{a_1^2}{g_1} + \frac{a_2^2}{g_2} + \ldots . = \left[\frac{aa}{g}\right] .$$

This form is the same as that obtained in equations with one measured quantity ¹), so that here also the weight of the result is found from the coefficients, which occur in the solution for $x, y, z \ldots .$ if the quantities $[g_1 \mathbf{X}_1 F_1]$ etc. in the normal equations are left undetermined.

Mineralogy. — *"On the behaviour of disthene and of sillimanite at high temperature."* By E. H. M. Beekman. (Communicated by Prof. Schroeder van der Kolk).

In nature occur three varieties of aluminium-silicate ($Al_2 Si O_5$) i. e. disthene, andalusite and sillimanite. Sillimanite and andalusite are orthorombic; disthene however triclinic. So the two first show parallel, the last oblique extinction.

According to the experiments made by Vernadsky ²), disthene is said to turn into sillimanite, at about 1350 degrees; the same temperature is said to turn also andalusite into sillimanite. As a proof that they had actually become sillimanite, he urged that, whereas before being heated, their hardness and specific gravity differed, they now showed the same. Moreover the extinction of disthene had become parallel.

The results to which he came are these:

Name.	S. G. before heating.	S. G. after heating.
Sillimanite	3.045 3.286	id.
Disthene	3.51 3.48	3.15 3 20
Andalusite	2 85	3.165

Directed by Prof. Schroeder van der Kolk, I experimented, as stated by Vernadsky, and came to the following results, as to their specific gravity:

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¹) See for instance Merriman, Method of least Squares, p. p. 83 and 84.

²) See Bulletin de la Société Min. de France (1889 et 1890).

Name.	S. G. before heating	S. G. after heating.
Sillimanite	3.152 3.161	3.157 3.159
Disthene	3.59 3 56	3.240 3.236
Andalusite	3.158 3.158	3.149 3.150

To determine the specific gravity, I made, as much as possible, use of the floating method. The fluids I used were methyl-iodide (spec. gr. 351) and acetylenetetrabromide (spec. grav. 2.84). The instrument I used to fix these spec. grav. was the "Westphal-balance", except when the fluids were too light, in which case I made use of a xylolareometer.

Consequently the results, as shown above, are pretty much the same, as those of VERNADSKY.

The extinction of disthene, after the heating, had become parallel also, however before the melting temperature of copper (1100 degr. C.) had been reached.

What is a strong argument against the change of disthene into sillimanite is its index, which I fixed in a way, indicated by Prof. SCHROEDER VAN DER KOLK, i.e. by using fluids of which the refractive index is known [1]). They were: methyl-iodide ($n = 1.74$); monobromine-naphtaline ($n = 1.66$); monochlorine-naphtaline ($n = 1.64$); mono-iodine-benzol ($n = 1.62$) and mixtures of them. The index of those fluids, I have fixed by using a Pulfrich with changeable refracting angle.

Thus I could fix the index of very small pieces and moreover acquire a precision up to the second decimal.

I have fixed the index only in the direction of the *c*-axis. The double refraction not being great, this was sufficient. That index is the greatest, since in sillimanite, the ellipse of intersection, with the indicatrix, has its long axis in the direction of the *c*-axis.

Before the heating process, the index of sillimanite was 1.68. Heating did not in the least affect it.

Andalusite remains equally unaffected by it, it has an index of 1.64.

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[1]) See „Tabellen zur Mikroskopischen Bestimmung der mineralien nach ihrem Brechungsindex" by Dr. J. L. C. SCHROEDER VAN DER KOLK.

The highest temperature to which I have submitted my materials, was acquired by blowing into an open Bunsen flame with an artificial blowpipe-apparatus.[1] The very small splinters of the mineral can be thus brought to a very high temperature probably to 2000° C. A platinum wire of $^1/_3$ mM. at once melted in it.

As investigation material for disthene, I used the blue variety (find-place Gängerhausen). Before the heating, the index was 1.73 and after it (I experimented in the way just described), it sank to 1.62; so far below that of sillimanite.

If disthene had actually turned into sillimanite, it should have kept its index (1.68); sillimanite submitted to the same temperature, not changing its index in the least. So this shows that heating does not turn disthene into sillimanite.

To try whether 1300° would bring the index to 1.68, I proceeded thus:

I took several earthen mugs, put in each a piece of disthene together with other metals of which the melting temperatures are known, heated the metals to a temperature that would keep them for a moment in melting condition and thus obtaining constant temperatures, I could fix the indices of disthene, which proved to be gradually lower. Lower than 1.62, it could not be reduced, in spite of continued heating. On the subjoined diagram, the different temperatures and indices are stated. On one of the axes are the indices, on the other the degrees from hundred to hundred. The line starting from 1.68, running parallel with the axis of the temperatures, represents the direction of the index of sillimanite. That line remained constant. The broken line marks the direction of the index of disthene. They cut each other, as will be seen, at about 1250° C.

The deviation in silver is probably caused, either by the not absolutely accurate melting temperature or by a slight inaccuracy in the index.

The reason of it is probably that we have a mixture of materials of which one more and more prevails; what pleads for this, is the growing intransparency of disthene, a fact noticed also by VERNADSKY.

At a degree of 1.62 disthene grows entirely opaque, consequently, it has got entirely amalgamated with the other material.

Of course this argument is open to discussion, but up to now, I have not been able to find a better one. This phenomenon, may be of some practical usefulness in making maxim-pyrometers, since it proves that a constant index may be obtained by heating to a certain temperature.

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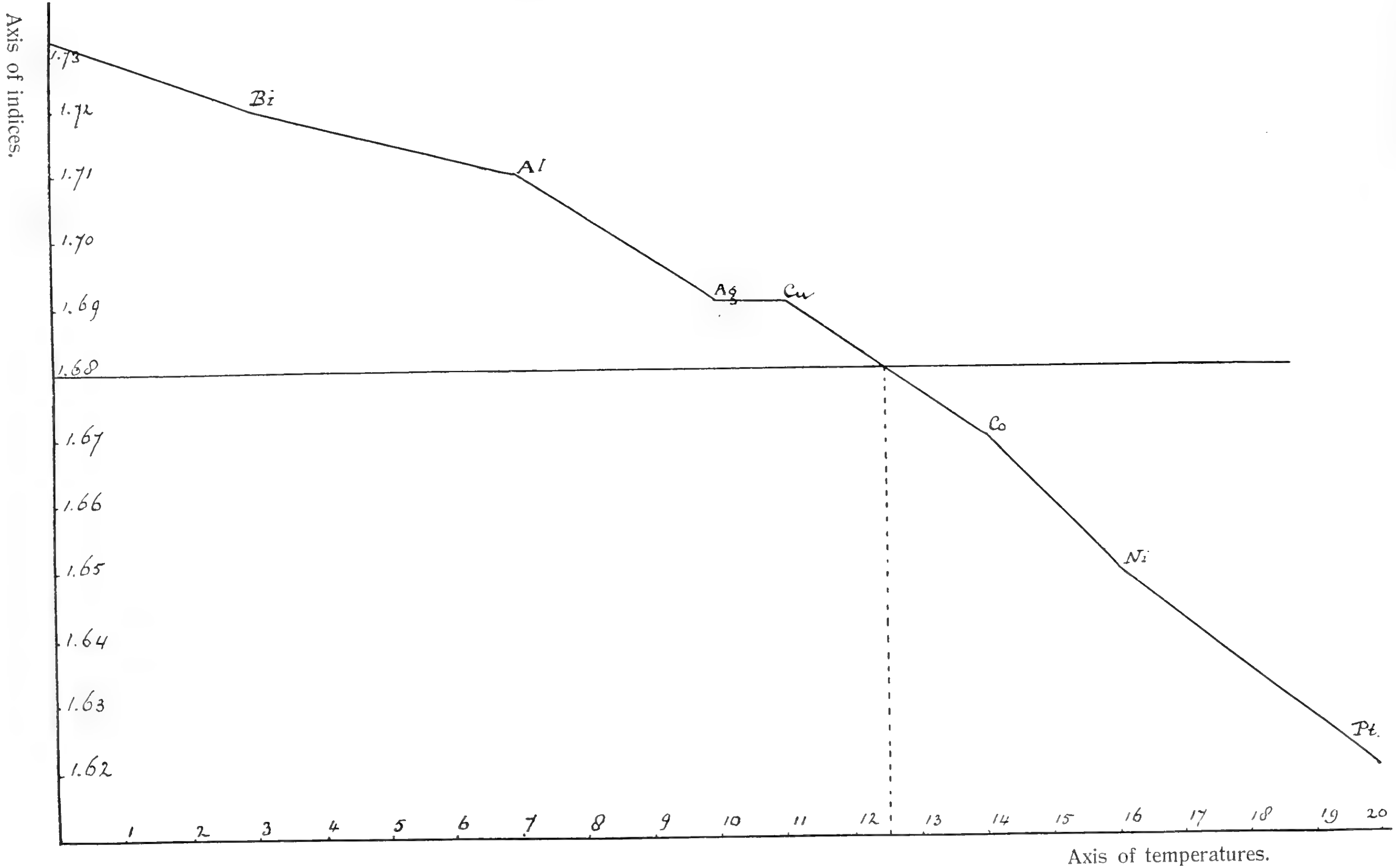
[1] To be had at ALTMANN's in Berlin.

E. H. M. BEEKMAN Mz., „On the behaviour of disthene and of sillimanite at high temperature.”



Physics. — "*Measurements on the magnetic rotation of the plane of polarisation in liquefied gases under atmospheric pressure. II. Measurements with methylchloride*" by Dr. L. H. Siertsema. (Communication n°. 80 from the Physical Laboratory at Leiden, by Prof. H. Kamerlingh Onnes).

(Communicated in the meeting of June 28, 1902).

I. In a previous communication n°. 57 [1]) an apparatus for the measurement of the magnetic rotation in liquefied gases under atmospheric pressure was described and a few results with methyl chloride were given. Further measurements with this apparatus have not fulfilled my expectations, so that it appeared to be necessary to make considerable modifications.

In the first place it was difficult to insulate the apparatus properly from heat. It had been packed in cotton-wool, yet it was not easy to obtain a perfectly quiet liquid, entirely free from rising bubbles. The pressure of as many as six glass-plates between the nicols was also very disturbing, owing to their depolarising influence. This was more noticeable after filling the apparatus when tensions appeared to arise in the plates, in contact with the cold liquid, which often rendered adjustment quite impossible.

To remedy this defect the nicols were immersed in the cold liquid in the tube marked *D* of the plate in the previous communication. The nicols were lying loose in this tube and were connected by a brass wire, running along the outside of the tube. One of the nicols could revolve in its holder and could be adjusted at a given angle before the apparatus was closed. The rotation for different wave-lengths could then be found by measuring the intensity of the current required to bring the dark band in the spectrum to that wave-length. The apparatus being arranged in this manner some measurements could be made with it, but always after some time the nicols appeared to have lost their transparency, either because the layer of canada-balsam was dissolved or became laminated. Nicols with a layer of linseed oil instead of canada-balsam lasted longer, and the layer seems not to dissolve so easily, but in the long run these too lose their transparency, perhaps in consequence of irregular deformation of the calcspar by the sudden and intense cold of the liquid gas.

2. Then a new apparatus was constructed, in which also the

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[1]) Proceedings Royal Acad. of Sciences. May 1900.

first mentioned difficulty was overcome, and with which some satisfactory measurements of the magnetic rotation dispersion in liquid methyl chloride have been made.

In this apparatus, shown in fig. 1, the experimental tube *D* and the nicols *C* are enclosed in a brass jacket *A* with double walls, filled with liquid methyl chloride, insulated from the heat of the coil by a layer of wool. The space within the jacket is closed on either side by the ebonite caps *N* of the previous apparatus, with the india-rubber rings *O* as packing-washers and 6 tightening rods. In these caps the glass plates *B* are fixed with the screw-rings *P*, and thin india-rubber leaf as packing. The other nuts and rings connected with them have remained unchanged.

The circulation of liquid methylchloride through the jacket is obtained from the cryogenic laboratory, where a connection with the methyl chloride reservoir with its compression pump can be made [1]). The liquid is supplied through a high pressure cock *E*, (see fig. 2) while the escaping vapour streams back to the cryogenic laboratory through the tubes *K K*. A float *F* enables us to know at any time whether the jacket is filled.

The experimental tube *D* consists of a glass tube of 35 c.m. having an opening *G* in the middle and closed by two glass plates 1 m.m. thick, fastened to it by means of fish glue. The nicols *C*, rotating in elastic brass rings, are mounted on either side. It is true that now there is glass between the nicols, and the unfavourable influence of this makes itself felt, however to a much smaller extent, so that adjustments can be now made.

The apparatus is filled through a steel capillary *H*, passing through an india rubber stopper in an aperture in the jacket and entering the testing tube.

The methyl chloride required to fill it is obtained by distilling the commercial article, which has been once distilled already, once more, the vapour passing through a drying tube into a spiral immersed in a reservoir of liquid methyl chloride under atmospheric pressure, supplied by the same tubes which were used for the liquid in the jacket described.

Liquid methyl chloride flows from this spiral through the steel capillary *H* connected with it, into the experimental tube under atmospheric pressure and hence having the same temperature as the jacket and the space within. The tube *I I* to which a piece of india rubber tubing is connected, serves to remove the vapour formed

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[1]) Comp. Communication N⁰. 14, These Proceedings. Dec. 1894.

inside the jacket. This arrangement proved very satisfactory, the liquid in the testing tube is perfectly quiet and free from bubbles of vapour.

At first the space round the nicols formed one continuous space with that round the testing tube, and so the nicols were also surrounded with an atmosphere of methyl chloride vapour. In consequence of this, vapour still condensed on the nicols and accurate adjustments could not be made. In order to avoid this the spaces round the nicols have been separated from that round the testing tube by the brass rings *L*, fastened on the testing tube by means of sealing wax and closed by means of india rubber rings on the jacket. As at the low temperature a considerable decrease of pressure is to be expected in the imperfectly closed nicol spaces, the caps *N* have been pierced by copper tubes *M*, connected to *U*-tubes with narrow openings and filled with pieces of sodium hydroxide.

Before closing the apparatus, the nicols have been adjusted at a given angle by fastening to one of them a long bent copper-wire, the end of which could be moved over a divided scale. This adjustment is not accurate and no use has been made of this angle in the calculation of the results, the rotations having been compared with those in water.

The rotation at different wave-lengths is again obtained by varying the strength of the current, by doing which, the dark band can be caused to move over the whole spectrum.

The optical and magnetical part is almost the same as that described in the previous communication, except that for the measurement of the current we have again used a D'ARSONVAL-galvanometer with shunt (comp. Comm. Suppl. 1 p. 25, Arch. Néerl, (2) 2 p. 305). By comparing it with a Weston-millivoltmeter it is found that the sensibility of the galvanometer is constant within the limits we had to fix for the accuracy.

Fig. 2 gives a general survey of the apparatus used. *C* represents an arc lamp, *B* ARONS-LUMMER's mercury electric lamp, *A* a collimator, *D* a water reservoir, *P* a prism and *Q* a telescope on a circle from MEYERSTEIN. Further *G* represents the coil with the methyl chloride apparatus, *E* the cock, by which the supply of liquid methyl chloride for the jacket is regulated.

The arrangements for regulating the current and measurement, with resistances and switches, are similar to those for the experiment on the magnetic rotation in gases [1]).

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[1]) Comm. Leiden Suppl. 1 p. 25; Arch. Néerl. (2) 2 p. 315.

3. For the measurements with methyl chloride of which the results are given below, the nicols were adjusted at an angle of 11 degrees from the crossed position.

The dark band moved from one end of the spectrum to the other as the strength of the current varied from 20 to 60 amp. The observations were made with the electric arc light and the calibration of the spectrum was obtained during the measurements by the brightest mercury lines, while the dispersion curve of the prism had been determined by means of sunlight. At each strength of the current three adjustments of the dark band were made and the means have been taken of the three pairs of readings of the galvanometer and the circle. Table 2 gives the galvanometer defections a so obtained, together with the wave-lengths λ of the position of the dark band in the spectrum.

Then on a subsequent day the testing tube was filled with water and the other parts of the apparatus remounted entirely unchanged. The dark band reappeared at strengths of the current deviating little from those found before, from which we could derive immediately that the rotation constants of liquid methyl chloride differed little from those of water. Thus the numbers of table 1 have been found, where a and λ have the same meaning as they had before, and r stands for the rotation constants in water. The latter have been derived from my measurements of communication n°. 73 [1]), and from them ar has been calculated, which quantity must be constant for all values of r, as it is equal to the rotation angle divided by the magnetic potential difference at the ends of the testing tube, and by the reduction factor of the galvanometer with its shunt.

TABLE 1.

a	λ	r	ar
235	588	0.01307	3.071
190	534	1612	3.062
208.5	554	1487	3.100
		mean	3.078

The mean value of ar, being 3.078, now served to derive the rotation constants ϱ of the methyl chloride from the a found. These values of ϱ have been plotted in a curve, from which $\varrho_D = 0'.01372$

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[1]) Arch. Néerl. (2) 6 p. 825 (1901).

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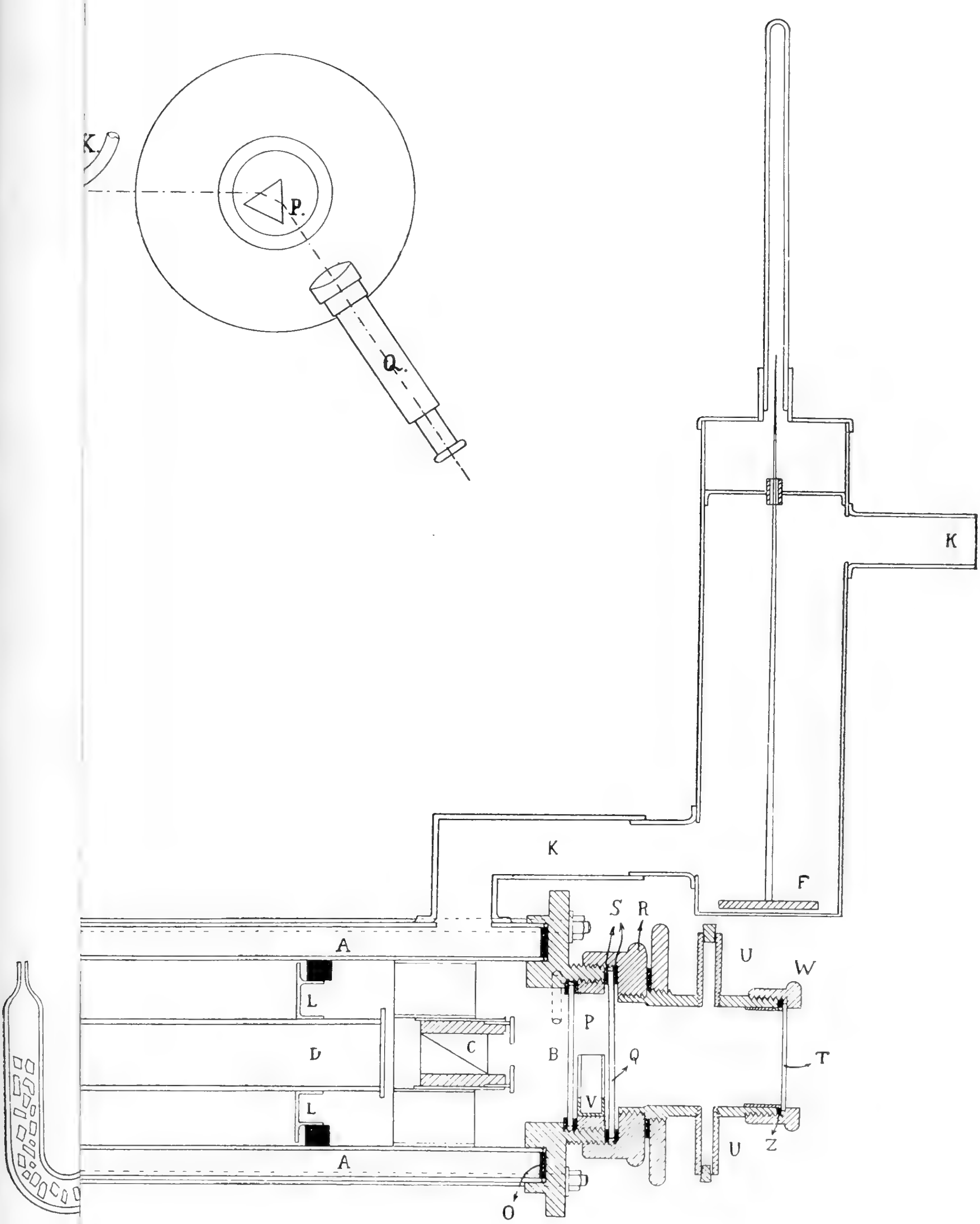

Proceedin

L. H. SIERTSEMA. „Measurements on the magnetic rotation of the plane of polarisation in liquefied gases under atmospheric pressure. II. Measurements with methyl chloride.”

Fig. 2.

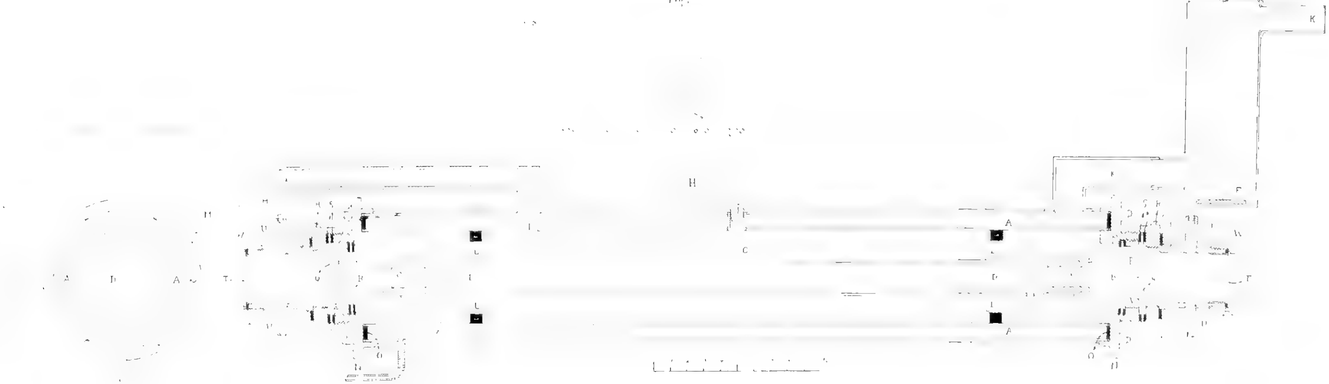

Fig 1.

is derived and the values ϱ/ϱ_D have been calculated finally, which values determine the dispersion of the magnetic gases. These different numbers are combined in table 2, while fig. 3 shows graphically the values of ϱ/ϱ_D.

TABLE 2.

a	λ	ϱ	ϱ/ϱ_D	a	λ	ϱ	ϱ/ϱ_D
112	420	0.02748	2.003	211.5	575	0.01455	1.061
116	431	2653	1 835	216	579	1425	1.039
124	446	2482	1 810	219.5	583	1402	1.022
130.5	458	2358	1.719		[589]	[1372]	1 000
165	510	1865	1.360	231	599	1332	0 971
166	512	1854	1.351	235.5	604	1307	0.953
176.5	527	1744	1.271	237	604	1299	0.947
184.5	536	1668	1.216	249.5	616	1234	0.899
189.5	543	1624	1.184	250	621	1231	0.898
196.5	554	1566	1.142	273	643	1127	0.822
196	555	1570	1.145	283	659	1089	0.794

In this calculation the rotation in the glass plates has been neglected. A simple calculation shows us that this is permissible; for it should be remembered that this is done both for the measurements with methyl chloride and with water.

As the result of this research I find that the magnetic rotation constant for liquid methyl chloride under atmospheric pressure for sodium light is 0'.01372, and that the rotation dispersion is normal, deviating little from that with gases and with water.

The research will be continued with other gases.

Physics. — *"Diffraction of Röntgen-Rays."* By Prof. H. HAGA and Dr. C. H. WIND; second communication.

In the March meeting 1899 we stated as the result of our experiments that Röntgen-rays show diffraction; with these experiments the rays passing through a narrow slit first fell on a second wedge-shaped slit, then on a photographic plate. The image proved not to be what was to be expected with rectilinear propagation but presented broadenings from which an estimation could be derived concerning the value of the wave-length which proved to be of the order of 0,1 $\mu\mu$.

In September of last year in one of the meetings of the "Deutsche Naturforscher Versammlung" at Hamburg Dr. WALTER[1]) protested against those experiments; he had arranged his experiments in entirely the same way as we had; moreover he had taken still greater precautions to get a steady mounting of the slits and the photographic plate and he had used stronger Röntgen-rays. WALTER obtained images quite similar to the second slit and attributed our broadenings to inaccuracies of the photografic plate brought about by long development.

These negative results gave rise to a renewed investigation on our side, now that we had greater means at our service than three years ago. We have succeeded in obtaining more clearly than before phenomena of diffraction, so that according to us one can no more doubt the character of Röntgen-rays to be that of disturbances in the ether.

The method of investigation has not changed in principle, but making use of the experience obtained by Dr. WALTER and ourselves we have been able to make improvements still in some respects.

On the upper surface width 5.5 cm. of an iron beam of I-shaped profile, long 2 m. and high 12.5 cm. three pieces of angle-iron were screwed down, one at the end, the two others 75 cm. and 150 cm. distant from it, the edge perpendicular on the length of the beam and the side of 3.5 cm. erect; in the figure the two first pieces of angle-iron are visible; against the vertical sides brass plates — 12 cm. high, 10 cm. wide and 4 mm. thick — were screwed. In the middle of plate I was the first slit, in the middle of plate II the wedge-shaped diffraction slit while against the third plate in a black envelope the photographic plate was clamped[2]). During the experiments the second and the third of these brass plates were enclosed in an oblong leaden case, which had to prevent the secondary Röntgen-rays or rays diffused by the air, from affecting the photographic plate and causing a fog.

The iron beam was fastened by means of plaster of Paris on two free-stone plates borne by free-stone columns; the columns were placed on a firm pillar; on this same pillar, likewise on a free-stone plate borne by a stone column, was the Röntgen-tube in a large leaden

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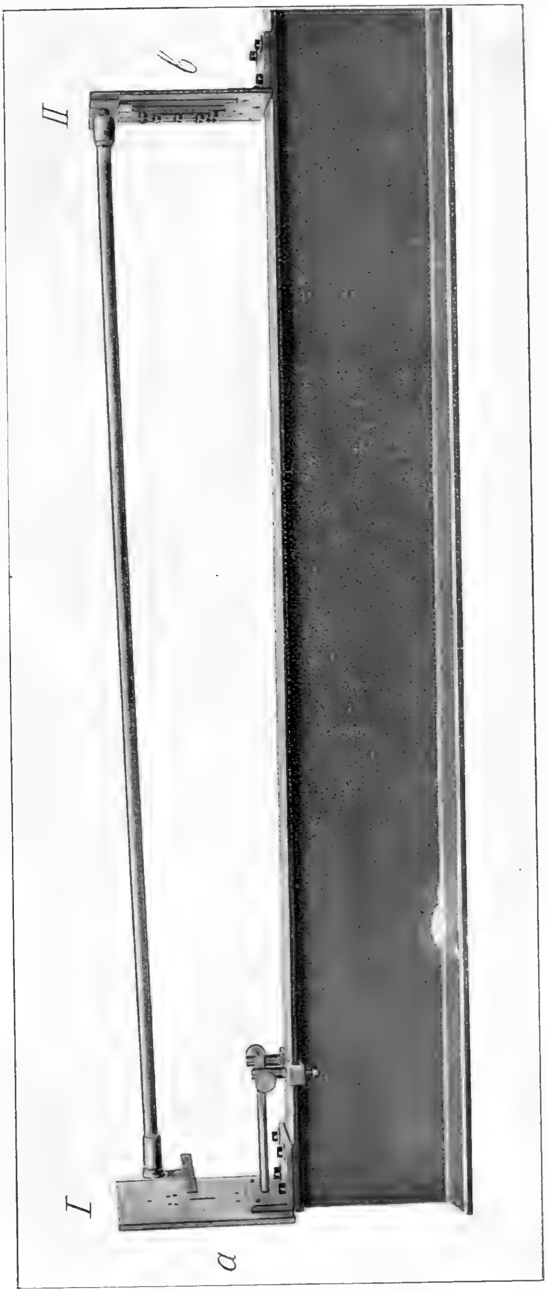
[1]) B. WALTER, *Physik. Zeitschrift* 3. p. 137, 1902.

[2]) SCHLEUSSNER's "Röntgenplatten" were used.

H. HAGA and C. H. WIND. „Diffraction of Röntgen-Rays."
(Second Communication).



case (thickness of the side 2 mm.); only the back of this case was left open for the connecting wires of the induction coil, whilst in the front a small aperture was made opposite the first slit to let the Röntgen-rays pass. The first slit was formed by two platina plates, thick 2 mm. and high 2 cM; a leaden screen left but the middle of it free over a height of 4 mm.; the width of this slit was 15 μ. The diffraction slit was formed by two platina plates thick $^1/_2$ mm., high 4 cm., tapering at the upper end from a width of 25 μ to nearly zero at the other. Greatest care was given to the grinding of the platina plates. For these slits, just as in our former experiments, the sides were everywhere equally thick and not ground wedge-shaped at the edge of the slit as is the case with slits for light-experiments.

To produce the Röntgen-rays an induction coil of Siemens and Halske was used with a sparklength of 60 cm., a primary with 4 coils and a Wehnelt-interruptor. The current was furnished by a battery of accumulators of 110 Volt. The newest Röntgen-tubes of Müller (Hamburg), were exclusively used; the anticathode being kept cool by water.

More care than formerly was taken to bring the passages of the two slits accurately into the same line. Peculiar difficulties are incident to this, which is a result of the extraordinarily great depth of the slits together with a width so slight that common light, on account of the arising phenomena of diffraction, cannot be used to fix accurately the direction of the passage. For this last reason we had to have recourse to Röntgen-rays to do so. And here again the slight width of the slits caused the pencils of rays passing through them to be so very faint, that in the case of the *first* slit, wide 15 μ, they could be observed on a fluorescent screen at the place where it was necessary, namely near the second slit only with an eye accustomed to complete darkness. The pencil of rays, allowed to pass through the most interesting part of the *second* slit viz. that part, where the width was about 5 μ, could be observed not even by this way, but only by the impression it made on a sensitive plate after a lengthy exposure (4 hours). In order to deduce from this impression a mark for the direction of the passage of the second slit, a small strip of brass was fastened near and slightly above the first slit; (see figure); in this strip, held by an arm fixed to plate II, some vertical rows of small holes had been drilled side by side, differing in number and size. A Röntgen-tube was placed behind plate II in *b* and a photographic plate between the brass strip and plate I; a small leaden screen left of the second slit but the part to be observed free. On the photographic impression one or two of the rows of the holes became visible and from this could be deduced without difficulty, which part of the strip was situated in the direction of the passage of the second slit. It was now easy to place plate II with its piece of angle-iron in such a way — the holes in the iron were somewhat larger than the diameter of the screws — that, seen from the centre of the second slit, the part of the strip, just now determined, appeared exactly above the first slit. Plate I being able to revolve round an axis through the first slit, the latter could be directed in such a way that the rays from a Röntgen-tube placed near *a* fell on the second slit; by means of a fluorescent screen we could make sure that this had been obtained. During the course of the diffraction experiments itself the exact position of the tube was several times controlled and if necessary corrected.

The width of the second and first slits were arrived at from photographs when the photographic plate was placed immediately behind plate II and the Röntgen-tube at *a* or the photographic plate at *a* against plate I and the Röntgen-tube at *b*; the photograph of the second slit was taken both before (namely April 10th, plate N°. 1) as after (namely Aug. 23rd, plate N°. 2) the experiments.

As has been mentioned before the self-regulating tubes with water-cooling were exclusively used; how well these tubes work and how excellent they are for the usual medical purposes, for the uncommon demands of this investigation only a few of them could be of service. For we wanted tubes which were "soft" and remained so for hours at a stretch, whilst the effect was so great that the cooling-water kept on boiling; most of the tubes became harder after a ten hours'use; when the discharges took place to the sides of the leaden case another tube had to be taken.

Three very good photographs were obtained, to be distinguished as *A*, *B* and *C*.

A, obtained on May 7th and 8th after an exposure of 9 hours and a half, principally by a very excellent tube furnishing very strong rays and of great softness; developed during three quarters of an hour in 200 ccm. of glycine [1]) 1 to 5.

B, obtained on July 8th, 9th, 10th, 12th; time of exposure 31 hours; two tubes were used, one of which was soft for four hours and after that became hard and the second continually hard; developed in one quarter of an hour with glycine 1 to 5.

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[1]) Vogel's Taschenbuch, 1901, pg. 128.

C, Aug. 14th, 15th, 16th, 17th, 18th; time of exposure 40 hours; two tubes used, one of which worked 10 hours and was pretty hard, the other a very good tube which remained soft for the remainder of the time; developed in 10 minutes with glycine 1 to 6.

There is scarcely any fog on the plates.

In order to enquire how wide that part of the diffraction slit was, through which the rays have passed that have worked upon the photographic plate at a definite point, small round holes were drilled just as in our preceding investigation in one of the sides of the second slit and close to it at the extreme ends and in the centre. On account of this on the plates N°. 1 and N°. 2 serving for the measurement of the second slit, circular images had appeared and elongated ones on the plates *A*, *B* and *C*. (From these pinhole-photographs of the active part of the anticathode, limited by the width of the first slit, is proved that this active part was only 2 mm. high). The distances between the centres of these images were divided by the dividing-machine into the same number of equal parts, so that the corresponding division-marks point to corresponding places of slit and image.

For the measurement of N°. 1 and N°. 2 object-glass *D* and measuring-eye-piece 2 were used where one division of the micrometer corresponds to 3,6 μ.

For the measurement of the image of the slit on *A*, *B* and *C* the microplanar I^a, 2 was used as object-glass and as eye-piece the compensation eye-piece 6; one division of the eye-piece-micrometer corresponds to 55 μ, the magnifying power was 27 with a distance of the image of 25 cm.

In the following table are mentioned for the successive division-marks indicated by their number in the first column:

in column 2: the mean of the values derived from N°. 1 and N°. 2 of the width of the second slit in micra;

in column 3: the double width of the second slit augmented by the width of the first slit (15 μ), thus the theoretic width of the image, without diffraction; the distance between the photographic plate and the first slit being double the distance between the first and second slit;

in column 4, 5 and 6: the width of the images respectively on *A*, *B* and *C* as measured in divisions of the eye-piece-micrometer (1 div. = 55 μ);

in column 7: the mean width of the images in micra (rounded off).

Number of the division-mark.	Width of the second slit.	Theor. width of image without diffraction	Measured width.			
			A.	B.	C.	Mean.
1	27 μ	69 μ	1.0	1.0	1.0	55 μ
2	22,5	60	0.85	0.85	0.9	50
3	19,5	54	0.75	0.75	0.8	40
4	18	51	0.6	0.7	0.7	40
5	17	49	0.55	0.7	0.7	35
6	16	47	0.45	0.65	0.65	30
7	14	43	0.4	0.6	0.65	30
8	12	39	0.35	0.5	0.6	25
9	9,5	34	0.3	0.4	0.6	25
10	8	31	0.3	0.35	0.5	20
11	6	27	0.4	0.4	0.55	
11½			0.6	0.45	0.6	
12	4	23	1	0.45	0.7	
12½			±1½	0.8	±1½	
13	3.5	22		±1½		

When considering these figures we must keep in view that the image on account of the width of the first slit is not sharply outlined but is hazy; this causes the measurement to remain uncertain and so somewhat deviating figures are found by different observers or by the same observer at various times; all measurements, however taken, proved, as can be noticed from the figures mentioned in the table, that for the *wide* part of the slit the figures of the third column are larger than the corresponding ones of the last column. The figures of this third column indicate the theoretic width of the image for the case that the plates have been affected to the *outer* edge of the rays to which they were exposed and that no diffraction, vibration, displacement or photographic irradiation has played a part; the latter three causes might bring about a broadening, yet this would necessarily have been greatest on the places of greatest influence thus at the *wide* part of the slit. Now that no broadening whatever is found *there*, the brush-shaped broadenings, whose width is 2 or 3 times greater than the theoretic, found on all the three plates at the narrow part of the slit, can certainly not be attributed to those three causes.

These broadenings, however, are exactly of a character as is to be expected in the case of diffraction; and therefore as long as another explanation is wanting, we can but consider our three plates as so many proofs of *diffraction of the Röntgen-rays*.

Of the most important parts of N°. 1, *A*, *B* and *C* we have made enlarged copies on glass by means of the microplanar, on which, if not so clearly as under the microscope, the broadening of the image of the slit is yet verydistinct; the difficulty of reproducing these enlargements well has made us refrain from publishing them; we are quite willing to send these copies to those who are interested in them.

As to the question to estimate the wave-lengths of these rays, various ways are open; but in no case can one attain at anything but a very rough estimation, as on one hand the real nature of the kind of radiation dealt with is unknown, so that it is uncertain with which kind of diffraction-image our images must be compared, and on the other hand it is very difficult to find out what is accurately the physical meaning of the limits of the image, on which is pointed when measuring.

If however we are forced to limit ourselves to a very rough estimation it is rather indifferent, as far as the result goes, which of the ways already indicated [1]) we take; the simplest method deserves recommendation, namely the one we followed in our first communication about this subject, based upon our estimating the tabular width v of the slit equal to 1.3 at the place where the broadening begins to make its appearance in the image. With a radiation of simple periodical disturbances this tabular width is connected with the wavelength and the linear width, and with the known distances a and b by means of the relation:

$$v_s = s\sqrt{\frac{2\,(a+b)}{a\,b\,\lambda}} \text{ or } \lambda = \frac{s^2}{v_s^2}\,\frac{2\,(a+b)}{a\,b}.$$

As in the experiments a and b both amounted to 75 cm. we obtain after substitution of the value of v_s

$$\lambda = 0{,}032\, s^2.$$

From the above table ensues for s: the width of the slit where the broadening begins to appear, respectively about 7, 4 and 6 μ for the plates *A*, *B* and *C*. From this would ensue for the

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[1]) H. Haga and C. H. Wind. These reports 7 page 500, 1899. C. H. Wind Wied. Ann. 68, page 896 and 69, page 327, 1899; Physik. Zeitschrift 2. p. 189, 265 and 292, 1901. A. Sommerfeld, Physik. Zeitschrift 1, pg. 105, 1900 and 2, pg. 58, 1900; Zeitschrift. f. Math. und Physik. 46, pg. 11, 1901.

wave-lengths if Röntgen-rays are simple periodical disturbances:

for plate A, B, C,
$\lambda = 0{,}16$ $0{,}05$ $0{,}12\ \mu\mu$.

Now that this supposition does certainly not hold, we shall have to consider these values as estimations of wave-lengths, which in the three different experiments have been more or less prominent in the curve of energy[1]) of the Röntgen-rays.

Mention ought to be made here, that, although not too much importance must be attached to the three values of λ as far as the absolute figures go, the difference they show is probably real and connected with the difference in hardness of the tubes. As was mentioned above the tubes used for plate B were distinguished by a considerable hardness from the others, which were relatively very soft.

Worth noticing is also the fact, that the values of λ found here are of the same order as those deduced from our former experiments.

Finally we wish to state emphatically that we continue to regard as the chief result of our investigations the proof they furnish that the Röntgen-rays ought to be considered as a phenomenon of radiation in the ether.

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Physics. — H. A. Lorentz. "*The fundamental equations for electromagnetic phenomena in ponderable bodies, deduced from the theory of electrons.*"

§ 1. In framing a theory that seeks to explain all electromagnetic phenomena, in so far as they do not take place in free aether, by means of small charged particles, electrons, we have to start from two kinds of equations, one relating to the changes of state in the aether, the other determining the forces exerted by this medium on the electrons. To these formulae we have to add properly chosen assumptions concerning the electrons existing in dielectrics, conductors and magnetizable substances, and the forces with which the ponderable particles act on the electrons in these several cases.

In former applications of the theory I have restricted myself to

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[1]) C. H. Wind. ll. cc.

the problem of the propagation of light in transparent substances, moving with a constant velocity. I shall now treat a more general case. I shall transform the original equations into a set of formulae, which, instead of quantities belonging to the individual electrons, contain only such as relate to the state of visible parts of the body and are therefore accessible to our observations. These formulae will hold for bodies of very different kinds, moving in any way we like.

The greater part of the results have already been established by POINCARÉ in the second edition of his *Electricité et Optique*. The mode of treatment is however rather different.

§ 2. With some exceptions, I shall use in the fundamental equations the same notation and the same units as on former occasions. The aether will again be supposed to remain at rest and to penetrate the charged particles; the equations of the electromagnetic field are therefore to be applied to the interior of the electrons, as well as to the spaces between them. We shall consider a distribution of the charges with a finite volume-density, whose value is a continuous function of the coordinates. If we speak of "electrons", we think of the charges as confined to certain small spaces, wholly separated from one another; however, in writing down our first equations, we may as well imagine a charge distributed over space in any arbitrary way.

We shall conceive the charges as being carried by "matter", though we might, if we chose, leave the latter out of consideration. We should then speak of the forces acting, not on charged matter, but on the charges themselves.

Let us call

ϱ the density of the charge,
$\mathfrak{v}$ the velocity of the charged matter,
$\mathfrak{d}$ the dielectric displacement, [1]
$\mathfrak{s}$ the current,
$\mathfrak{h}$ the magnetic force,
V the velocity of light.

Then we shall have

$$Div\, \mathfrak{d} = \varrho, \quad \ldots \ldots \ldots \ldots \quad (I)$$

$$\frac{\partial \varrho}{\partial t} + Div\,(\varrho\, \mathfrak{v}) = 0\,, \quad \ldots \ldots \ldots \ldots \quad (II)$$

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[1] The dielectric displacement, the current and the magnetic force are here represented in small type, because we wish to keep in reserve large type for corresponding quantities which we shall have to introduce later on.

$$\mathfrak{s} = \dot{\mathfrak{d}} + \varrho\, \mathfrak{v}, \qquad (1)$$

$$Rot\, \mathfrak{h} = 4\, \pi\, \mathfrak{s}, \qquad (III)$$

$$-4\, \pi V^2\, Rot\, \mathfrak{d} = \dot{\mathfrak{h}}, \qquad (IV)$$

$$Div\, \mathfrak{h} = 0, \qquad (V)$$

and the electric force $\mathfrak{f}$, i. e. the force acting on the charged matter per unit charge, will be given by

$$\mathfrak{f} = 4\, \pi V^2\, \mathfrak{d} + [\mathfrak{v} . \mathfrak{h}] \qquad (VI)$$

§ 3. If it were possible, by means of our observations, to penetrate into the molecular structure of a ponderable body, containing an immense number of charged particles, we should perceive within and between these an electromagnetic field, changing very rapidly and in most cases very irregularly from one point to another. This is the field to which the equations (I)—(V) must be applied, but it is not the field our observations reveal to us. Indeed, all observed phenomena depend on the mean state of things in spaces containing a very large number of particles; the proper mathematical expressions for such phenomena will therefore not contain the quantities themselves appearing in the formulae (I)—(V) but only their mean values. Of course, the dimensions of the space for which these values are to be taken, though very large as compared with the mutual distance of neighbouring particles, must at the same time be very much smaller than the distance over which one must travel in the body in order to observe a perceptible change in its state. We may express this by saying that the dimensions must be *physically infinitely small.*

Let P be any point in the body and σ a physically infinitely small closed surface of which it is the centre. Then we shall define the mean value at the point P of a scalar or vectorial quantity A by the equation

$$\overline{\mathrm{A}} = \frac{1}{\mathrm{S}} \int \mathrm{A}\, d\,\tau, \qquad (2)$$

in which the integration has to be extended to all elements $d\tau$ of the space S, enclosed by σ. It is to be understood that, if we wish to calculate the mean value for different points P, P', the corresponding spaces S, S′ are taken equal, of the same form and in the same position relatively to P, P'. The result $\overline{\mathrm{A}}$ will depend on the coordinates of the point considered; however, the above mentioned rapid changes will have disappeared from it; it is only the slow changes from point to point, corresponding to the perceptible changes in the state of the body, that will have been preserved in the mean value.

It is easily seen that

$$\frac{\partial \bar{A}}{\partial x} = \overline{\frac{\partial A}{\partial x}}, \text{ etc.,} \qquad \frac{\partial \bar{A}}{\partial t} = \overline{\frac{\partial A}{\partial t}}.$$

Hence, if we take the mean values of every term in the equations (I)—(V) and (1), as we shall soon do, we may replace $\dot{\mathfrak{d}}$ and $\dot{\mathfrak{h}}$ by $\overline{\dot{\mathfrak{d}}}$ and $\overline{\dot{\mathfrak{h}}}$, $\overline{Div\, \mathfrak{d}}$ by $Div\, \bar{\mathfrak{d}}$, etc.

§ 4. Before proceeding further, it is necessary to enter into some details concerning the charged particles we must suppose to exist in ponderable bodies.

Each of these particles calls forth in the surrounding aether a field, determined by the amount, the distribution and the motion of its charges, and it may be shown that, if x, y, z are the coordinates relatively to an origin *O* taken somewhere within the particle, and if the integrations are extended to the space occupied by it, the field, at distances that are large as compared with the dimensions of the particle, is determined by the values of the expressions

$$\int \varrho\, d\tau, \qquad (3)$$

$$\int \varrho\, \mathrm{x}\, d\tau, \quad \int \varrho\, \mathrm{y}\, d\tau, \quad \int \varrho\, \mathrm{z}\, d\tau, \qquad (4)$$

$$\int \varrho\, \mathfrak{v}_x\, d\tau, \quad \int \varrho\, \mathfrak{v}_y\, d\tau, \quad \int \varrho\, \mathfrak{v}_z\, d\tau, \qquad (5)$$

$$\int \varrho\, \mathfrak{v}_x \mathrm{x}\, d\tau, \quad \int \varrho\, \mathfrak{v}_x \mathrm{y}\, d\tau, \quad \int \varrho\, \mathfrak{v}_x \mathrm{z}\, d\tau, \text{ etc.,} \qquad (6)$$

Now, we might conceive particles of such a nature that for each of them all these quantities had to be taken into consideration. For the sake of clearness, it will however be preferable to distinguish between different kinds of particles, the action of each of these kinds depending only on some of the integrals (3)—(6).

a. If the charge of a particle has the same algebraic sign in all its points, the actions corresponding to the integrals (3) and (5) will far surpass those that are due to (4) and (6); we may then leave out of consideration these latter integrals. Such particles, whose field is determined by their charge and their motion as a whole, may be called *conduction-electrons*. We shall imagine them to be crowded together at the surface of a charged conductor and to constitute by their motion the currents that may be generated in metallic wires.

b. In the second place, we shall consider particles having in one part of their volume or surface a positive and in another part an equal negative charge. In this case, for which a pair of equal and opposite electrons would be the most simple example, the surrounding field is due to (4) and (5). We shall say that a particle of this kind is *electrically polarized* and, denoting by $\mathfrak{r}$ the vector drawn from the origin towards the element of volume $d\tau$, we shall call the vector

$$\int \varrho\, \mathfrak{r}\, d\tau = \mathfrak{p} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (7)$$

the *electric moment* of the particle. In virtue of the supposition

$$\int \varrho\, d\tau = 0,$$

this vector is independent of the position of the origin of coordinates. From (7) we may infer immediately

$$\int \varrho\, \mathrm{x}\, d\tau = \mathfrak{p}_x, \text{ etc.} \quad , \quad \int \varrho\, \mathfrak{v}_x\, d\tau = \dot{\mathfrak{p}}_x, \text{ etc.}$$

In all dielectrics, and perhaps in conductors as well, we must admit the existence of particles that may be electrically polarized. We shall refer to their charges by the name of *polarization-electrons.*

c. Finally, let there be a class of particles whose field is solely due to the expressions (6), the integrals (3), (4), (5) being all 0. If we suppose the values of

$$\int \varrho\, \mathrm{x}^2\, d\tau, \quad \int \varrho\, \mathrm{x}\, \mathrm{y}\, d\tau, \quad \int \varrho\, \mathrm{x}\, \mathrm{z}\, d\tau, \text{ etc.}$$

not to vary in the course of time, we can express all the integrals (6) by means of the vector

$$\frac{1}{2} \int \varrho\, [\mathfrak{r} \cdot \mathfrak{v}]\, d\tau = \mathfrak{m}, \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (8)$$

i. e. of the vector whose components are

$$\mathfrak{m}_x = \frac{1}{2} \int \varrho\, (\mathrm{y}\, \mathfrak{v}_z - \mathrm{z}\, \mathfrak{v}_y)\, d\tau, \text{ etc.},$$

Indeed, we shall have

$$\int \varrho\, \mathfrak{v}_x\, \mathrm{x}\, d\tau = 0, \quad \int \varrho\, \mathfrak{v}_x\, \mathrm{y}\, d\tau = -\, \mathfrak{m}_z, \quad \int \varrho\, \mathfrak{v}_x\, \mathrm{z}\, d\tau = +\, \mathfrak{m}_y, \text{ etc.} \quad (9)$$

The field produced by a particle satisfying the above conditions may be shown to be identical to the field due to a small magnet whose moment is $\mathfrak{m}$. For this reason, we shall speak of a *magnetized particle* and we shall call $\mathfrak{m}$ its *magnetic moment.*

According to the view here adopted, this moment is caused by rotating or circulating motions of the charges within the particle, similar to AMPÈRE's molecular electric currents. If, for the product $e\mathfrak{v}$ of a charge e and its velocity, we introduce the name of "quantity of motion of the charge", the integral in (8) may be said to represent the moment about the origin O of the quantities of motion of all the charges present.

A very simple example is furnished by a spherical shell, rotating round a diameter, and enclosing an immovable, concentric sphere, the shell and the sphere having equal and opposite charges, uniformly distributed.

Whatever be the motion of the charges which call forth the moment $\mathfrak{m}$, we may properly apply to them the denomination of *magnetization-electrons*.

§ 5. In the determination of the mean values of the quantities in (I), (II) and (1), the following considerations and theorems will be found of use.

a. Consider a space containing an immense number of points Q, whose mutual distances are of the same order of magnitude as those between the particles of a ponderable body. Let N be the number of these points per unity of volume. If the density of the distribution gradually changes from point to point — in a similar way as may be the case with the observed density of a body — the value of N belonging to a point P is understood to be derived from the number of points Q lying within a physically infinitely small space of which P is the centre.

Draw equal and parallel vectors $QR = \mathfrak{r}$ from all the points Q, and consider a physically infinitely small plane $d\sigma$ whose normal, drawn towards one of its sides, is n. The question is to find the number of the vectors QR that are intersected by the plane, a number which we shall call positive if the ends of the vectors, and negative if their starting points lie on the side of $d\sigma$ indicated by n.

If N has the same value throughout the whole space, and if the points Q are *irregularly* distributed, like the molecules of a liquid or a gas, the number in question will be the same for all equal and parallel planes, whence it is easily found to be

$$N \mathfrak{r}_n \, d\sigma \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

The problem is somewhat less simple if the points Q have a regular geometric arrangement, such as those one considers in the theory of the structure of crystals. If, in this case, the length of the vectors QR is smaller than the mutual distance d of neighbouring points, it may come to pass that there are a certain number of intersections with one plane $d\sigma$ and none at all with another plane of the same direction. We shall meet this difficulty by irregularly undulating the element of surface, in such a way that the distances of its points from a plane $d\sigma$ are of the same order of magnitude as the distance δ, and that the direction of the normal is very near that of the normal n to this plane; so that the extent of the element and the normal to it may still be denoted by $d\sigma$ and n. It is clear that, if N is a constant, the number of intersections of the vectors QR with such an undulated element may again be said to depend only on its direction and magnitude, and that it may still be represented by the formula (10).

The same formula will hold in case the value of N should slowly change from point to point, provided we take for N the value belonging to the centre of gravity of the element.

b. Let us apply the above result to the elements $d\sigma$ of a closed surface σ. Let $\mathfrak{n}_1$ be the number of ends R, and $\mathfrak{n}_2$ the number of starting points Q lying within σ.

Supposing the normal n to be drawn in the outward direction, we may write for the difference of these numbers

$$\mathfrak{n}_1 - \mathfrak{n}_2 = -\int N \mathfrak{r}_n \, d\sigma \, , \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

an expression, which of course can only be different from 0, if N changes from point to point.

c. Leaving the system of points, we pass to a set of innumerable equal particles, distributed over the space considered. Let q be a scalar quantity, whose values in the points $A_1, A_2, \ldots A_k$ of one of the particles are $q_1, q_2, \ldots q_k$, the position of these points and the values of q being the same in all particles, and these values being such that

$$q_1 + q_2 + \ldots + q_k = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

We proceed to determine the sum Σq of the values q, belonging to all the points A that lie within the above mentioned closed surface σ. Of course, the particles lying completely within the surface will contribute nothing to this sum. Yet, it may be different from 0, because a certain number of particles are cut in two by the surface, so that only a part of the values $q_1, q_2, \ldots q_k$ belonging to each of these are to be taken into account.

Assume in each particle an origin O (having the same position in each) and regard this as composed of k points $O_1, O_2, \ldots O_k$. Attach to these the values $-q_1, -q_2, \ldots -q_k$. Then, in virtue of (12), we may, without changing the sum Σq, include in it not only the points A, but likewise the points O. Now, if the vectors $O_1 A_1$, $O_2 A_2$, . . . $O_k A_k$ are denoted by $\mathfrak{r}_1, \mathfrak{r}_2, \ldots \mathfrak{r}_k$, the part of Σq due to the points O_1 and A_1 will be

$$-\int N q_1 \mathfrak{r}_{1n}\, d\sigma,$$

as may easily be inferred from (11). There are similar expressions for the parts of the sum corresponding to O_2 and A_2, O_3 and A_3, etc. Hence, if we introduce for a single particle the vector

$$\mathfrak{q} = \Sigma q \mathfrak{r} \,. \qquad (13)$$

and if we put

$$N \mathfrak{q} = \mathfrak{Q}, \qquad (14)$$

the final result will be

$$-\int \mathfrak{Q}_n\, d\sigma \qquad (15)$$

In this formula, the vector $\mathfrak{Q}$ is to be considered as a function of the coordinates because the number N may gradually change from one point to another (this §, a) and the vector $\mathfrak{q}$ may vary in a similar way. If now the surface σ is taken physically infinitely small, though of so large dimensions that it may be divided into elements, each of which is large in comparison with molecular dimensions, the expression (15) may, by a known theorem, be replaced by

$$-\, Div\, \mathfrak{Q} \,.\, S, \qquad (16)$$

S being the space within the surface σ.

d. It has been assumed till now that the quantity q occurs only in a limited number of points within each particle. By indefinitely increasing this number k, we obtain the case of a quantity q continuously distributed. We shall then write $q d\tau$ instead of q, and replace the sums by integrals. The condition (12) becomes

$$\int q\, d\tau = 0,$$

which we shall suppose to be fulfilled for each separate particle, the vector $\mathfrak{q}$ is now to be defined by the equation

$$\mathfrak{q} = \int q \mathfrak{r}\, d\tau, \qquad (17)$$

and the sum Σq, whose value we have calculated, becomes $\int q\, d\tau$, taken for the space enclosed bij σ. If we still understand by $\mathfrak{Q}$ the vector given by (14), the value of the integral for a physically infinitely small space will be

$$-\, Div\, \mathfrak{Q}.\, S.$$

Now, according to the definition of mean values (§ 3), division of this by S will give the mean of q; hence

$$\overline{q} = -\, Div\, \mathfrak{Q}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (18)$$

This result may even be extended to a state of the body, in which the distribution of the values of q is not the same in neighbouring particles. In this case we may again apply to each particle the formula (17), but $\mathfrak{Q}$ can no longer be calculated by (14). We have now to define this vector by

$$\mathfrak{Q} = \frac{1}{S} \Sigma\, \mathfrak{q}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (19)$$

the sum being taken for all the particles that lie wholly in the space S, without attending to those that are cut in two by the surface. We may express this in words by saying that $\mathfrak{Q}$ is the sum of all the vectors $\mathfrak{q}$, reckoned per unit of volume.

e. The case still remains that a quantity q, given for every point, has such values that the integral $(q) = \int q d\tau$, taken for a single particle, is not 0. If this quantity were constant throughout the space occupied by a particle, it would be unnecessary to take into account those which are cut in two by the surface σ and we should have

$$\overline{q} = N\, (q).$$

The most general case may be reduced in the following way to this case and to those that have already been disposed of before. If q is distributed in some arbitrary manner, we begin by calculating for a single particle the mean value $q_1 = \frac{1}{s}\, (q)$, s being the volume of the particle, and we put in every point $q - q_1 = q_2$. We shall then have

$$\overline{q} = \overline{q_1} + \overline{q_2}\, .$$

The problem is therefore reduced to the determination of two mean values, one of which may be found by what has just been said, and the other by applying the formula (18).

§ 6. The mean value of each of the quantities ϱ and $\varrho\, \mathfrak{v}$ in the equations (I), (II) and (1) may be decomposed into three parts, belonging to the conduction-electrons, the polarization-electrons and the magnetization-electrons. In determining them, we shall suppose the ponderable matter to have a visible motion with velocity $\mathfrak{w}$, and we shall write $\mathfrak{v}$ for the velocity the charged matter may have in addition to this. We have therefore to replace $\mathfrak{v}$ by $\mathfrak{w} + \mathfrak{v}$, and to determine separately $\overline{\varrho\, \mathfrak{w}}$ and $\overline{\varrho\, \mathfrak{v}}$.

a. Conduction-electrons. The mean value of ϱ, in so far as it depends on these, may be called the (*measurable*) *density of electric charge;* we shall denote it by ϱ_1.

The mean value $\mathfrak{E}$ of $\varrho\,\mathfrak{w}$ may be represented by

$$\mathfrak{E} = \varrho_1\,\mathfrak{w}.$$

This is the *convection-current,* and the vector

$$\mathfrak{J} = \overline{\varrho\mathfrak{v}}\,,$$

taken for the conduction-electrons, may fitly be called the *conduction-current.*

b. Polarization-electrons. Let the body contain innumerable particles electrically polarized, each having an electric moment $\mathfrak{p}$. The vector defined by the equation

$$\mathfrak{P} = \frac{1}{S}\,\Sigma\,\mathfrak{p}\,, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (20)$$

where the sign Σ is to be understood in the same sense as in the formula (19), is the *electric moment for unit volume* or the *electric polarization* of the body. Replacing q by ϱ in the formulae of § 5, *d*, and taking into account (7); we find for the part of $\overline{\varrho}$ that is due to the polarization-electrons,

$$\varrho_2 = -\,Div\,\mathfrak{P}.$$

We may next remark that the visible velocity $\mathfrak{w}$ is practically the same in all points of a particle. Since, for the space occupied by it,

$$\int \varrho\, d\,\tau = 0,$$

we have likewise

$$\int \varrho\,\mathfrak{w}_x\,d\,\tau = \int \varrho\,\mathfrak{w}_y\,d\,\tau = \int \varrho\,\mathfrak{w}_z\,d\tau = 0,$$

so that the values of $\overline{\varrho\,\mathfrak{w}_x}$, $\overline{\varrho\,\mathfrak{w}_y}$, $\overline{\varrho\,\mathfrak{w}_z}$ may be found by means of (18). The result is

$$\overline{\varrho\,\mathfrak{w}_x} = -\,Div\,(\mathfrak{w}_x\,\mathfrak{P}),\ \text{etc.} \quad . \quad . \quad . \quad . \quad . \quad (21)$$

We have finally to determine $\overline{\varrho\,\mathfrak{v}}$. Now, the quantities $\varrho\mathfrak{v}_x$, $\varrho\mathfrak{v}_y$, $\varrho\mathfrak{v}_z$ are of the kind considered at the end of § 5, *e*. However, there are cases, especially if the velocities $\mathfrak{v}_x$, $\mathfrak{v}_y$, $\mathfrak{v}_z$ and the dimensions of the particles are sufficiently small, in which the parts of $\overline{\varrho\mathfrak{v}_x}$, $\overline{\varrho\mathfrak{v}_y}$, $\overline{\varrho\mathfrak{v}_z}$ corresponding to $\overline{q_2}$ of § 5, *e*, may be neglected. Confining ourselves to such cases, we shall determine $\overline{\varrho\mathfrak{v}}$ without taking into consideration the particles intersected by the surface σ.

For a single particle we may write

$$\int \varrho\,\mathfrak{v}\,d\tau = \frac{d\mathfrak{p}}{dt},$$

and for a physically infinitely small space, partaking of the visible motion

$$\int \varrho\,\mathfrak{v}\,d\tau = \frac{d}{dt}\,\Sigma\,\mathfrak{p}.$$

On account of (20) this is equal to

$$\frac{d}{dt}(S\,\mathfrak{P}),$$

so that

$$\overline{\varrho\,\mathfrak{v}} = \frac{1}{S}\int \varrho\,\mathfrak{v}\,d\tau = \frac{1}{S}\,\frac{d}{dt}(S\,\mathfrak{P}).$$

In performing the differentiation we must attend to the change of $\mathfrak{P}$ in a point that moves with the velocity $\mathfrak{w}$. If $\dot{\mathfrak{P}}$ relates to a fixed point of space, we have

$$\frac{d\mathfrak{P}}{dt} = \dot{\mathfrak{P}} + \mathfrak{w}_x\frac{\partial\mathfrak{P}}{\partial x} + \mathfrak{w}_y\frac{\partial\mathfrak{P}}{\partial y} + \mathfrak{w}_z\frac{\partial\mathfrak{P}}{\partial z},$$

and, since

$$\frac{dS}{dt} = S\,.\,Div\,\mathfrak{w}\,,$$

$$\varrho\mathfrak{v} = \dot{\mathfrak{P}} + \mathfrak{w}_x\frac{\partial\mathfrak{P}}{\partial x} + \mathfrak{w}_y\frac{\partial\mathfrak{P}}{\partial y} + \mathfrak{w}_z\frac{\partial\mathfrak{P}}{\partial z} + \mathfrak{P}\,Div\,\mathfrak{w}.$$

Combining this with (21), we get for the mean value of the current corresponding to the motion of the polarization-electrons

$$\dot{\mathfrak{P}} + Rot\,[\,\mathfrak{P}\,.\,\mathfrak{w}].$$

c. Magnetization-electrons. If the body contains magnetized particles (§ 4, *c*), we have nothing to add to $\overline{\varrho}$ and $\overline{\varrho\mathfrak{w}}$. There will however be a new part of $\overline{\varrho\mathfrak{v}}$. We can calculate it by applying (18), because the quantities (5) vanish for every particle.

Let us first replace, in the formulae of § 5 *d*, q by $\varrho\mathfrak{v}_x$. We then find

$$\mathfrak{q}_x = 0, \qquad \mathfrak{q}_y = -\,\mathfrak{m}_z, \qquad \mathfrak{q}_z = +\,\mathfrak{m}_y,$$

and, if we denote by $\mathfrak{M}$ the *magnetic moment for unit volume* or the *magnetization*, a vector that is to be defined in a similar way as $\mathfrak{P}$,

$$\mathfrak{Q}_x = 0, \qquad \mathfrak{Q}_y = -\,\mathfrak{M}_z, \qquad \mathfrak{Q}_z = +\,\mathfrak{M}_y.$$

Finally, by (18),

$$\overline{\varrho\mathfrak{v}_x} = \frac{\partial\mathfrak{M}_z}{\partial y} - \frac{\partial\mathfrak{M}_y}{\partial z},$$

with similar expressions for $\varrho\mathfrak{v}_y$ and $\varrho\mathfrak{v}_z$.

The mean value of the current, in so far as it is due to the magnetization-electrons, is therefore

$$Rot\ \mathfrak{M}.$$

It may be called the *current equivalent to the magnetization.*

§ 7. It remains to take together the different parts of the second member of (1). Putting

$$\mathfrak{D} = \bar{\mathfrak{d}} + \mathfrak{P}, \quad \dots \dots \dots \quad (22)$$

$$\mathfrak{B} = \dot{\mathfrak{D}}, \quad \dots \dots \dots \quad (23)$$

and

$$\mathfrak{R} = Rot\ [\mathfrak{P}\,.\,\mathfrak{w}], \quad \dots \dots \dots \quad (24)$$

we have

$$\bar{\mathfrak{s}} = \mathfrak{B} + \mathfrak{J} + \mathfrak{C} + \mathfrak{R} + Rot\ \mathfrak{M}.$$

Now, we might understand by the *current in the ponderable body* the whole of this vector. Conformly to general usage we shall however exclude from it the last term. We therefore define the current as the vector

$$\mathfrak{S} = \mathfrak{B} + \mathfrak{J} + \mathfrak{C} + \mathfrak{R}, \quad \dots \dots \dots \quad (25)$$

so that

$$\bar{\mathfrak{s}} = \mathfrak{S} + Rot\ \mathfrak{M} \quad \dots \dots \dots \quad (26)$$

We may call $\mathfrak{D}$ the *dielectric displacement in the ponderable body,* and $\mathfrak{B}$ the *displacement-current.* As to the total current $\mathfrak{S}$, the formula (25) shows that it is composed of the displacement-current, the conduction-current $\mathfrak{J}$, the convection-current $\mathfrak{C}$ and the fourth vector $\mathfrak{R}$, for which POINCARÉ has proposed the name of *Röntgen-current,* because its electromagnetic effects have been observed in a well-known experiment of RÖNTGEN.

§ 8. We shall now write down the equations that arise from (I)—(V) and (1) if every term is replaced by its mean value. In order to obtain these formulae in a usual form, we shall put

$$\bar{\mathfrak{h}} = \mathfrak{B}, \quad \dots \dots \dots \quad (27)$$

$$\bar{\mathfrak{h}} - 4\pi\,\mathfrak{M} = \mathfrak{H}, \quad \dots \dots \dots \quad (28)$$

$$4\pi V^2\,\bar{\mathfrak{d}} = \mathfrak{E}, \quad \dots \dots \dots \quad (29)$$

these quantities being the *magnetic induction,* the *magnetic force in the ponderable body* and the *electric force in the body.*

Beginning with the equation (I), and writing ϱ instead of ϱ_1 for the (measured) density of electric charge, we find

$$Div\ \bar{\mathfrak{d}} = \varrho - Div\ \mathfrak{P},$$

whence

$$Div\ \mathfrak{D} = \varrho \quad \dots \dots \dots \quad (I')$$

We may further deduce from (1), taking into account (I) and (II),

$$Div\,\mathfrak{s} = 0,$$

and consequently

$$Div\,\overline{\mathfrak{s}} = 0.$$

Now the expression $Rot\,\mathfrak{M}$ we have found for the current that is equivalent to the magnetization, shows immediately that the distribution of this current, taken by itself, is solenoïdal. We conclude from this that

$$Div\,\mathfrak{S} = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (\text{II}')$$

From (III) we may deduce, if we introduce the value (26),

$$Rot\,\mathfrak{B} = 4\,\pi\,\mathfrak{S} + 4\,\pi\,Rot\,\mathfrak{M},$$

or, taking into account the relation

$$\mathfrak{B} = \mathfrak{H} + 4\,\pi\,\mathfrak{M}$$

which results from (27) and (28),

$$Rot\,\mathfrak{H} = 4\,\pi\,\mathfrak{S} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (\text{III}')$$

Finally we find by (IV)

$$Rot\,\mathfrak{E} = -\,\dot{\mathfrak{B}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (\text{IV}')$$

and by (V)

$$Div\,\mathfrak{B} = 0. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (\text{V}')$$

We have thus been led back to the equations of the electromagnetic field in a form that has long been known. In this form we may use them without even thinking of the individual electrons. As soon however as we seek to penetrate into the mecanism producing the phenomena, we must keep in mind the definitions that have been given of the different quantities appearing in the equations and the manner in which they are connected with the distribution and the motion of the elementary electric charges. The formulae (27) and (28) e. g. show the precise meaning that is to be attached in the theory of electrons to the terms "magnetic force" and "magnetic induction".

The equations (I')—(V') may be applied to all bodies indifferently. It is otherwise with the formulae expressing the relation between $\mathfrak{S}$ (or $\mathfrak{D}$) and $\mathfrak{E}$, and that between $\mathfrak{B}$ (or $\mathfrak{M}$) and $\mathfrak{H}$ [1]; the form of these depends entirely on the particular properties of the bodies considered. I shall not here discuss these more special formulae; in order to deduce them from the theory of electrons it is necessary to consider the forces acting on the electrons in a conductor, the "molecular motion" of these particles and the circumstances which determine the electric and magnetic moments of a single molecule or atom.

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[1] See Voigt, Electronenhypothese und Theorie des Magnetismus. Nachr. d. Ges. d. Wiss. zu Göttingen, 1901, Heft. 3.

Astronomy. — *"Preliminary investigation of the rate of the standard clock of the observatory at Leyden* HOHWÜ *N°.* 17 *after it was mounted in the niche of the great pier."* By Dr. E. F. VAN DE SANDE BAKHUYZEN.

1. In a preceding paper on the clock HOHWÜ 17 I communicated the investigations I had made on an inequality of a yearly period noted in its rate which does not depend on the actual temperature.

Besides the periods 1861—1874 and 1877—1898 I discussed also the period 1899—1902 when the clock had been mounted in the hall of the observatory in a niche cut out for this purpose from the great pier. From the mean daily rates during periods of about a month each, I derived formulae for the rate in two different ways, and this research clearly brought to light that during this period the rate of the clock had become considerably more regular than before and now satisfies high demands.

Since that time the same formulae have been compared with the daily rates observed during much shorter periods and an investigation has been undertaken about the barometer coefficient, for which purpose the monthly rates were less appropriate.

The latter calculations have so clearly shown the excellence of the clock also with regard to its rate during periods of a few days, that it seemed to be of interest briefly to give here the results to which they led.

2. The results we obtained from the previous investigations may be resumed thus.

Under all the conditions in which the clock HOHWÜ 17 has been placed, its rate, after correction for the influence of the temperature, has always shown a residual yearly inequality. As the former influence had been derived from the yearly variation of the temperature, the residual inequality must necessarily show a difference of phase of three months with respect to the temperature.

If the influence of the temperature had been derived and accounted for in the form $c_1 (t—t_0) + c_2 (t—t_0)^2$, whether we had found for c_2 a small negligible value, as in the period 1862—1874 or an obviously real quantity as in the period 1899—1902,, the residual inequality could with sufficient accuracy be expressed by a simple sinusoid. If on the contrary only a linear influence of the temperature had been accounted for, while an investigation of c_2 showed it to have an appreciable value, the residual inequality showed a half-yearly term besides. This could be expected; for as long as only the yearly variation of the temperature is concerned, a quadratic influence of the latter and a half-yearly inequality are completely equivalent.

3. For the rate of the clock during the period 1899—1902 I derived in the first place the formula:

$$D.\ R. = -0^s.169 + 0^s.0140\ (h - 760).$$
$$- 0^s.0253\ (t - 10^\circ) + 0^s.00074\ (t - 10^\circ)^2.$$
$$+ 0^s.0465\ \cos 2\pi \frac{T - May\ 3}{365} \quad \ldots\ldots\ldots \quad I)$$

secondly the formula:

$$D.\ R. = -0^s.157 + 0^s.0140\ (h - 760).$$
$$- 0^s.0220\ (t - 10^\circ) + Suppl.\ inequal \quad \ldots\ldots \quad II)$$

The supplementary inequality in the second formula was represented by a curve. Yet it can as well be represented by a yearly and a half-yearly term. We then find:

$$Suppl.\ Inequ. = +0^s.0471\ \cos 2\pi \frac{T - Apr.\ 29}{365}$$
$$- 0^s.0198\ \cos 4\pi \frac{T - Apr.\ 16}{365} \quad \ldots \quad II')$$

From the term depending on the square of the temperature found by the first method of calculation and from the yearly variation of the temperature in the clock-case, which is approximately represented by

$$t = +11^\circ.6 + 6^\circ.54\ \sin 2\pi \frac{T - May\ 4}{365}\ ^{1)}$$

we derive for the half-yearly term

$$- 0^s.0158\ \cos 4\pi \frac{T - May\ 4}{365}$$

which is in sufficient agreement.

The two formulae must however give different results, as soon as the accidental variations of the temperature become of importance, and therefore it was of interest to compare the rates during short periods with either.

4. Hence two comparisons were made for the three years 1899 May 3—1902 May 3. ²)

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¹) For the next term we find: $+0^\circ.55\ \sin 4\pi \frac{T - June\ 9}{365}$.

²) In this and the following calculations the supplementary inequality for formula II was read from the curve.

Within that period I could dispose of 182 time-determinations at average intervals of 6 days, giving 181 values for the daily rate. We can assume as mean error of the result of a time-determination, largely accounting for systematic errors such as variations of the personal errors of the observers, $\pm 0^{s}.04$.

I do not give here in full the results of the comparison of these 181 observed rates with the two formulae and only lay down the mean values found in both cases for a difference: observation—computation.

I found:

Formula I M. Diff. $= \pm 0^{s}.0333$
" II $\pm 0\ .0344$

Hence this mean difference is nearly the same for the two formulae; indeed, if the three years are kept apart, it is found to be a little greater for formula I in two of the three years.

We may therefore say that the two are in equally good agreement with the observations and for the investigation of the barometer coefficient it was sufficient to use either.

I chose formula II (linear influence of the temperature) and I proceeded in the following way. The rates reduced with that formula to 760 m.m. and 10° and freed from the supplementary inequality were divided into five groups according to the barometric pressure and for each group the mean of those reduced rates was calculated. The results are laid down in the following table, where the first column gives the number of rates from which each mean has been derived.

Number.	Barom.	Reduced. D. R.	O.—C.
17	752.8	$-0^{s}.174$	$-0^{s}.002$
31	757.6	162	+ 02
68	762.6	154	+ 01
44	767.4	145	+ 02
21	772.2	141	— 02

From these results I derived as correction for the barometer coefficient:

$$\Delta\, b = +\, 0^{s}.0017$$

while I found for the daily rate for 760 mm. — $0^s.160$. With these values we obtain a very good agreement with the observations as appears from the differences obs.—comp. contained in the last column of the foregoing table. Hence it appears that the value for the barometer coefficient $b = + 0^s.0157$ is determined with great precision [1]).

For the constant term of the formula we find from all the rates $- 0^s.161$, while, if we put $b = + 0^s.0157$ also in formula I, the constant term here becomes $- 0^s.173$.

5. With the formulae thus modified:

$$D.\ R. = - 0^s.173 + 0^s.0157\,(h-760).$$
$$- 0^s.0253\,(t-10^\circ) + 0^s.00074\,(t-10^\circ)^2.$$
$$+ \textit{Supplementary inequality} \;.\;.\;.\;.\;.\;. \quad (\mathrm{I}a).$$
$$D.\ R. = - 0^s.161 + 0^s.0157\,(h-760).$$
$$- 0^s.0220\,(t-10^\circ) + \textit{Supplem. inequal.} \;.\;.\;, \quad (\mathrm{II}a).$$

we have again compared all the observed rates and this time the comparison has been extended to 1902 Sept. 20 i. e. till almost five months after the period from which the formulae were derived. Besides the observations have been compared with a third calculation. This we obtained by applying the formula II*a* so that we did not use the actual mean temperature but that of five days earlier. It is obvious that in doing so also the value of the supplementary inequality must be altered. An assumed lagging behind of the influence of the temperature of five days is equal, so far as the general variation of the temperature (as found above) is concerned, to 0.27 × the yearly supplementary term. Hence the latter had to be diminished by this part of its amount. The formula thus modified I call II*b*.

The results of these three comparisons are given in full in the following table. The first column gives the dates of the time determinations, the next column gives the mean temperature for the period between the date of one line above and of that on the same line, while the third, fourth and fifth columns give the differences between the observed rates for those periods and the computations I*a*, II*a* and II*b* respectively. These differences are expressed in thousandth parts of seconds.

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[1]) According to the investigations of Mr. WEEDER a value little different from this follows for the period 1882—1898.

	Temp.	Obs. — I*a*	Obs. — II*a*	Obs. — II*b*		Temp.	Obs. — I*a*	Obs. — II*a*	Obs. — II*b*
1899					1899				
May 3					Nov. 12	+12.6	— 12	— 14	— 28
» 12	+10.5	— 11	— 18	— 10	» 20	11.0	— 3	— 8	+ 3
» 17	12.0	+ 33	+ 23	+ 9	» 28	10.8	— 42	— 51	— 63
» 30	12.7	0	— 12	— 1	Dec. 7	10.4	— 9	— 22	— 19
June 3	13.9	— 17	— 32	— 40	» 13	6.8	+ 83	+ 83	+140
» 8	14.8	+ 43	+ 33	— 3	» 16	3.7	+ 76	+103	+170
» 14	14.8	+ 27	+ 14	+ 23	» 19	3.0	— 19	+ 16	+ 52
» 22	15.4	+ 36	+ 22	+ 12	» 23	2.3	— 24	+ 21	+ 31
» 27	16.5	+ 20	+ 11	+ 5	» 31	3.1	— 52	— 19	— 38
July 7	16.5	+ 7	— 3	+ 7	1900				
» 11	16.4	— 17	— 29	— 28	Jan. 8	5.3	— 32	— 26	— 62
» 14	18.1	+ 57	+ 57	+ 13	» 20	5.4	— 44	— 39	— 36
» 17	18.6	+ 56	+ 60	+ 29	» 25	6.0	— 36	— 36	— 62
» 25	19.6	+ 78	+ 91	+ 71	Febr. 4	6.1	— 12	— 9	— 2
» 31	19.6	+ 39	+ 50	+ 60	» 8	4.9	— 22	— 6	+ 8
Aug. 3	19.4	+ 30	+ 38	+ 45	» 20	4.3	— 28	— 2	+ 3
» 9	19.6	+ 66	+ 76	+ 71	March 2	6.9	— 4	0	— 28
» 14	19.1	+ 21	+ 28	+ 44	» 9	6.3	— 18	— 7	+ 23
» 21	18.7	+ 26	+ 30	+ 34	» 16	6.7	— 40	— 30	— 34
» 26	17.7	— 3	— 4	+ 12	» 20	6.8	— 30	— 20	— 10
Sept. 3	18.3	+ 17	+ 25	+ 11	» 26	6.6	— 25	— 12	— 1
» 8	18.3	+ 9	+ 22	+ 18	» 30	6.1	— 45	— 26	— 7
» 13	17.7	+ 34	+ 44	+ 50	April 2	6.0	— 52	— 32	— 18
» 21	16.3	— 14	— 9	+ 7	» 4	6.1	— 38	— 19	— 11
Oct. 5	14.4	— 35	— 32	— 24	» 12	7.2	— 12	— 1	— 11
» 9	13.1	+ 3	+ 7	+ 15	» 18	9.0	— 29	— 29	— 49
» 16	11.9	— 9	— 5	+ 8	» 21	9.9	+ 37	+ 34	+ 25
» 19	11.1	— 42	— 37	— 30	» 24	10.7	+ 17	+ 9	— 11
» 24	10.9	— 19	— 14	— 17	» 28	10.1	— 16	— 20	— 1
» 31	11.4	— 15	— 12	— 35	May 1	9.8	+ 14	+ 10	+ 35
Nov. 5	12.3	+ 4	+ 6	— 21	» 4	10.4	— 71	— 77	— 83

	Temp.	Obs. — I*a*	Obs. — II*a*	Obs. — II*b*
1900				
May 10	+12.1	— 12	— 22	— 43
» 14	11.7	— 16	— 26	— 3
» 23	11.2	— 19	— 30	— 12
» 26	12.5	— 11	— 22	— 46
June 2	13.0	— 27	— 40	— 43
» 9	14.9	— 9	— 19	— 44
» 12	16.3	— 26	— 31	— 48
» 18	17.3	+ 33	+ 33	+ 15
» 23	17.1	— 29	— 33	— 21
» 28	16.6	— 11	— 20	+ 2
July 2	16.2	— 46	— 58	— 45
» 10	16.3	— 31	— 43	— 36
» 13	16.4	— 29	— 40	— 40
» 17	18.1	+ 18	+ 18	— 24
» 21	19.8	+ 31	+ 46	— 4
» 25	20.8	+ 41	+ 68	+ 39
» 31	20.7	+ 11	+ 35	+ 36
Aug. 7	19.0	— 39	— 35	— 4
» 11	17.5	— 43	— 51	— 21
» 14	17.1	— 63	— 74	— 61
» 17	17.6	— 46	— 51	— 60
» 23	18.8	+ 4	+ 12	— 25
» 28	18.4	— 28	— 22	— 11
» 31	17.4	— 34	— 34	— 8
Sept. 4	16.9	— 25	— 27	— 20
» 12	16.4	— 48	— 48	— 44
» 16	16.2	— 32	— 29	— 35
» 19	16.5	+ 3	+ 11	— 1
» 29	16.4	— 31	— 20	— 27
Oct. 6	15.3	— 24	— 14	— 6
» 16	14.6	— 12	— 3	— 3
1900				
Oct. 19	+12.6	— 7	— 3	+ 34
» 29	11.6	— 9	— 6	— 3
Nov. 3	11.8	— 50	— 48	— 67
» 7	11.3	— 13	— 13	— 14
» 16	10.3	— 1	— 2	+ 6
» 23	9.2	+ 22	+ 20	+ 22
» 27	8.8	— 12	— 14	— 20
Dec. 7	8.3	+ 21	+ 17	+ 14
» 10	8.9	— 62	— 75	—106
» 15	9.3	+ 23	+ 6	— 14
» 19	9.5	+ 50	+ 29	+ 14
» 29	8.7	+ 55	+ 34	+ 42
1901				
Jan. 3	7.4	+ 69	+ 57	+ 64
» 6	5.2	+ 96	+103	+162
» 11	3.1	+ 59	+ 91	+146
» 14	3.0	— 32	+ 2	0
» 17	3.2	+ 27	+ 57	+ 50
» 23	4.7	+ 37	+ 51	+ 18
Febr. 1	6.8	+ 47	+ 43	+ 18
» 4	6.0	+ 26	+ 31	+ 49
» 11	5.1	+ 32	+ 46	+ 67
» 20	4.4	+ 15	+ 39	+ 55
March 5	5.4	+ 28	+ 44	+ 27
» 13	7.2	+ 4	+ 9	+ 14
» 21	7 2	— 10	— 3	+ 1
» 25	6 3	+ 1	+ 17	+ 50
Apr. 1	5.8	— 28	— 6	+ 13
» 4	7.3	— 5	+ 6	— 24
» 7	8.2	+ 12	+ 16	— 14
» 17	9.3	+ 3	+ 2	— 2

		Temp.	Obs. — I*a*	Obs. — II*a*	Obs. — II*b*
1901					
Apr.	20	+ 9.3	+ 21	+ 20	+ 35
»	23	10.5	+ 38	+ 32	+ 12
»	29	11.6	+ 49	+ 41	+ 24
May	3	11.7	+ 13	+ 4	+ 18
»	8	11.6	— 5	— 15	— 3
»	11	11.5	+ 1	— 8	+ 8
»	14	11.7	— 1	— 11	- 3
»	20	11.9	— 8	— 19	— 12
June	2	14.0	+ 15	+ 5	— 15
»	7	16.4	+ 17	+ 14	0
»	18	15.6	— 30	— 39	— 10
»	25	15.3	— 28	— 42	— 43
July	3	16.8	— 16	— 24	— 38
»	10	17.7	— 19	— 22	— 30
»	15	19.1	— 6	+ 3	— 24
»	20	19.8	— 2	+ 14	+ 2
»	31	20.2	+ 1	+ 21	+ 23
Aug.	9	19.5	— 28	— 18	— 11
»	12	19.6	+ 14	+ 25	+ 16
»	16	19.4	— 4	+ 7	+ 3
»	22	18.9	— 37	— 30	— 22
»	27	18.5	— 25	— 18	— 13
Sept.	5	16.8	— 24	— 27	— 7
»	16	15.8	— 22	— 23	— 26
»	20	15.5	+ 9	+ 11	+ 16
»	26	16.2	+ 20	+ 29	+ 7
Oct.	1	16.7	— 5	+ 9	— 8
»	11	15.5	+ 6	+ 18	+ 30
»	16	13.1	+ 7	+ 12	+ 32
»	22	12.9	+ 2	+ 6	— 4
»	26	12.6	— 16	— 13	— 16
1901					
Nov.	1	+11.9	+ 6	+ 8	+ 11
″	4	10.6	+ 26	+ 29	+ 48
»	15	9.9	+ 15	+ 19	+ 11
»	22	9.6	+ 37	+ 35	+ 37
»	26	9.0	+ 53	+ 50	+ 51
Dec.	6	8.4	— 3	— 7	— 10
»	16	7.8	+ 9	+ 1	+ 7
»	25	5.5	+ 1	+ 7	+ 25
1902					
Jan.	5	6.6	— 6	— 11	— 43
»	11	8.6	+ 20	0	— 19
»	18	8.1	— 24	— 40	— 30
»	28	7.9	+ 18	+ 5	+ 5
Febr.	1	6.4	+ 36	+ 37	+ 70
»	7	4.9	— 3	+ 13	+ 45
»	12	4.6	— 44	— 24	— 15
»	15	4.2	— 36	— 11	0
»	20	3.2	— 68	— 29	— 2
»	24	4.0	— 7	+ 23	+ 12
March	4	5.6	— 14	+ 1	— 25
»	10	7.0	— 15	— 9	— 23
»	14	7.1	+ 9	+ 16	+ 25
»	19	7.7	+ 12	+ 15	+ 12
Apr.	3	8.3	+ 12	+ 14	+ 21
»	8	8.2	— 3	+ 1	+ 11
»	12	8.0	— 14	— 7	+ 8
»	18	9.3	+ 32	+ 31	+ 16
»	25	11.3	+ 41	+ 34	+ 10
»	28	12.1	+ 37	+ 29	+ 26
May	3	11.0	— 6	— 14	+ 22
»	9	10.7	+ 2	— 7	+ 12

	Temp.	Obs. — Ia	Obs. — IIa	Obs. — IIb		Temp.	Obs. — Ia	Obs. — IIa	Obs. — IIb
1902					1902				
May 24	+10.4	— 10	— 18	— 9	July 31	+17.1	— 52	— 63	— 55
» 31	12.7	+ 26	+ 12	— 13	Aug. 5	16.8	— 54	— 68	— 61
June 11	15.9	+ 37	+ 32	+ 16	» 11	16.9	— 40	— 53	— 56
» 17	14.6	— 34	— 48	— 19	» 15	16.0	— 52	— 70	— 50
» 23	15.1	— 13	— 29	— 34	» 20	16.5	— 14	— 28	— 38
» 28	16.8	+ 7	0	— 28	» 25	16.8	— 49	— 55	— 66
July 5	18.4	+ 14	+ 18	0	Sept. 3	17.1	— 16	— 19	— 36
» 12	17.9	— 20	— 21	— 7	» 8	17.8	— 25	— 18	— 31
» 15	17.4	— 31	— 38	— 21	» 14	16.7	— 19	— 16	— 3
» 23	17.7	— 26	— 32	— 47	» 20	15.2	— 27	— 28	— 7

From these differences we derive the following mean errors of a rate computed by means of the three formulae:

	Form. *Ia.*	Form. *IIa.*	Form. *IIb.*
1899 May—1900 April......	$\pm 0^{s}.0343$	$\pm 0^{s}.0345$	$\pm 0^{s}.0424$
1900 May—1901 April.... .	345	387	447
1901 May—1902 Sept	251	266	274
1899 May—1902 April......	± 0.0311	± 0.0327	± 0.0385
1899 May—1902 Sept......	± 0.0311	± 0.0332	± 0.0382

First let us compare the mean errors of the three formulae inter se and with the corresponding values formerly obtained for the formulae I and II with the uncorrected barometer coefficient.

Then it appears in the first place from the values for the period 1899 May—1902 April that the correction of the barometer coefficient has markedly improved the agreement with the observations. 1) Secondly it would appear that the quadratic formula now represents the observations a little better than the linear formula, and thirdly we find that the supposition of a lagging behind of the influence of the temperature markedly impairs the agreement.

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1) Each of the three years separately also leads to the same result.

A consideration of the differences obs.—II*a* and obs.—II*b* shows however, that the latter conclusion does not equally hold good for all parts of the year and that the agreement with formula II*b* is especially bad in the winter months. In order to investigate this more closely, I divided the observations into groups of two months and calculated for each group the mean value of the differences, first for each year separately, then after combining the corresponding groups of the different years. The latter values follow here.

	Form. II*a*.	Form. II*b*.
January, February	$\pm 0^s.0402$	$\pm 0^s.0549$
March, April	208	214
May, June	285	284
July, August	423	368
September, October	215	232
November, December	369	559

They lead to the singular result that during the four winter months formula II *b* agrees much less with the observations than II*a*, whereas in the middle of the summer the agreement with II*b* seems to be better, and in the other months both formulae may be said to agree equally well. In this respect the different years practically lead to the same conclusion and hence we cannot say that this has been brought on by entirely accidental causes. However this may be, we are not entitled yet to assume a lagging behind of the influence of the temperature.

Let us now consider separately the results for formula I*a*, which seems to represent the observations with the greatest precision (those for II*a* do not essentially differ from them). It will be seen immediately that during the last seventeen months the rate has been considerably more regular than during the first two years[1]; a smaller M.E. has been reached although the 5 last of these 17 months were not included for the derivation of the formula. Thus the feature observed before, i.e. the gradual improvement of the regularity of the rate after the mounting of the clock, shows itself once more. The mean result for the whole period (M. E. = $\pm 0^s.0311$) may already be regarded as very satisfactory, and the great regularity represented by a mean difference of $\pm 0^s.0251$ between a daily rate from a 6 days interval and a relatively simple formula gives us a high sense of the supe-

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[1] Already at the beginning we had left out the first 4 months after the remounting.

riority of Hohwü 17 in its present state. That this regularity markedly surpasses the one reached formerly is shown also by the results of an investigation of the years 1886—87, which are among those of the greatest regularity in the period 1877—1898. This investigation was made in a similar manner as the present one, the mean interval between the time determinations used was 5 days and the mean error found was ± $0^s.0365$.

6. We may also investigate the rates of a clock in such a manner that only the irregularities of a very short period are considered. A simple process for attaining this is to calculate the mean value of the difference between two consecutive reduced daily rates.

Applying this method to Hohwü 17 during the period under consideration [1]) I found:

Mean difference 1899 May—1902 Sept. ± $0^s.0313$.
" " 1901 May—1902 Sept. ± $0^s.0253$.

From these mean values considered in connection with the mean errors of the rates in 6-daily and in monthly intervals formerly found we can draw some, albeit rough, conclusions about the amount of the perturbations of longer and shorter periods.

The values found, as well those for the whole period as those derived for the last year only, are given in the following table. The columns *A* contain the values found directly, the columns *B* those diminished by the amount that can be ascribed to the errors of observation, assuming ± $0^s.04$ as the total mean error of a time-determination. M. E. β of a 6-daily rate stands for the total mean difference from the formula Ia, found above, M. E. α represents the error derived from the mean differences between two consecutive rates. The mean errors of the monthly rates differ a little from those of my previous paper as they now also refer to formula Ia.

	1899—1902.		1901—1902.	
	A.	B.	A.	B.
M. Diff. of two 6 d. r.	± $0^s.0313$	± $0^s.0267$	± $0^s.0253$	± $0^s.0193$
M. E. α of 6 d. r.		189		137
M. E. β of 6 d. r.	314	297	251	233
M. E. of monthl. r.	209	208	164	163

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[1]) The rates were reduced by means of formula IIa, but a reduction according to Ia would practically have led to the same result.

Although these calculations are inaccurate owing also to the fact that the intervals between the time determinations often differ rather much from 6 days, yet it is evident that the M. E. β are much larger than the M. E. α and hence that considerable perturbations of long period exist, as, indeed, a glance at the table of the obs.—comp. also shows. It would be possible to account tolerably well for the values found for the three different mean errors by assuming, quite arbitrarily of course, that there are two kinds of perturbations, one constant during 6 days and another constant during a month. We should then have to assign for the whole period an average value to both of $\pm 0^s.02$ and for 1901—1902 alone one of $\pm 0^s.015$.

There are not many clocks about which investigations have been published, which allow us directly to compare the regularity of their rates with that of HOHWÜ 17 and most of these embrace but a short period.

An investigation extended over 4 years about the standard-clock of the observatory at Leipzig DENCKER 12 has been published by Dr. R. SCHUMANN [1]). He uses 224 time determinations at mean intervals of $6^1/_2$ days and derives for the rate a formula containing a linear influence of the temperature and of the barometric pressure and besides a term varying with the time elapsed since a zero-epoch. As mean value of the difference obs.—comp. he finds $\pm 0^s.059$ and there is no evidence of a residual yearly inequality. I calculated also the mean value of a difference between two consecutive rates and found $\pm 0^s.055$.

In the latter respect we possess also data about the four normal clocks of the Geodetic Institute at Potsdam. An investigation by Mr. WANACH [2]), about the rates during last year gave the following mean differences between consecutive rates after correction for the barometric pressure, while the temperature was kept very nearly constant:

STRASSER 95	$\pm 0^s.054$
RIEFLER 20	± 0.062
DENCKER 27	± 0.047
DENCKER 28	± 0.049.

These values are considerably larger than that for HOHWÜ 17, but respecting the Potsdam clocks we must keep in view that DENCKER

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[1]) R. SCHUMANN. Ueber den Gang der Pendeluhr F. DENCKER XII. (Ber. Sächs. Gesellsch. d. Wiss. 1888).

[2]) Jahresbericht des Direktors des Königlichen Geodätischen Instituts für die Zeit von April 1901 bis April 1902, pg. 35.

27 and 28 had lately been cleaned, while STRASSER 95 during the period of observation had twice been replaced and meanwhile had been exposed to great differences of temperature. For DENCKER 12 at Leipzig also some perturbations from outside shortly before and during the period under consideration are noted.

7. For a clock which is used for astronomical fundamental determinations the regularity of the rate during the 24 hours of the day is of the very highest importance, but it is obvious that only long continued observations reduced with the greatest possible care can give us any information on this subject.

As yet I can only state that we may confidently expect HOHWÜ 17 not to be inferior in this respect to other clocks kept at constant temperature, seeing that, while the amplitude of the yearly variation of temperature has diminished comparatively little in its present place, the daily variation has almost entirely disappeared.

This will be seen from the following values of the difference between the temperature at 4 o'clock in the afternoon and the mean of the temperatures of the preceding and the following 8 hours in the morning. These differences taken for about 240 days have been combined in 6 two-monthly groups, and their means follow here:

	Temp. 4h—Temp. 20h
January, February	+ 0°.09
March, April	+ 0.13
May, June	+ 0.12
July, August	+ 0.20
September, October	+ 0.14
November, December	+ 0.08

The mean difference is greatest in summer, but even then very small, while no difference ever reaches to 0°.5.

(October 22, 1902).

KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN TE AMSTERDAM.

PROCEEDINGS OF THE MEETING

of Saturday October 25, 1902.

(Translated from: Verslag van de gewone vergadering der Wis- en Natuurkundige Afdeeling van Zaterdag 25 October 1902, Dl. XI).

CONTENTS.

The following papers were read:

Chemistry. — *"A representation in space of the regions in which the solid phases, which occur, are the components, when not forming compounds."* By Prof. H. W. Bakhuis Roozeboom.

(Communicated in the meeting of September 27, 1902).

In the course of my researches, I have often made use of special kinds of graphical representations to indicate the limits of the existence of single phases or complexes of phases. It was only after the year 1896, when it could be taken for granted that the general character of the equilibria between liquid and vapour in binary systems had become fully understood, that efforts could be made to construct a complete graphical representation of the conditions of equilibrium in which solid phases occur.

The simplest possible case is found when only the two components of the binary system occur as solid phases. For such a case, I have since 1896 arrived at the representation in space of which photographs are given in the accompanying figures. For the case that chemical compounds or mixed crystals occur as solid phases other figures have been constructed which, however, may be deduced in a simple manner from the present ones.

In this figure the length represents the temperature, the breadth the concentrations x of the mixtures which can exist as vapour or liquid, the component A being placed at the left and the component B at the right. The height represents the pressure. The figure does not represent any particular case, but is so constructed that the different details come out plainly and the dimensions are not too great.

We start from the equilibria between liquid and vapour, which researches on the critical constants of mixtures have proved to be capable of representation by a surface of two sheets, the upper part of which represents the liquids and the lower part the vapours. The coexisting conditions of these two must have equal values of p and t and are therefore, situated on a horizontal line which is parallel to the x-axis. The said surfaces meet at the left side in the vapour-pressure line $O_A C$ of the liquid A, at the right side in the vapour-pressure line $O_B D$ of the liquid B and in front in the critical curve CD.

The points in the space between the two surfaces indicate complexes of liquid and vapour. In the representation, this space is massive, like all other spaces which represent complexes of *two* phases.

The surface of two sheets for liquid + vapour is so constructed that A is the substance with the greatest vapour pressure. It has further been assumed that the liquids are miscible in all proportions and that no maxima or minima occur in the equilibrium pressure.

Descending continuously, the surface would reach the absolute zero if A or B or both did not solidify first.

The pure liquids A and B solidify in O_A and O_B; from there the vapour-pressure lines $O_A I$ and $O_B K$ of the solid substances run in the left and right vertical side-plane.

Considering now the liquid-mixtures with an increasing amount of B, solid A can only be deposited at temperatures lower than O_A. At each temperature there is a definite liquid and a definite vapour which coexist with the solid phase A at a definite pressure which is larger than the vapour-pressure of solid A alone, but the same for each of them. The three coexisting phases are represented by the lines O_AG, O_AF, O_AE respectively standing for solid, gas and liquid. They are situated together on a cylindrical surface, because for equal t, also p is equal. The part FO_AE is also a limitation of the surface of two sheets.

In the same manner we have for the equilibrium of solid B with liquid and vapour the three lines O_BH, O_BE, O_BF, for solid, liquid and gas respectively, again situated on a cylindrical surface, while the part EO_BF thereof forms below a second limitation of the surface of two sheets. This cylindrical surface first rises from O_B but afterwards falls again.

The surface of two sheets terminates, as far as the liquid-surface is concerned, finally in E, the gas-surface in F. This liquid and this vapour may exist in contact with solid A (point G) and also with solid B (point H). As the points G, F, E, H belong to the same values of p and t, they are situated on a horizontal line and represent the only possible complex of four phases.

To the gas-line O_AF a second gas-surface joins, representing the vapours capable of coexisting with solid A, when the quantity of B in the vapour increases; also to O_BF the gas-surface for the vapours in equilibrium with solid B with increasing amounts of A. From the melting points of the pure substances down to the temperature of the quadruple-point $GFEH$ these two gas-surfaces are not in contact with each other, but each of them singly is in contact with the gas-surface of the surface of two sheets.

Below that temperature they intersect each other immediately, forming the line FL which represents the vapours capable of coexisting with solid A + solid B. To this belong the lines GM for solid A and HN for solid B which are again situated on a cylindrical surface.

All complexes of the solid phase A and of the coexisting vapours are situated within the space formed by the gas-surface IO_AFL, the surface of the solid phase IO_AGM and the two cylindrical surfaces GO_AF and $MGFL$. All complexes of the solid phase B and the vapours which can exist in contact with it, are situated in the space bounded by the gas-surface KO_BFL, the surface of the solid phase KO_BHN and the cylindrical surfaces HO_BF and $NHFL$.

Both spaces extend to the absolute zero if no new phases are formed.

The three surfaces representing the equilibria of gas with liquid, with solid A and with solid B meet each other in the point F. In the same way, two other liquid-surfaces must join in the point E at which the liquid surface coming from higher temperatures ends, namely those which indicate the p, t, x values of the liquids which can coexist with solid A or solid B. The lower limits of these surfaces are the lines $O_A E$ and $O_B E$ which represent the equilibrium of solid and vapour. Setting out from these lines the vapour disappears when the pressure is increased. On account of the small changes which the composition of the liquid undergoes with an increase of pressure, the liquid-surfaces $O_A EPU$ and $O_B EPV$ will rise almost vertically. They terminate to the left and the right in the melting point lines $O_A V$ and $O_B V$ of the solid substances A and B, whilst they intersect each other in the line EP which indicates the liquids which at different p, t values can coexist with solid A and B. To this line belong the p, t lines GQ and HR for the solid phases, which again form a cylindrical surface with EP.

In this way we arrive for the complexes of solid A + liquid at the space included between the liquid-surface, the surface of the solid A, $O_A UQG$ and the cylindrical surfaces $GO_A E$ and $GEPQ$. A similar space includes, at the right, the complexes for solid B + liquid.

Finally, the region of the complexes of solid A + solid B is situated behind the cylindrical surface $GHRQ$ and above the cylindrical surface $NHGM$.

The spaces last described terminate in the figures at the back at an arbitrary temperature and above at an arbitrary pressure. One must suppose that, in reality they continue their course.

The remaining space outside the massive parts constitutes the regions of homogeneous liquids and vapours which pass into each other beyond the critical curve. The other six massive parts represent complexes of two phases, the states of matter forming the complex being represented by two side surfaces.

They further are connected with each other by four cylindrical surfaces on which three lines are always situated representing the systems of three coexisting phases and these cylindrical surfaces intersect each other in one straight line on which is situated the only possible complex of four phases.

If for any system of two substances the figure described were studied completely, it would enable us for each mixture at each temperature and each pressure to read off, of what phases it has been built up and as far as liquid and vapour are concerned it would also show their separate composition.

H. W. BAKHUIS omponents when not forming compounds.

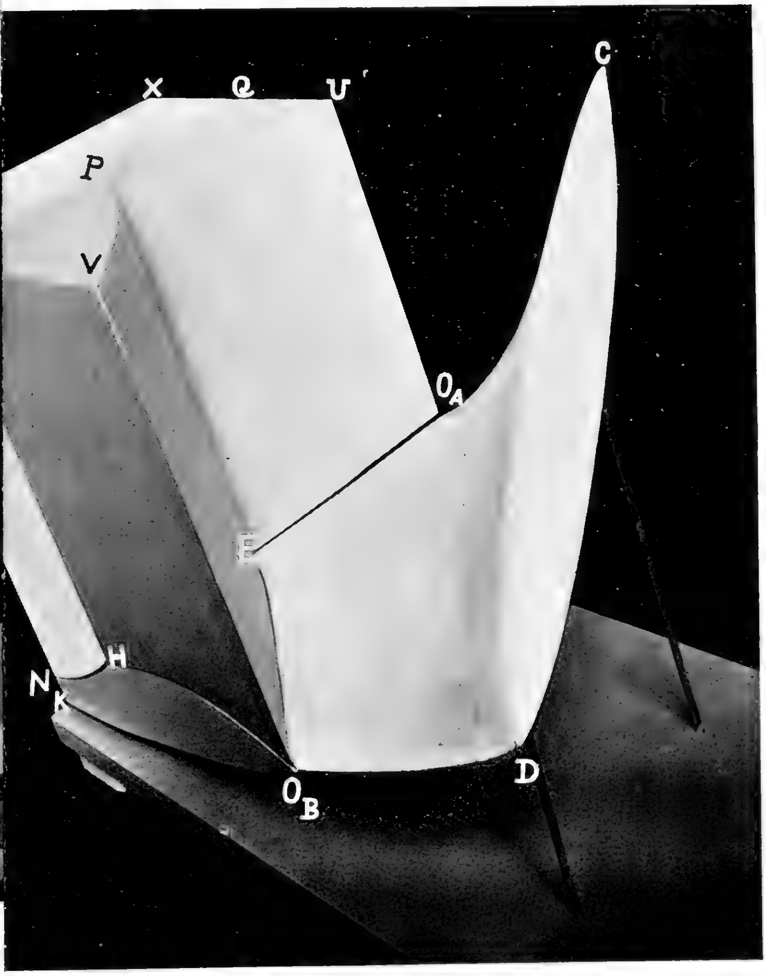

Fig. 2.

H. W. BAKHUIS ROOZEBOOM. A representation in space of the regions in which the solid phases, which occur, are the components when not forming compounds.

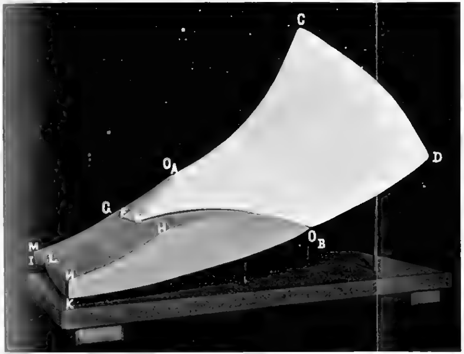

Fig. 1.

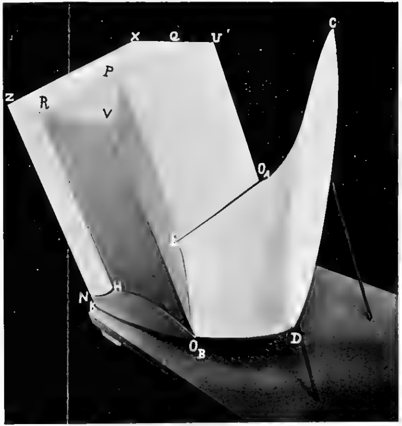

Fig. 2.

For the complexes of *two* phases, the relative proportions may also be read off in the figure; for those of *three* or *four* phases it would be necessary to also know the relation of the volumes.

The figure also makes it possible to ascertain what changes a mixture will undergo, when the temperature, pressure[1]) or concentration are changed.

Chemistry. — "*Equilibria of phases in the system acetaldehyde + paraldehyde with and without molecular transformation*". By Prof. H. W. Bakhuis Roozeboom.

(Communicated in the meeting of September 27, 1902).

The character of the equilibria of phases is exclusively determined by the number of independently variable constituents — components — of which the system is built up.

Sometimes this is equal to the number of the different kinds of molecules. It may also be smaller, if there are among the molecules those which may pass into each other as in the case of associating, ionizing or isomeric substances. If these molecular changes proceed more rapidly than the equilibria of the phases, they exercise no influence on them.

Although water, for example, is a mixture of at least two kinds of molecules, its freezing point is quite as sharply defined as that of a single substance.

If however, the velocity of the molecular change is small, the system on being treated rapidly will behave like one with more components than it shows if treated more slowly. The effect of this on the phenomena of solidification has already been mentioned by Bancroft in 1898 and by myself in 1899. So far, however, no suitable example has been found which would enable us to consider

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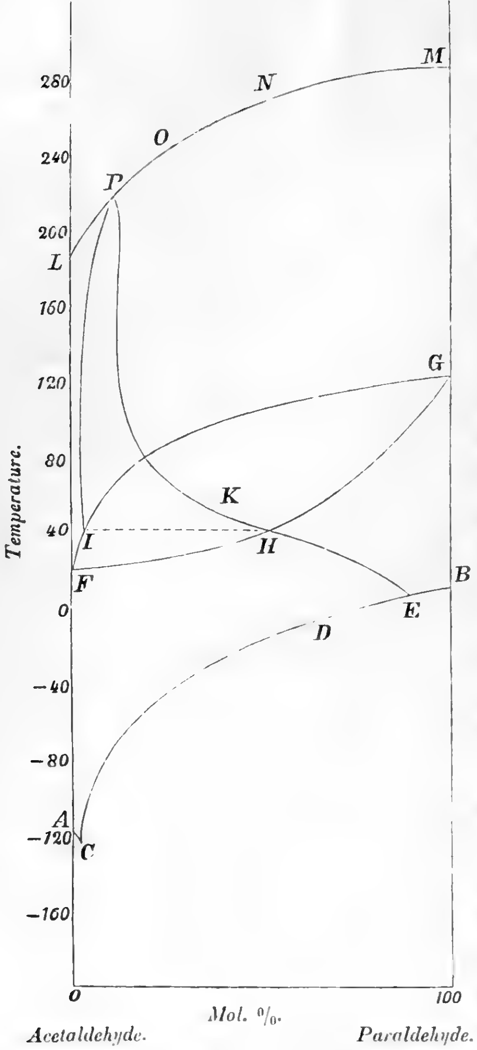
[1]) It demonstrates, for instance, in a simple manner that on compressing vapour mixtures with a sufficient amount of A, the component B first deposits in the solid state in increasing quantity, but then again completely disappears at a certain pressure to make room for a liquid phase.

This phenomenon has recently been observed by Kuenen (Phil. Mag. July 1902) with solid CO_2 mixed with C_2H_6.

It must always show itself with the component which in the liquid-mixtures is the least volatile: in this case B. When however, the liquid-surface has a maximum pressure as in the instance cited by Kuenen, the phenomenon will be noticed with both components. If the surface has a minimum pressure it can only occur with one of the two.

Fig. 1.



the whole of the equilibria of phases from that point of view.

Such a system has now been investigated in my laboratory by Dr. Hollmann of Dorpat. It is the system acetaldehyde+paraldehyde, which has the further advantage of not undergoing molecular transformation except in the presence of a catalyzer and so behaves like a system with two components, whilst it undergoes transformation rapidly enough on addition of a trace of sulphuric acid to appear as a system with only one component. It becomes possible, thus, for the first time to obtain a general insight into the position which equilibria with apparently one component occupy among the systems with two components.

The chief results of the research are the following.

First of all the solidification phenomena of mixtures of acetaldehyde and paraldehyde were investigated. As is well known, paraldehyde in a pure state melts at 12°.55 (point *B*). This melting point is lowered by addition of acetaldehyde along to the curve *BEDC*, which continues until the liquid consists almost entirely of acetaldehyde.

With the aid of the apparatus of Prof. Kamerlingh Onnes [1]) the melting point of acetaldehyde was determined at — 118°.45 (*A*). The melting point line of acetaldehyde does not extend further than — 119°.9 (*C*) where it meets that of the paraldehyde. *C* is therefore a eutectic point,

	Melting point.	$^0/_0$ Paraldehyde.
B	+ 12°.55	100
E	+ 6 .8	88.1
D	— 4 .0	67.6
C	—119 .9	1.4
A	—118 .45	0

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[1]) Ladenburg gave — 120°.

The boiling points of the mixtures were next determined at a pressure of 1 atmosphere and the composition of the vapour of these boiling mixtures was also determined by means of a special apparatus. The former form the line *FHG*, the latter the line *FIG* of which the following points are the most important:

F	20°.7	boiling point of acetaldehyde		
I	41 .7	vapour	2.5 °/₀	paraldehyde
H	41 .7	liquid	53.5 〃	〃
G	123 .7	boiling point of paraldehyde.		

On account of the great difference in volatility of the two components the liquid- and vapour lines are situated far from each other. The vapour of a boiling mixture is much richer in acetaldehyde than the liquid, for which reason the two are readily separated by fractionation.

In the third place the critical temperatures of the components and of a few mixtures were determined. (Only that of acetaldehyde had been previously found by Prof. VAN DER WAALS to be 184°).

Result:

Critical	temp.	°/₀ Paraldehyde.
L	188°	0
P	221°	11.0
O	241°	22.0
N	270°	50.0
M	286°	100.0

These are the relations when there is no transformation of acetaldehyde into paraldehyde, or the reverse.

If, however, a trace of a catalyzer is added, acids in particular, the two molecules can be converted into each other, till the condition of equilibrium corresponding to p and t has been reached [1]).

It appeared that by these means the boiling point of *all* mixtures came in a very short time to 41°.7 and as this point according to the line *FHG* is situated at 53.5 °/₀ of paraldehyde, it represents the relation of equilibrium in the liquid condition at that temperature and 1 atm. pressure. As the corresponding vapour according to point *I* of the vapour line *FIG* only contains 2.5 °/₀ of paraldehyde a rational explanation has thus been found of the long-known fact

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[1]) A little meta-aldehyde is also formed but the quantity remaining in solution is so very trifling that its influence on the system considered may be utterly neglected. It must still be ascertained what place meta-aldehyde occupies in regard to the two forms at high temperatures.

that on distilling paraldehyde with a little sulphuric acid, nearly pure acetaldehyde is collected.

At temperatures below 41°.7, the equilibrium appeared to be displaced along the line *HE*, which at 6°.8 and 88.1 °/₀ of paraldehyde meets the melting point line of paraldehyde.

The consequence is that, from whatever mixture we may start, paraldehyde will always crystallise out on adding a trace of sulphuric acid and cooling to 6°.8 and as the transformation of acetaldehyde into paraldehyde proceeds very rapidly even at this temperature, the whole mixture becomes at last a solid mass of paraldehyde. This even proved to be the case when pure acetaldehyde was taken as starting point. On the other hand paraldehyde in the presence of a trace of a catalyzer does not melt at 12°.5 but at 6°.5 owing to partial conversion into acetaldehyde.

We have no knowledge of the equilibrium in the vapour at these low temperatures but something can be said regarding higher temperatures.

The lines *F H G* and *F I G* have regard to 1 atm. pressure. Similar lines might however, be determined for a higher pressure and in that manner the displacement of the points *H* and *I* with the pressure would be determined. Finally, we should thus arrive at the critical line *LM* and here the compositions of the vapour and liquid, which indicate the relation of equilibrium, must become the same. It appeared from a series of determinations that the point *P* at 221° and 11°/₀ of paraldehyde is this very point.

At these high temperatures, the equilibrium is also reached after some time without a catalyzer.

It appears from the position of *P* that the line which gives the composition of the liquid when equilibrium is attained slopes in the beginning very rapidly, with rising temperature, towards the acetaldehyde side of the figure (portion *E H K*)[1] but afterwards much less rapidly.

The line of equilibrium of the vapour certainly does retrograde, for at 41° the vapour still contains 2.5°/₀ of paraldehyde, at 100° less, and at 221° again 11°/₀. In this case the influence of the pressure prevails obviously. As paraldehyde is a triple polymer, the influence of the pressure is very marked.

If we make a representation in space of the whole figure, like the one mentioned in the previous communication, it will be noticed that the equilibria where the possibility of the mutual transformation of acetaldehyde and paraldehyde is admitted, are lines on the surface

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[1] The point *K* has been determined by TURBABA at 50°.5 and 39.4°/₀.

which represents the case that the two components are not subject to transformation.

For this another new representation may be given which considers the matter from a more general point of view.

Taking p, t and x as coordinates, a surface may be constructed which shall represent the equilibrium between the two kinds of molecules in a homogeneous phase, vapour or liquid.

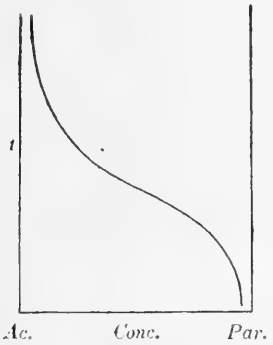

Fig. 2.

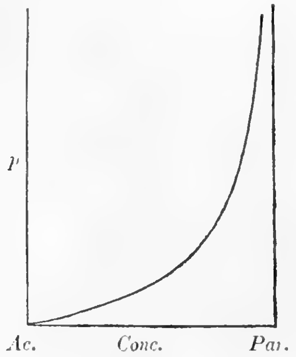

Fig. 3.

The general form of such a surface of equilibrium for the system acet-paraldehyde may be readily deduced from analogy with other known equilibria in the gaseous condition, if one considers that paraldehyde requires heat to pass into acetaldehyde and may be reobtained from the same by compression.

The general course of the equilibrium line at a constant pressure is indicated in fig. 2, that at constant temperature in fig. 3. If we now imagine that on the different points of the t, x-line in a horizontal plane, p, x-lines are erected in vertical planes, we obtain a p, t, x surface of a very peculiar shape which gives the equilibrium relation between acetaldehyde and paraldehyde for every temperature and pressure.

The course may be theoretically calculated for the vapour if the pressure is not too large. With greater pressures and for the liquid state this becomes a difficult matter but the general course remains fairly certain. We might therefore, imagine this equilibrium surface first of all at temperatures higher than those of the critical curve *LM*. Here, the surface would for some time extend itself undisturbed both vertically and horizontally. At lower temperatures, the surface, on account of its form, must necessarily meet first of all the surface for liquid-vapour; according to the investigation this takes place in the point *P*. From here to lower temperatures, the equilibrium surface which was at first continuous will become discontinuous and break up into an equilibrium surface for the vapour state and another for the liquid state.

The lines of intersection of these two surfaces with the surface of two sheets are the lines PI and $PKHE$ in fig. 1. To these must, of course, also be added lines of intersection with the other gas- and liquid surfaces, which have been mentioned in the previous communication.

In this manner, it appears that special equilibria, which occur when transformation between the two components is possible, may be always considered to originate from the intersection of the general space figure for the equilibria of phases with the surface of equilibrium for the molecular equilibria in each phase.

Chemistry. — "*On the action of sulphur on toluene and xylene.*"

By L. Aronstein and A. S. van Nierop. (Communicated by Prof. J. M. van Bemmelen).

(Communicated in the meeting of September 27, 1902.)

The researches on the molecular weight of sulphur according to the boiling point method of L. Aronstein and S. H. Meihuizen [1]) showed that this molecular weight was found to agree with the formula S_8 and this in liquids the boiling point of which varied from 45° to 214°. But when toluene and xylene were used as solvents for sulphur the determination of the molecular weight had given values which corresponded with those calculated from formulae ranging between S_7 and S_8. It was then suspected that this difference might be due to chemical causes. In the following lines we will communicate the results of our efforts to trace those causes.

Action of sulphur on toluene. It had already been noticed that on boiling a solution of sulphur in xylene hydrogen sulphide was given off which was shown by means of lead acetate. A similar evolution of hydrogen sulphide was not noticed on boiling sulphur with toluene. As the chemical action of sulphur on toluene at the usually observed boiling point could probably not amount to much, a preliminary experiment was made by heating a solution of sulphur in toluene in sealed tubes at 250°—300° so as to accelerate the action until on

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[1]) Proc. Kon. Akad. Wetensch. 1898. First section VI, 3.

cooling the tubes no crystallisation of sulphur took place. In the case of a mixture of 2 grams of sulphur and 10 grams of toluene, this lasted 10 days; in the interval the tubes were repeatedly opened to allow the accumulated hydrogen sulphide to escape. The product obtained was freed from undecomposed toluene by distillation; a preliminary investigation of the residual mass showed with certainty the presence of stilbene, thionessal and probably also of tolallyl sulphide. As moreover the contents of the tube had a strong odour of mercaptane it was supposed that the action had taken place in one of the following ways. Firstly, benzyl sulphydrate might have been formed by a direct addition of sulphur according to the equation:

$$C_6 H_5 CH_3 + S = C_6 H_5 CH_2 S H$$

and this on losing hydrogen sulphide according to the equation:

$$2 C_6 H_5 C H_2 S H = (C_6 H_5 CH_2)_2 S + H_2 S$$

might have yielded benzyl sulphide, which according to Forst [1]) may yield as final products stilbene, totallyl sulphide and thionessal.

Secondly, the sulphur, according to the equation:

$$C_6 H_5 CH_3 + 2 S = C_6 H_5 C S H + H_2 S$$

might have yielded thiobenzaldehyde or rather $(C_6 H_5 C S H)_x$, which[2]) according to the equation:

$$2 C_6 H_5 C S H = C_{14} H_{12} + 2 S$$

might have formed stilbene, which then might have formed thionessal according to the equation:

$$2 C_{14} H_{12} + 3 S = C_{28} H_{20} S + H_2 S.$$

In order to test the accuracy of these theories 4 grams of sulphur were boiled in a reflux apparatus with 150 cc. of toluene for 120 hours, care being taken that any hydrogen sulphide which might have been formed and the non-condensed benzylsulphydrate were carried off by means of a current of carbon dioxide and passed through an alcoholic solution of lead acetate. Although perceptible quantities of lead sulphide were precipitated during that time not a trace of the well-known yellow lead mercaptide was found. Both the toluene solution and the crystalline mass obtained therefrom were carefully tested for the presence of benzyl sulphydrate and also of thiobenzaldehyde but notwithstanding the delicate tests for these substances their presence could not be demonstrated. But from the toluene solution we succeeded in isolating stilbene melting at 124° and from this was prepared the characteristic dibromide (m. p. 235—236°) by

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[1]) Liebig's Annalen, Band 178. P. 370.

[2]) Baumann & Klett. Ber. D. Chem. Ges. Band 24, P. 3307.

means of an ethereal solution of bromine. The result justified the belief that the formation of stilbene had taken place in a more simple manner than was formerly supposed, and according to the equation:

$$2\,C_6H_5CH_3 + 2\,S = C_6H_5CH : CH\,C_6H_5 + 2\,H_2S$$

The thionessal found in the preliminary experiments might then have originated from the action of sulphur on the stilbene which according to BAUMANN and KLETT readily takes place at 250°. Fresh experiments in which toluene was heated with sulphur for hundreds of hours in sealed tubes at 200° yielded as sole crystallisable product a large quantity of stilbene which was obtained in a perfectly pure condition and of which the bromine addition product with the correct melting point was prepared. In connection with the results of the action of sulphur on xylene to be mentioned presently, we took into consideration the possibility that as a first product not stilbene but dibenzyl might have been formed according to the equation:

$$2\,C_6H_5CH_3 + S = C_6H_5CH_2\,CH_2\,C_6H_5 + H_2S$$

and efforts were made to isolate this if possible. As, however, according to the researches of RADISZEWSKI[1]), sulphur converts dibenzyl very readily into stilbene and as we had found by special experiments that this already takes place at 200° when a solution of dibenzyl in benzene is heated with sulphur and as we had also proved that this action does *not* take place at a temperature of 140—145° we have heated sulphur with toluene in a sealed tube for eight days at 140°. As sole product we obtained stilbene besides hydrogen sulphide from which fact we are justified in concluding that by the action on the toluene two atoms of hydrogen are directly withdrawn and the two remaining groups are condensed to stilbene.

Action of sulphur on p-xylene. When a solution of sulphur in *p*-xylene is boiled there is a much more perceptible evolution of hydrogen sulphide than on boiling a solution of sulphur in toluene. If, as in the previous experiment with toluene, the gas evolved was removed by means of a current of carbon dioxide and passed through an alcoholic solution of lead acetate 16 milligrams of lead sulphide (equal to 2.1 milligrams of sulphur) were obtained after boiling for an hour and a half. Here again there was no sign of any lead mercaptide; neither did the xylene solution contain a mercaptane as was plainly shown by the fact that no reaction was obtained with mercuric oxide. We next proceeded to heat one gram of sulphur with 30 cc of *p*-xylene in sealed tubes for 120 to 160 hours at 200 to 210° similarly to what was done in the experiment with

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[1]) Ber. D. Chem. Ges. Band 8. P. 758.

toluene. On opening the tubes much hydrogen sulphide escaped and from the liquid obtained the xylene was distilled off. The residue became quite solid and apparently consisted of sulphur and a crystallised hydrocarbon. To remove the greater part of the sulphur, the hydrocarbon was dissolved in ether which was then distilled off. By recrystallising the residue from alcohol a mass was soon obtained which melted at 81—82°. Two determinations of the molecular weight by the freezing point method with benzene gave, respectively the values 200 and 205. No change took place on heating with hydrogen iodide in sealed tubes and no addition product was obtained on adding an ethereal solution of bromine. The product in fact appeared to be identical with p.p. dimethyldibenzyl p—$CH_3C_6H_4CH_2.CH_2C_6H_4CH_3$ — p. which MORITZ and WOLFFENSTEIN [1]) had obtained by the oxidation of *p*-xylene with potassiumpersulphate.

The result which was not analogous to that obtained with toluene caused us to repeat the experiment which now yielded a crystallised product which unlike the first substance was found to consist of a mixture of hydrocarbons. In order to completely eliminate the sulphur the mixture was boiled with solution of sodium sulphite, then dissolved in ether and after distilling off the same, the residue was treated with cold alcohol. The alcoholic solution again contained p.p. dimethyldibenzyl (m. p. 81— 82°) as was proved by repeated recrystallisations. The portion insoluble in cold alcohol was solved in boiling alcohol and by repeated recrystallisation a product was obtained which melted at 176—177°, yielded, on adding an ethereal solution of bromine, a bromine product melting at 208° and proved to be identical [2]) with p.p. dimethylstilbene p — $CH_3C_6H_4CHCHC_6H_4CH_3$ — p.

In order to find out the cause of the difference in these results a further investigation took place. As far as we were aware, the only difference between the two experiments was that this time the tubes had been repeatedly opened thus causing the removal of the greater part of the hydrogen sulphide. The temperature during the experiment was in both cases the same and constant between 200 and 210°; the heating was also continued for about the same length of time. It was now possible that originally in both cases p.p. dimethylstilbene had been formed. Whilst in the first experiment this substance might have been almost completely reduced to p.p. dimethyldibenzyl by the action of the hydrogen sulphide, this reaction could only have occurred in a limited degree in the second experiment.

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[1]) Ber. D. Chem. Ges. Band 32. P. 2531.

[2]) GOLDSCHMIDT & HEPP. Ber. D. Chem. Ges. Band 5. P. 1504.

For this investigation a solution of p.p, dimethylstilbene in benzene was saturated with hydrogen sulphide, introduced into tubes the air of which was totally displaced by hydrogen sulphide and after sealing the tubes, the contents were heated for 40 hours at 200°. From these tubes there indeed was obtained, besides unaltered p.p. dimethylstilbene, a product which proved to be identical with p.p. dimethyldibenzyl. This showed that under the given circumstances the expected reaction might have taken place.

On the other hand, dimethyldibenzyl was heated with a solution ot sulphur in benzene for 40 hours at 200° and, although it was not yielded in a quantity sufficient to admit of a thorough purification, p.p. dimethylstilbene was obtained; at all events a hydrocarbon melting between 140° and 150° which absorbed bromine and yielded a product melting between 185° and 192°, whereas the melting point of p.p. dimethylstilbene dibromide is situated at 208°. From these experiments it is, therefore, probable that the formation of stilbene is here the primary and that of dibenzyl the secondary reaction, but we here got no certainty about this.

On repeating the experiments on the action of sulphur on *p*-xylene in sealed tubes some of which were opened from time to time unequal proportions of stilbene and dibenzyl were still obtained, but the result of the first experiment (nearly exclusive formation of dibenzyl) was never again obtained.

It should be mentioned here that p.p. dimethylstilbene was often obtained in two different forms. Generally, it was a coarse crystalline powder, but occasionally it consisted of very thin leaflets with a silky lustre and showing a violet-coloured fluorescence. The original form of both was retained after recrystallisation from alcohol. Once we succeeded after a good deal of trouble to convert the coarse granular form by grafting, into the silky condition. The melting point of both forms was identical. On treating them with an ethereal solution of bromine they both gave the same bromine addition product. To see whether this was a case of stereo-isomery, solubility determinations were made of both modifications in absolute alcohol at 25°. In both instances the same solubility value was found, namely 0.21 part per 100 parts of alcohol [1]. Notwithstanding the difference in appearance which was also retained in these solubility experiments, a stereo-isomery has thereby been rendered very improbable.

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[1] Elbs (Journal f. Pract. Chemie. Neue Folge Band 39. P. 299 and Band 47. P. 46) gives the solubility of p.p. dimethylstilbene in alcohol at the ordinary temperature as 0.76 per 100.

Action of sulphur on m.-xylene. Sulphur boiled with *m*-xylene not only gave a much smaller evolution of hydrogen sulphide than in the case of *p*-xylene but the amount was even less than that obtained on boiling sulphur with toluene. *m*-Xylene which had been boiled for a considerable time with sulphur was quite as free from mercaptane as the similarly treated toluene and *p*-xylene.

We now proceeded to heat sulphur and *m*-xylene in sealed tubes at 200°. After the heating had lasted for 70 hours, the sulphur had totally disappeared and the tubes could be opened. Streams of hydrogen sulphide escaped. From the liquid obtained the xylene was distilled off and the liquid non-crystallisable residue was freed from sulphur by boiling with solution of sodium sulphide. As it was not improbable that both m.m. dimethylbenzyl and dimethylstilbene might have been formed (to judge from the behaviour of *p*-xylene) and as the first named substance is, according to VOLLRATH [1]) and MORITZ and WOLFFENSTEIN [2]), a liquid and the unknown m.m. dimethylstilbene probably a crystallisable substance it was tried (although in vain) to effect a separation of these two substances by heating in a current of steam, by fractional distillation at ordinary pressure and also by solvents. The suspected presence of a stilbene in that liquid was, however, soon proved when bromine was added to its ethereal solution and the whole placed in a freezing mixture. A bromine-addition product now crystallised in abundance. The addition of bromine was continued until a small excess was present. The crystallised product after being recrystallised twice from xylene had a constant melting point of 167—168°. A bromine determination according to CARIUS gave 44.02 % of bromine, the calculated quantity for dimethylstilbene dibromide being 43.50 %.

The dibromide was used to prepare the hydrocarbon itself. For this purpose it was dissolved in xylene and boiled with molecular silver or sodium wire for 6 hours in a reflex apparatus. From the xylene solution obtained the xylene was removed by distillation; the residual liquid crystallised on cooling and the crystalline mass could be readily purified by recrystallisation from alcohol. The substance is very difficult to burn; the combustion only succeeded by intimately mixing it with lead chromate and potassium bichromate. The elementary analysis gave the following result:

Found . . . . . , ...	C. 92.19 %	H 7·91 %
Calculated for $C_{16}H_{16}$	C. 92.30 %	H 7.70 %

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[1]) Zeitschr. f. Chemie 1866. P. 489.

[2]) Ber. D. Chem. Ges. Band 32. P. 2532.

The melting point was constant at 55—56°.

That the obtained hydrocarbon was really m.m. dimethylstilbene was proved by adding bromine to its ethereal solution which immediately yielded crystals of the dibromide with the previously found constant melting point of 167—168°.

The ethereal liquid from which the dimethylstilbene bromide was precipitated, contained, of course, free bromine from which it was freed by treatment with aqueous potash. After distilling off the ether, the liquid was submitted to fractional distillation when hydrogen bromide was evolved owing to the presence of brominated products. The hydrogen bromide present in the distillate was removed by treatment with aqueous potash and the liquid distilled once more. When it appeared that this distillate, passing over between 298° and 302° was not yet free from bromine it was dissolved in toluene and boiled for three hours with sodium wire which completely removed the bromine. The liquid then showed a constant boiling point ot 298°. On analysis was found:

C 91.38 % H. 8.64 %

Calculated for $C_{16}H_{18}$. . . . , . C 91.43 % H. 8.57 %

Two determinations of the molecular weight by means of the lowering of the freezing point in benzene gave 201 and 199; calculated 210°. All data agree with those of VOLLRATH and those of MORITZ and WOLFFENSTEIN for m.m. dimethyldibenzyl. Only the boiling point was found to be two degrees higher.

From this it, therefore, appears that *m*-xylene on treatment with sulphur yields stilbene as well as dibenzyl as discomposition products.

To ascertain whether stilbene was here also the first product, m.m. dimethyldibenzyl was submitted to the action of sulphur by boiling it with this in a reflex apparatus. The product of the reaction dissolved in ether and treated with bromine did not yield a trace of the characteristic m. m. dimethylstilbene dibromide. This substance could not even be recognised by means of the microscope.

From this we think we may come to the conclusion that during the action of sulphur on *m*-xylene the first product is most probably stilbene and that dibenzyl is a secondary product formed by the reducing action of hydrogen sulphide.

The results of this research are, as we believe, a confirmation of the opinion expressed by ARONSTEIN and MEIHUIZEN in their treatise on the molecular weight of sulphur. A trifling action of the sulphur on toluene and xylene must cause a derivation of the molecular weight in the direction previously found. One mol. of sulphur causes the formation of 8 mols. of hydrogen sulphide and 4 mols of stilbene.

Although hydrogen sulphide is volatile and most of it escapes during the boiling, the increase of the number of molecules formed during that action (however small this may be) is large enough to account for the observed difference. The fact that the deviation has been found larger in the case of toluene than with *m*-xylene as solvent is also in agreement with the observed fact that more hydrogen sulphide is evolved in the first than in the second case.

Our research on the action of sulphur on *p*-xylene was not conducted merely with the idea of confirming the researches of ARONSTEIN and MEIHUIZEN (we were not quite sure whether the *m*-xylene then used had been completely free from *p*-xylene) but also to throw more light on the mechanism of the process and particularly on the question of the primary formation of stilbene and the secondary formation of dibenzyl.

Chemical Laboratory of the Polytechnical School.

DELFT, September 1902.

Physiology of Plants. — "*Investigations of Glucosides in connection with the Internal Mutation of plants,*" by mr. TH. WEEVERS. (Communicated by Prof. C. A. LOBRY DE BRUYN).

(Communicated in the Meeting of 27 September 1902.)

The purpose I had in view in this investigation was to trace for some plants, whether the amount of glucosides remains unchanged during the development or not; and to investigate in the latter case by what conditions these changes are determined.

At the same time the manner in which those changes took place formed another subject for study: whether glucosides were transported as such, or whether a decomposition could be stated, and in the latter case what were the components in which this took place.

Salix species and Aesculus hippocastanum L. were especially used for the investigations; Gaultheria procumbens L. and Fagus sylvatica were also submitted to a prefatory study.

The glucosides to be mentioned here are salicine for the Salix species, gaultherine for Gaultheria and Fagus, aesculine and moreover some glucosides not yet chemically determined for Aesculus hippocastanum.

As for salicine the quantitative valuations were made as follows. The salicine was entirely extracted by boiling water from the parts to be examined and the extract treated with basic lead acetate. The surplus was removed by dinatriumphosphate and the liquid then obtained reduced to a definite volume. In this two estimations of sugar were made, one before, the other after allowing emulsine to work in upon it for 48 hours. Prefatory experiments with pure salicine had proved that in this way it was completely decomposed: the increase of the reduction after inversion was to be attributed only to the glucose formed of salicine. [1]).

From this increase of the glucose the quality of the salicine could then be calculated.

This same method was followed in order to state the salicine in various parts of the plant; then however, after inversion the liquid was extracted with ether, so that saligenine might enter into it. This substance is easily recognised by the physic qualities of its crystals and by the substitute of bromine obtainable with brominewater and moreover by its salt of copper. The efforts to point out salicine in the tissue itself were unsuccessful; the method formerly used by **Theorin** [2]), namely that of adding concentrated sulphuric acid, proved impracticable, as it during the produced erroneous results.

For the above mentioned Salix species salicine is found in the bark of the branches, but not in the wood; young buds are rich in it, likewise the assimilating leaves. It appears in young ovaries but disappears during the process of ripening.

Although an inverting enzyme was not to be extracted, it proved necessary to kill the parts immediately in boiling water, otherwise considerable alterations in the quantity of salicine presented themselves. Thus e. g. after slow drying 25 pCt. disappeared out of the bark.

The following series of determinations for the purpose of investigating the quantity of salicine during the budding period, was made with *one* specimen to exclude individual differences.

The total quantity in various successive stages was calculated by taking a branch with a definite number of sidebuds as object. The weight of the different parts of this branch together with the procentic values of the quantity of salicine in corresponding parts of the same object in the successive stages gave the total quantity of salicine of this branch in those stages [3]).

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[1]) Before inversion a solution of salicine does not reduce even with boiling; neither does saligenine formed by means of inversion at the same time as glucose.

[2]) See Theorin Öfversigt af Kongl Vetenskaps. Akademiens Förhandlingen 1884. No. 5. Concentrated $H_2 SO_4$ gives with salicine a coloring of red.

[3]) In corresponding parts of *one* object was an equal quantity.

Under observation were only branches without genitals; those with catkins gave a different result [1]).

Branches of $1^1/_2$—4 mM. diameter (wood and bark together).

March 24th 3.2 pCt. [2])
April 17th 2 „
May 21st 0.4 „

Branch of 4—8 mM. diameter (only bark; hence the quantity is higher).

March 24th 4.1 pCt.
April 17th 2.8 „
May 21st 2.1 „

For Salix Helix L. the figures for the bark of branches were

March 24th 4.4 pCt.
April 17th 2.7 „

The quantity of glucose is a little variable; however, it does not rise above 0.5 pCt.; the quantity of fecula diminishes when budding from 9.5 pCt. to 6 pCt.

In the young buds of Salix purpurea there is before the budding 4.4 pCt. and of Salix Helix 6.2 pCt. During the budding this quantity decreases greatly, disappears even for S. purpurea entirely (17 April) but rises again quickly, when assimilation begins, to 3.7 pCt in leaves and 3 pCt. in young shoots (21 May).

Of the absolute quantity of salicine in a branch with 300 buds

± 36 pCt. disappeared from 24 March—17 April
± 18 „ „ „ 17 March—21 May,

the assimilation, begun already before May 21, having given rise to new salicine.

Experiments with branches placed in the dark in water [3]) showed the following:

After the roots have been formed, a number of long etiolated shoots bud forth, consuming by their development besides the fecula also a great quantity of the salicine in the bark (± 70 pCt.).

At first the young shoots contain a great quantity 7.2 pCt., this, however, keeps on decreasing; the absolute quantity calculated for 100 young shoots also diminishes:

for 100 young shoots long 18 mM. there is 28 mG. salicine
„ „ „ „ „ 125 „ „ „ 15 „ „

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[1]) The quantity of salicine is at the same instant lower in branches with catkins than in those without; the salicine diminishes more quickly.

[2]) These procentic values are calculated for dry weight.

[3]) These were branches of 6—10 m.M. diameter, the young shoots coming from sleeping buds.

These quantities are small compared to the entire quantity consumed ± 330 mG. for 100 young shoots.

When the young buds were budding forth saligenine was found in them, the branches were immediately killed in boiling water, the extract after cooling down extracted with ether; so all influence of enzyme could be excluded. It becomes very probable that the salicine is analysed before the consumption, on account of saligenine being found; the quantity, however, is so small that if really the analysis of salicine were to take place as indicated, and a decomposition to precede the consumption, saligenine can only be an intermediate stage. Either the aromatic half disappears as such, or another aromatic substance must be the definite product of the decomposition.

In the young leaves developing normally, salicine soon makes its appearance again after having disappeared for a moment; we can expect that this increase is connected with and due to the assimilation, as etiolated shoots do not show it. In order to state whether the leaves were really the place of a new formation and the light really had a part in it, the quantity of salicine before and after darkening was compared.

The quantity in the leaves was determined in the evening after sunset and in the morning before sunrise (*one* specimen). Likewise in the evening leaves were halved, one half with midrib left on the plant, the other half analysed. The following morning the remaining half was cut off from the midrib and also analysed[1]). Provided that a sufficient number, 100 or 200 leaves were halved, a comparison could very well be made.

For a small-leafed specimen a 100 leaves

8 P. M. 7 Aug.	47.5	mG. glucose	87.2	mG.	salicine
4 A. M. 8 „	27.4	„ „	60.2	„	„

For a big-leafed specimen a 100 leaves

8 P. M. 7 Aug.	80	mG. glucose	177.7	mG.	salicine.
4 A. M. 8 „	31.9	„ „	142.7	„	„

So in both cases we see a decrease during an 8 hours' summer night of respectively 30 and 20 % of the salicine in the leaf in the evening.

For experiments with entire leaves of *one* specimen:

8 P. M. 7 Aug.	4.6 %	salicine.
4 A. M. 8 „	3.2 %	„
8 A. M. 8 „	4.6 %	„

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[1]) See Lotsy. Mededeelingen 's Lands Plantentuin XXXVI.

Thus here too a decrease of 30 °/₀ during the night followed up by an equal increase on the following day. If branches on the plant are enveloped in black waxed paper the decrease amounts after 48 hours only to 35 °/₀, no great difference with that of 8 hours; increase, however, did not take place, so light proves to be a necessary factor. The experiments of etiolating told the same.

If this quantity of salicine disappearing from the leaves was removed to the bark, an increase would have to be observed there. This was indeed the case, for branches rich in leaves the increase of the quantity of salicine of the bark amounted in *one* night to 2.5 °/₀; for branches with few leaves to 1.1 °/₀.

From the etherextract prepared in the above described manner, of the parts of Salix purpurea still another substance could be isolated by means of subliming. According to the micro-chemic qualities this was a substance resembling phenol and qualified by its compound of lead and of lime, besides reaction with tetrachloorchinon as an ortho-derivate [1]). The substance did not show Aldehydreactions. The further micro-chemical qualities corresponded to those of the simplest ortho-phenol, catechol. After a repeated crystallisation out of benzol the melting-point proved to be 104°. Elementary analysis and determination of molecular weight confirmed the fact, that it was catechol.

As the material which furnished the substance was quickly killed both in boiling water and in boiling alcohol and the etherextract already showed the crystals before sublimation, influence of enzym [2]) is not probable and formation out of resin is not possible.

Treatment with ferrichloride followed by additon of natrium hydrocarbonate also furnished in the tissue the reaction of catechol. The red colour was clearly visible in the unopened cells of the sections of the bark, young etiolated shoots showed them faintly, older ones more. Catechol is like salicine only to be found in the bark [3]).

The supposition was aroused that catechol might be the aromatic substance, remaining there as definite product of decomposition of the salicine. In order to test the accuracy of this supposition, an investigation had to be made whether the quantity of catechol of the parts of Salix purpurea were varying.

For a quantitative determination of the catechol the method of

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[1]) According to an investigation of Prof. H. Behrens which will shortly appear, communicated to me by Miss Grutterink.

[2]) The black colour of the dying leaves is caused by the influence of a "tyrosinase" on catechol.

[3]) Catechol was also obtained out of Salix Helix L., S. babylonica L., S. vitellina L, Populus alba L., P. monilifera Ait, sometimes only very little.

Degener (Journal f. Prakt. Chemie 1879) could not be used on account of a flavon-like colouring matter not closer examined, and also precipitated by a basic leadacetate. So the method of Prof. **Behrens** to determine Indigo was followed. The sublimate of a solution of catechol of a known strength in absolute alcohol was compared with that of the alcoholic solution of the remainder of the ether evaporated dry. Now it was examined how much this liquid had to be diluted to obtain an equivalent sublimate. The sublimation was performed by means of the brass table described by Prof. **Wijsman**. Under certain precautions the determination could be accurately made to milligrammes.

The quantity of catechol of the leaves was in the evening 0.6 pCt. } with *one*
〃 〃 〃 〃 〃 〃 〃 〃 〃 〃 morning 0.1 〃 } specimen
〃 〃 〃 〃 〃 〃 bark 〃 〃 〃 evening 0.6 〃 } with the same
〃 〃 〃 〃 〃 〃 〃 〃 〃 〃 morning 0.4 〃 } specimen.

So the quantity of the catechol here proved to change in reverse order as that of the salicine. In the leaves the salicine diminishes in the night, the catechol increases, and in the bark the catechol diminishes and the salicine increases. Is there any connection between the extent of these changes?

For that purpose for one and the same object catechol was determined as well as salicine.

200 halves of leaves 8 P. M. 225 mGr. salicine (4.5%) ± 32 mG. catechol (0.65%)
〃 〃 〃 〃 4 A. M. 162 〃 〃 (3.3%) ± 52 〃 〃 (1.05%)

So 63 mG. salicine less, 20 mG. catechol more.

The proportion of these values, given the degree of accuracy of the determination of catechol, pretty well agrees with the proportion of the molecular weights.

A comparison was also made of the change in salicine with that in catechol for leaves budding forth in the dark.

17 Gr. bark before budding 351 mGr. salicine 36 mGr. catechol
17 〃 〃 after 〃 232 〃 〃 55 〃 〃
budding etiolated shoots 55 〃 〃 4 〃 〃

(a great increase in the bark, in the young shoots only a small part of the catechol thus formed to be found) 64 mG. salicine was used, 23 mGr. catechol was formed.

These two values stand in the ratio of 36 to 100, the molecular weights in that of 38 to 100.

So it is very natural to assume here a decomposition of the salicine into sugar and catechol with saligenine as intermediate stage (see above). For this then a CH_2 group out of the lateral chain would have to be decomposed, as saligenine is orthoöxybenzylalcohol and catechol is the orthodiphenol.

Corresponding to this the quantity of catechol of the bark is large in May(1.1 pCt.), a greater part of the salicine then having disappeared, much lower in July (0.3 pCt.) when the loss has been repaired 1). Where now has the decomposition taken place?

Pfeffer says Kap. VIII, Pflanzenphysiologie 2e Auflage: „vielleicht dienen die esterartigen Verbindungen der Kohlenhydrate mit Phenolkörpern zur Herstellung von schwer diosmirende Verbindungen bei deren Zerspaltung im allgemeinen der Phenolkörper in der Zelle intact verbleibt, um fernerhin wieder zur Bindung von Zucker benutzt zu werden."

The facts are excellently explained in the following way:

The decomposition of the salicine takes place in every cell, the glucose is conveyed in the direction of the green parts, the catechol remains in the cell and binds glucose, coming from cells situated closer to the bark, to salicine.

Glucose is transportmatter and salicine is transitory reservematter.

The glucose being comsumed in young parts in greater quantities than its supply is, catechol must be found, but only so much as corresponds to the decrease of the absolute quantity of salicine.

100	young shoots	18 m.M.	long	28 m.G.	salicine,	traces of	catechol.
100	„ „	85 m.M.	„	21,6 m.G.	„	2 m.G.	„

6.4 m.G. salicine corresponds when calculated to 2,5 m.G. catechol, when observed to 2 m.G.

This correspondence adds great strength to the hypothesis. 2)

In the bark the loss of consumed glucose is not repaired, so catachol increases greatly.

As for Aesculus, here it was especially the germination which was studied. The glucosides found in the ripe seedlings being not yet chemically determined, it was only necessary to base the method of the quantitative definition on the quantity of sugar formed by inversion. I had to trace whether the quantity of sugar bound in glucoside decreased during the germination.

To this end the seedlings were ground and extracted with methylalcohol, of this extract the alcohol was evaporated, and the watery liquid

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1) I here mean the quantity in the bark of thicker leafless branches where no difference between night and day is observed.

2) Also the facts observed at the change of night and day can be excellently explained in this way.

extracted with ether to get rid of oil and resin. The extracted liquid served as definition of the reduction *before* and *after* inversion by boiling it for 2 hours with HCl [1]).

From the difference of this reduction the quantity of reducing sugar originating from the glucoside could be calculated; it amounted to 13 pCt.

During the germination this quantity decreased in cotyledons by 60 or 70 pCt. Fecula and albumen by 70 or 80 pCt. The germinating plants contained only 1 or 2 pCt. of glucose bound in the shape of glucoside, the consumption of the glucosided sugar during the germination could be regarded as proved by the 70 pCt. decrease of the absolute quantity.

The localisation of aesculine was observed by fluorescence of its watery solution, to be seen when there are not too few sections. Aesculine was to be found in ungerminated seeds only sporadically in the plumule; when germinating it appears in greater quantity in the stalks of cotyledons, not in the cotyledons themselves. Stalk and hypocotyledon internodium contain aesculine when germinating in the dark as well as in the light, so light is not necessary for the formation.

The stalks of the leaves show the aesculine only when developing in the light and not in the dark; this seems to point to the fact, that the aesculine of the normal germinating plant originates from two sources: that it is formed for the greater part by reforming of substances out of the cotyledons and side by side with this, that it is prepared independently in the stalks of the leaves from substances assimilated by the leaves. Experiments with full-grown plants, in the light and in the dark, with coloured and with normal leaves made this the more propable, but full certainty can only be given by means of later quantitative definitions.

Studies on Gaultheria procumbens showed what changes took place in the quantity of the gaultherine, the investigations have however not yet been brought to an end. The method of quantitative definitions was founded on the observation of the quantity of methylsalicylate which could be formed out of it. This was redistilled with vapour out of the parts, caught in alcoholic potash and saponificated with it. The kaliumsalicylate formed in this way was determined according to the method of MESSINGER and VORTMANN [2]). For smaller quantities the colorimetric method of determination was used with $Fe\,Cl_3$.

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[1]) After inversion and neutralisation the liquid was treated with leadacetate.

[2]) MESSINGER and VORTMAN, Zeitschrift f. Anal. Chem. 38 bl. 292.
Ber. d. deutschen chem. Gesellschaft. Berlin. Bd. 22. 2313.

With Fagus sylvatica where TAILLEUR [1]) found methylsalicylate only in the germinating plant, the latter method showed that it was also present in the full-grown plant. Methylsalicylate is to be found sporadically in the buds of the beech shortly before budding, during that process it is found in the young leaves and shoots as well as in the branches of the preceding year. Young long branches are richest in it, 0.02 pCt. As soon as the leaves have unfolded, this substance begins to disappear again and is nowhere to be found in a week's time.

Further particulars to be looked for in the dissertation to appear shortly.

Physics. — "*Some observations on the course of the molecular transformation.*" By Prof. J. D. VAN DER WAALS.

As is well known, acetic acid may be considered as a mixture of simple and double molecules and we find a decreasing number of double molecules when we investigate the saturated vapour of this substance at increasing temperature. The same applies also to NO_2. We are apt to conclude from these two best known instances of molecular transformation that this course is the only one that is possible. We may, however, easily convince ourselves that also the opposite course may occur, and it appears to me that we may conclude from figure (1) of the communication of Prof. H. W. BAKHUIS ROOZEBOOM in the Proceedings of the previous session, that for the transformation of acetaldehyde and paraldehyde this opposite course perhaps occurs.

Let us take the equation for the molecular transformation, as it occurs Cont. II, pag. 29, namely:

$$log \frac{(v-b)x}{(1-x)^2} = \frac{2(E_1-E_2)}{R_1T} + 1 - \frac{2(H_1-H_2)}{R_1}$$

The quantity $1-x$ of this equation represents the quantity of the substance expressed in grams which occurs in the form of simple molecules, x therefore that which occurs in the form of double molecules. If molecules were formed consisting of n simple molecules, the equation would be modified into the following one:

$$log \frac{(v-b)^{n-1}x}{(1-x)^n} = \frac{A}{T} + B.$$

It is true that we only find the equation in this simple shape if

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[1]) TAILLEUR, Comptes Rendus A. Sc. Tome 132 p. 1235.

we make suppositions concerning the quantities a and b, which can only be satisfied if the multiple molecules may be considered to be mere complexes of simple molecules, which can be formed without further radical modifications in the structure of the molecules themselves. But as I will apply the given formula only in the case of saturated vapour at a pressure which is not very high, in which case the influence of the quantities a and b may be neglected, we may consider it to be sufficiently accurate for our aim.

We may deduce from it:

$$(n-1)\frac{dv}{vdT}+\frac{dx}{dT}\left(\frac{1}{x}+\frac{n}{1-x}\right)=-\frac{A}{T^2}.$$

For saturated vapour at a pressure which is not too high, we have:

$$pv=R_1T\left(1-\frac{n-1}{n}x\right),$$

from which follows:

$$\frac{dp}{pdT}+\frac{dv}{vdT}=\frac{1}{T}-\frac{\frac{n-1}{n}\frac{dx}{dT}}{1-\frac{n-1}{n}x}.$$

If we substitute for $\frac{1}{v}\frac{dv}{dT}$ the value found above, we get the equation:

$$T\frac{dx}{dT}\frac{1}{x(1-x)(1-\frac{n-1}{n}x)}=(n-1)\left(\frac{T}{p}\frac{dp}{dT}-1\right)-\frac{A}{T}.$$

Whether the number of multiple molecules in the saturated vapour increases or decreases with the temperature, depends therefore on the fact whether the value of the expression:

$$(n-1)\left(\frac{T}{p}\frac{dp}{dT}-1\right)$$

is more or less than $\frac{A}{T}$.

For a normal substance $\frac{T}{p}\frac{dp}{dT}$ is approximately equal to $7\frac{T_{cr}}{T}$. For a substance in which molecular transformation takes place, the factor 7 is to be modified and this factor will even vary more or less with the temperature. But if a perfectly accurate numeric determination is not required, and if we only ask: Can both ways in which x may be thought to vary with the temperature occur? then we may state what follows:

"When the heat developed by the combination of n simple molecules to a complex one is so great, that it far exceeds the quantity $(n-1)\, 7\, T_{cr}$ — as is the case for acetic acid — then the saturated vapour will at higher temperature be associated in a lower degree. If on the other hand that quantity of heat is much smaller than $(n-1)\, 7\, T_{cr}$ then the reverse will take place."

When we proceed to saturated vapours of greater density and when we approach the critical temperature, then this difference in the course will no longer exist.

If we consider in the equation:

$$(n-1)\frac{T}{v-b}\frac{dv}{dT}+T\left(\frac{1}{x}+\frac{n}{1-x}\right)\frac{dx}{dT}=-\frac{A}{T}$$

the value of $-\dfrac{T}{v-b}\dfrac{dv}{dT}$ for the saturated vapour at all temperatures between 0 and T_{cr}, we see that this quantity has a minimum value for a certain value of T. For very low temperatures it may be equated to $f\dfrac{T_{cr}}{T}$ and for the absolute zero it is therefore infinite.

But also for $T=T_{cr}$ it will be infinite, for $-\dfrac{dv}{dT}$ is infinite in the critical point. The value of T for which this minimum value occurs, would for normal substances be the same fraction of T_{cr}. For substances with molecular transformation we find a different value for this fraction. It may be calculated for many substances from the experiments of SIDNEY YOUNG at least approximately.

Above the temperature for which $-\dfrac{T}{v-b}\dfrac{dv}{dT}=\dfrac{A}{T}$ for acetic acid also $\dfrac{dx}{dT}$ is again positive. For substances which behave as acetic acid therefore a minimum value of x occurs. The fig. (1) of BAKHUIS ROOZEBOOM presents in fact such a minimum for paraldehyde, and from this would follow, that this transformation is of the same type as that of acetic acid. Yet it seems possible to me that an accurate direct investigation would prove this minimum not to exist. If it really exists, then it will probably occur at a much higher value of T.

But even if this transformation would also prove to be of the same type as that of acetic acid, yet it seems not superfluous to me to point out, that also the other type may possibly occur. The abnormality of substances as the alcohols, water, etc. is ascribed to a possible molecular transformation, and yet the saturated vapour of these substances appears to follow the laws of the perfect gases the more accurately as the temperature at which it is investigated is lower. So the density of saturated vapour of water at 100°, appears to be $2^1/_2$ pCt. higher than would follow from the application of the laws for perfect gases; whereas the saturated vapour of water at ordinary temperature presents a density which does not deviate noticeably from that, which follows from the laws of BOYLE and GAY-LUSSAC. If for molecular transformation the type of acetic acid were the only one which could occur in nature, then the supposition that water is also subjected to this transformation would involve that the deviation would be found to increase when the temperature is lowered. It is highly probable that the deviation of $2^1/_2$ pCt. of saturated vapour of water at 100°, which cannot be accounted for by the ordinary deviation from the laws of BOYLE and GAY-LUSSAC which also normal substances present, must be ascribed to the presence of more complex molecules; but at the same time we must then assume, that the heat of transformation lies below the limit which we have indicated above.

The equation which we have used here, is taken from Cont. II, p. 29 and there it had been obtained by the direct application of the principle of equilibrium, according to which a given quantity of matter at a given temperature in a given volume will arrange itself in such a way that the free energy is a minimum. It is therefore that we had to take a fixed quantiy of the substance, e. g. a unit of weight, which might be divided into $1-x$ grams simple, and x grams double molecules. When x varies, the total quantity of the substance remains constant.

We may, however, also consider a mixture, consisting of a number of $1-x$ simple and x multiple molecules and then we may apply the thesis that, when equilibrium is established the thermodynamic potential for a molecular quantity of the multiple molecules must be n times greater than that for the simple molecules. The linear function of x, however, which in other cases may be omitted, must in this case of course be preserved. If we then put:

$$\zeta = MRT\,\{\mu + (1\text{-}x)\,l\,(1\text{-}x) + x\,l\,x\} + T\,\{\alpha\,(1\text{-}x) + \beta\,x\} + \gamma\,(1\text{-}x) + \delta\,x$$

then we have:

$$\zeta - x\,\frac{\partial\zeta}{\partial x_{pT}} = MRT\,\{\mu - x\mu'_x + l\,(1-x)\} + \alpha T + \gamma,$$

and $$\zeta + (1-x)\,\frac{\partial\zeta}{\partial x_{pT}} = MRT\,\{\mu + (1-x)\,\mu'_x + lx\} + \beta T + \delta.$$

From $\zeta + (1-x)\,\dfrac{\partial\zeta}{\partial x_{pT}} = n\,\left\{\zeta - x\,\dfrac{\partial\zeta}{\partial x_{pT}}\right\}$ we deduce:

$$log \frac{x}{(1-x)^n} = (n-1)\{\mu - x\mu'_x\} - \mu'_x + B + \frac{A}{T}.$$

This last equation yields the results we have obtained, in a still simpler way than that which we have made use of originally. It has moreover the advantage, that the usual signification of x and μ, as it is established in the theory of a binary system, may be kept unchanged.

Reactions like that of acetaldehyde and paraldehyde, reactions which we can bring about at pleasure by means of a catalyzer and in which the composition may be determined experimentally are of course of the highest importance for the investigation of the course of the molecular transformation. For reactions as that of acetic acid the density is the only criterion for the degree of the transformation; and this criterion fails as soon as we work in circumstances in which the deviations from the laws for the perfect gases are considerable. The experimental investigation will therefore not be able to prove the occurrence of a minimum in the number of the double molecules in the saturated vapour of acetic acid. At the temperature at which the theory predicts that minimum and which lies probably between 0.8 T_{cr} and 0.9 T_{cr}, the density of the saturated vapour is already so great that it is nearly impossible to deduce reliable conclusions concerning the course of the transformation.

Physics. — *"Critical phenomena in partially miscible liquids."* By Prof. J. D. VAN DER WAALS.

I have read with great interest the communication of Prof. KUENEN under the above title, which occurs in the Proceedings of the previous session, and it induces me to draw attention to the following considerations.

In my paper of March 25th 1899 I started from the thought, that the series of plaitpoints, which may occur at different temperatures, whether we arrange them to a plaitpoint curve or assign a place to them in the x, v plane, must form one or more continuous curves — of course continuous in the mathematical sense.

When therefore the experiment yielded, e.g. for ethane and ethylalcohol two separate plaitpoint curves, I have connected them by means of a theoretical part.

If we wish to connect the two pieces of curves found to one curve, we may perform this in two simple ways. In the first place we may connect them in such a way that the curve is continuous also as to its direction. In the second place we may, between the ends of the pieces which are experimentally determined, trace a curve which presents in those ends abrupt changes of direction and which has about the same course as the three-phase pressure, though it lies everywhere lower than that pressure.

I then thought that the two pieces of the plaitpoint curve were to be connected in the first manner. The experiment had shown that the peculiarities which must then occur, namely the existence of a minimum and of a maximum temperature, were possible and really occurred in nature; at any rate the minimum temperature. The peculiarity, on the other hand, which occurs, if we make the connection in the second manner, namely the abrupt change of the direction, was never observed.

Now when we have made a choice and when we wish to examine its meaning, all conclusions must of course be in accordance with the choice we have made. Here I will mention the following conclusions from the first way of bringing about the connection: 1st. A mixture with minimum critical temperature exists. 2nd. A mixture with maximum critical temperature exists. 3rd. Plaitpoints occur outside the borders of the three-phase temperature, which cannot be observed, as they lie above the empirical ψ-surface.

In this case a plait must necessarily at a certain temperature be separated from the principal plait, which at higher temperature (the maximum critical temperature) has contracted to one point. In short then the phenomenon quite corresponds to the description I have given Cont. II, p. 187. If therefore KUENEN accepts the way in which the connection of the two pieces of the plaitpoint curve he has determined experimentally, is brought about, then I cannot but consider it to be inconsistent, if he raises objections to the interpretation.

But more important is the question whether the choice we have made is the right one; whether, therefore, the connection between the two pieces of the curve should not rather be brought about with two abrupt changes in the direction. This has at the same time the following meaning: Is the plaitpoint the course of which is indicated by the theoretic curve, perhaps quite another plaitpoint as that whose course is indicated by the experimental curve? Now I read in the paper of KUENEN p. 321 that he has obtained the figure I have originally given, with the aid of other curves. But I think that this must be understood in such a way that he has succeeded in pointing out, that the two ends of the experimental branches may be connected. The way in which the connection must be established can here, after my opinion, not be decided. I have already doubted some time as to this question. The first way of connecting requires that as well a mixture with a maximum, as a mixture with a minimum critical temperature occurs. And though I expressed in my paper of 1899 the expectation, that it would be possible to account for this, yet I must acknowledge, that a further investigation has made me consider the occurrence of a maximum critical temperature more and more improbable.

After my opinion the question is decided by that part of the plaitpoint curve KUENEN has determined experimentally, which starts at the critical point of methylalcohol and which indicates the course of a plaitpoint belonging to a plait which has its summit towards the side of the small volumes. The fact that $\frac{dp}{dT}$ is negative or at any rate smaller than $\left(\frac{\partial p}{\partial T}\right)_v$ quite agrees with the circumstance, that $\left(\frac{d^2 v}{dx^2}\right)$ is positive.

If this plait had its summit on the side of the large volumes, then it would be possible to explain the course also for the case of ethane and methylalcohol by admitting the existence of a maximum and a minimum T_{cr}. As this is however not the case it seems to me that we cannot but assume with KUENEN, that the theoretical part of the plaitpoint curve indicates the course of a point, drawn i. a. by KORTEWEG (Archives Neérl. XXIV, p. 305, fig. 12) and which belongs to a sideplait if we trace the connodal curve of the sideplait also in the unstable region. The discontinuity in the direction of the curve ensues then from the fact that the theoretic part represents the course of another plaitpoint than the experimental part.

If we return to the case of ethane and methylalcohol then we must admit that above T_B the spinodal curve possesses a protuberance towards the side of the small volumes, accompanied by a new connodal curve, which if we trace it also in the unstable region, presents a new plaitpoint. Or, what comes to the same: the existing plaitpoint splits up into two plaitpoints. This second plaitpoint lies on the side of ethane and in the beginning it will move with great velocity. At higher values of T the sideplait extends and in consequence thereof that part of the principal plait which has a plaitpoint on the side of ethane contracts. At the moment that that part would vanish the second plaitpoint has coincided with the plaitpoint which is indicated by the point A (see fig. (1) of p. 319). This description differs in details from that of KUENEN, but a great number of figures would be required in order to show this difference clearly, but then also in order to bring us into agreement.

For the case of ethane and methylalcohol the theoretical plaitpoint belonging to the sideplait of the side of alcohol coincides at T_A (see fig. 2, p. 326) with the practical plaitpoint of the side of ethane. At lower value of T it is displaced in the x,v-plane towards the side of alcohol and when the temperature continues to decrease it approaches asymptotically to the plaitpoint with which it forms a "système double hétérogène" (after the terminology of KORTEWEG). If we draw this series of points in the plaitpoint diagram, it must of course satisfy the condition which follows from the fact, that they lie below the three-phase triangle, namely on the side of the small pressures. At low temperatures it lies even in the region of the negative pressures.

Fig. 2 of KUENEN p. 326 must therefore be completed with a theoretic curve which starts at point A, retrogrades immediately to lower temperatures and lies below the curve of the three-phase pressure. The theoretical branch approaches to the same asymptote as the highest branch that starts at C_2. For the theoretic branch also $\left(\frac{d^2v}{dx^2}\right)$ must be positive, and therefore we have:

$$\frac{dp}{dT} < \left(\frac{\partial p}{\partial T}\right)_v .$$

The rapid rising of this branch at low values of T seems to be contradictory to this explanation. But if we take into account that also $\left(\frac{\partial p}{\partial T}\right)_v$ approaches to an infinitely great value for values of v which approach to the limiting volume, this apparent contradiction disappears.

What is surprising, at least to me, is that these theoretic plaitpoints serve to make the course of the practical plaitpoints continuous. But on the other hand the circumstance, that also for the course of these theoretic plaitpoints a so important and at the same time a so simple meaning has been found, confirms my opinion that now the true description of the phenomenon has been given, at least for those cases, in which the longitudinal plait has its summit on the side of the small volumes.

But though the accuracy of the description of the phenomenon has increased, we must acknowledge that the chance to find a satisfactory explanation for the phenomenon is not greater than before; on the contrary it has diminished. The circumstance in which a mixture of two substances has a maximum and a minimum critical temperature needs now no longer be inquired into. The question whether the size of the molecule of the normal substance has influence on the course, has also lost its direct importance. For mixtures of ethane with an alcohol the separation between the two types lies between methyl- and ethylalcohol; the question whether this separation takes place between two higher terms of the alcohol series, if we take instead of ethane a higher term of the series of carbonhydrogene compounds, which seemed very important before is now no longer of primary interest [1]). It seems to me that I have to return in many respects to my original meaning, namely that we have to inquire after the circumstance which causes the spinodal curve to show a protuberance towards the side of the small volumes. In mixtures of a normal substance with an associating one this cause can perhaps be found in the circumstance that the quantity $\left(\frac{\partial p}{\partial x}\right)_v$ can obtain abnormous high values for such a mixture. As the equation:

$$-\frac{\partial p}{\partial v}\frac{\partial^2\psi}{\partial x^2}=\left(\frac{\partial p}{\partial x}\right)^2$$

applies to the spinodal curve, the value of $-\frac{\partial p}{\partial v}$ may also be abnormously high in this case. If this is really the case an explanation for the protuberance is given which is certainly satisfactory. Yet a great distance exists between this observation and an adequate calculation.

In any case these experiments of KUENEN, to which I hope that he will add many others, are an important contribution to our knowledge of the critical phenomena of not miscible substances.

Physics. — "*The influence of variation of the constant current on the pitch of the singing arc.*" By J. K. A. WERTHEIM SALOMONSON. (Communicated by Prof. P. ZEEMAN).

In the course of some experiments on the physiological action of alternating currents of very high frequency, I tried the currents generated by means of DUDDELL's singing arc. A constant current arc between solid carbons shunted by a self-inductive resistance and a condenser emits a note, the pitch of which corresponds with the frequency of the alternate current generated in the condenser-circuit.

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[1]) An experiment in order to investigate whether for propane the limit lies between ethyl- and propylalcohol was already in preparation for a long time in the laboratory of Amsterdam. But other labour which could not be delayed prevented each time those who would undertake the investigation.

DUDDELL believed that the frequency was determined by the self-induction and the capacity according the well-known formula: $p = 2\pi\sqrt{cL}$.

PAUL JANET thought the same and proposed, as DUDDELL had already done before, to use the singing arc for measuring small coefficients of self-induction.

In the way proposed by JANET, this seems to be impossible as the frequency depends not only on the self-induction and the capacity but i. a. also on the strength of the constant current.

I have investigated the variation of the frequency caused by varying the constant current, the results being stated in this paper.

The experiments were carried out after PEUKERT's method. The $P\ D$ at the solid carbons was measured by a Weston-instrument, that showed the Volts of the constant current only, and at the same time by a hot-wire Voltmeter. Lastly the current in the condenser-circuit was measured by means of a hot-wire amperemeter. The three readings being E_1, E_2 and I_2, the frequency may be calculated by

$$p = \frac{I_2}{2\pi c\sqrt{E_2^2 - E_1^2}},$$

c being the capacity of the condenser in farads.

The necessary correction of the instruments was known and has already been applied in the tables. The arc-lamp used was a small shunt-regulator by KÖRTING & MATTHIESEN.

Series 1. Capacity 2,68 mF. Selfinduction: bronze wire spiral of 80 windings; air isolation; diameter 25 centimeter, height 50 centimeter.

The table contains in the

1st column: I_1 the constant current through the arc.
2nd 〃 E_1 the constant current PD of the carbons.
3rd 〃 E_2 the hot-wire voltmeter reading.
4th 〃 E_a the value of $\sqrt{E_2^2 - E_1^2}$ being the superposed alternating volts.
5th 〃 I_2 the alternating current strength.
6th 〃 p the number of complete alternations p. s. calculated by PEUKERT's formula.

TABLE I.

I_1	E_1	E_2	E_a	I_2	p.
1.9	37.0	44.0	23.7	1.8	4520
2.2	37.0	46.0	27.4	2.4	5230
2.6	37.5	43.0	21.1	2.1	5960
2.8	37.5	44.0	23.0	2.4	6450
3.2	38.0	42.7	19.6	2.5	8000
3.7	38.0	41.0	15.5	2.7	10390
4.1	38.0	40.0	12.8	3.0	13980

Series 2. The same as in Series 1. Capacity reduced to 1.68 mF.

TABLE II.

I_1	E_1	E_2	E_a	I_2	p.
1.7	38	46	26	1.7	6200
2.4	39	46	24.5	2.1	8130
2.8	39	44	20.4	2.1	9820
3	38	42.7	19.6	2.3	11200
3.5	38.5	42	16.75	2.4	13590
3.7	38	42	18.3	2.7	13980

Series 3. Capacity 1 mF. Selfinduction: coil of 160 windings in 4 layers; wire 2 millimeters. Length of coil 8 centimeters, external diameter 3.5 centimeter.

TABLE III.

I_1	E_1	E_2	E_a	I_2	p.
1.9	38	47.7	28.7	2.4	14950
2.3	38	47	26	2.6	17240
2.6	38	45	24.5	2.9	18820
2.9	38	43	20.1	2.8	22200
3.3	37	42	19.8	3.3	26600
3.6	37	42	19.8	3.5	28160
4.1	38	41	15.4	3.4	35100

Series 4. The same as Series III. Capacity reduced to 0.5 mF.

TABLE IV.

I_1	E_1	E_2	E_a	I_2	p.
1.9	35	47	31.3	2.51	25200
2.4	36	42	21.6	2.51	36800
2.7	35	40	19.4	2.7	44300
3.1	35	39	17.2	3	55550
3.4	35	37	12	3.2	84700
3.7	35	36.5	10.36	3.3	97700
3.9	35	36.5	10.36	3.4	100500

Series 5. Capacity 1 mF. Selfinduction: coil of 40 windings in 2 layers; wire $3^1/_2$ mm. Length of coil 8 centimeter, external diameter 3.5 centimeter.

.TABLE V.

I_1	E_1	E_2	E_a	I_2	p.
1.9	38	50.4	33.2	4.68	22400
2.2	38	50.4	33.2	5.16	24700
2.6	38	50.4	33.2	5.55	26700
2.9	38	46	26.0	5.20	31800
3.2	37.6	46	26.5	6.15	37000
3.6	37	44	23.8	6.15	41200
3.7	38	43.2	22.8	6.24	43600
4.2	38	41	15.4	5.70	59200

Series 6. The same conditions as in Series 5. The capacity reduced to 0.3 mF.

TABLE VI.

I_1	E_1	E_2	E_a	I_2	p.
2.1	35	50	35.7	4.1	61300
2.4	36	47.5	31	4.2	71900
2.9	35	42	23.2	4	91600
3.6	36	40.2	17.9	4.4	130000
4.2	35	36.3	9.75	3.6	196000

Duddell attained frequencies of 500—10000 complete periods p. s. Simon increased the number of alternations so much, that the note emitted by the arc ceased to be audible. He speaks of a limit of 30000—40000 vibrations. From my tables will be seen that I have attained much higher frequencies, so high that I first distrusted them. But as yet I have not been able to find any inaccuracy either in the principle of the method or in its application. So I must think that my numbers are exact, the more so as they seem to be confirmed by a physiological estimate. With small frequencies, say up to 10000, the pitch of the note may be easily estimated by the ear when we produce two notes in rapid succession. In Series 1 I found that increasing the current from 1.9 to 2.2 ampere caused the pitch to rise about a "second". By increasing from 2.2 ampere to 3.2 ampere the successive notes sounded as with a quint-interval. The later calculation of the frequencies from the galvanometer readings agreed fairly well with the estimated increase of pitch.

The limit of audibility as calculated from the readings agreed equally with the limit as determined by the aid of a recently graduated Galton-whistle by Prof. Edelmann, the graduation-table being verified on different points by myself. I found as a limit for the audibility about 43500 d. v. p. s. My arc-lamp ceased to emit an audible note when the frequency of 42000 was reached. In the 6th series no sound was heard at all. In the series 1, 2 and 3 the sound was heard throughout. In the series 4 I heard the note distinctly at 2.4 ampere; at 2,7 ampere I did not always hear the sound; only every now and then I got the impression of a very faint and high whistling sound. At 3.1 ampere I did not hear the sound. In the 5th Series the sound was always present at 3.6 ampere and sometimes at 3.7 ampere.

As these results agree, I think that the method is a correct one, and that the higher numbers may also be relied upon.

The sound of the singing arc may prove perhaps valuable in physiological researches on sound.

The highest frequency with my apparatus was attained with a primary constant current of 4.2 ampere, $E_1 = 36$ Volt, $E_2 = 37.3$ Volt, $I_2 = 0.49$ ampere, $C = 0.03$ m.F., E_a being 9.7 Volt and $p =$ **268000**. Of course much higher frequencies may probably be attained. But the resistance of my hot-wire amperemeter was rather high, and I believe that therein lies an obstacle for my surpassing this limit.

How are we to interpret the increase of the frequency caused by an increase of the constant current? There is some analogy with the rise in pitch of electromagnetically driven tuningforks when the intensity of the currents is increased; and also with the rise of the pitch of harmoniumreeds when the air-pressure is increased. Yet there is already some difference in the origin of these last two phenomena, so as to forbid anything more than considering the analogy. The only allowed consequence is, that the electrical system consisting of a capacity and a selfinduction does in this special case not vibrate in its proper period and that this proper period might only be expected to be brought about by a hypothetic infinitely small constant current through the arc.

Increasing the P. D. at the carbons seems to lower the pitch and at the same time to increase the intensity of the sound; if the P.D. rises too much the whistling ceases all at once. As I worked with a constant E. M. F. of 110 Volts from an accumulator-battery, the primary current strength was regulated by inserting resistance or withdrawing it from the circuit. When without changing the resistance, the P. D. at the carbons rises, the current falls off and so causes the frequency to diminish at the same time. Yet by keeping the current constant, by lengthening the arc and withdrawing resistance at the same time an unmistakable lengthening of the period may be observed.

From the Tables I—VI curves have been plotted connecting the frequency with the current-strength.

It is not impossible, that a simple relation might express this connection. Yet an experimental formula as

$$p = a + b\,I + c\,I^2$$

is only possible when b is negative; as in this case there is a minimum for $I = \frac{b}{2\,c}$ this formula does not seem to be very plausible.

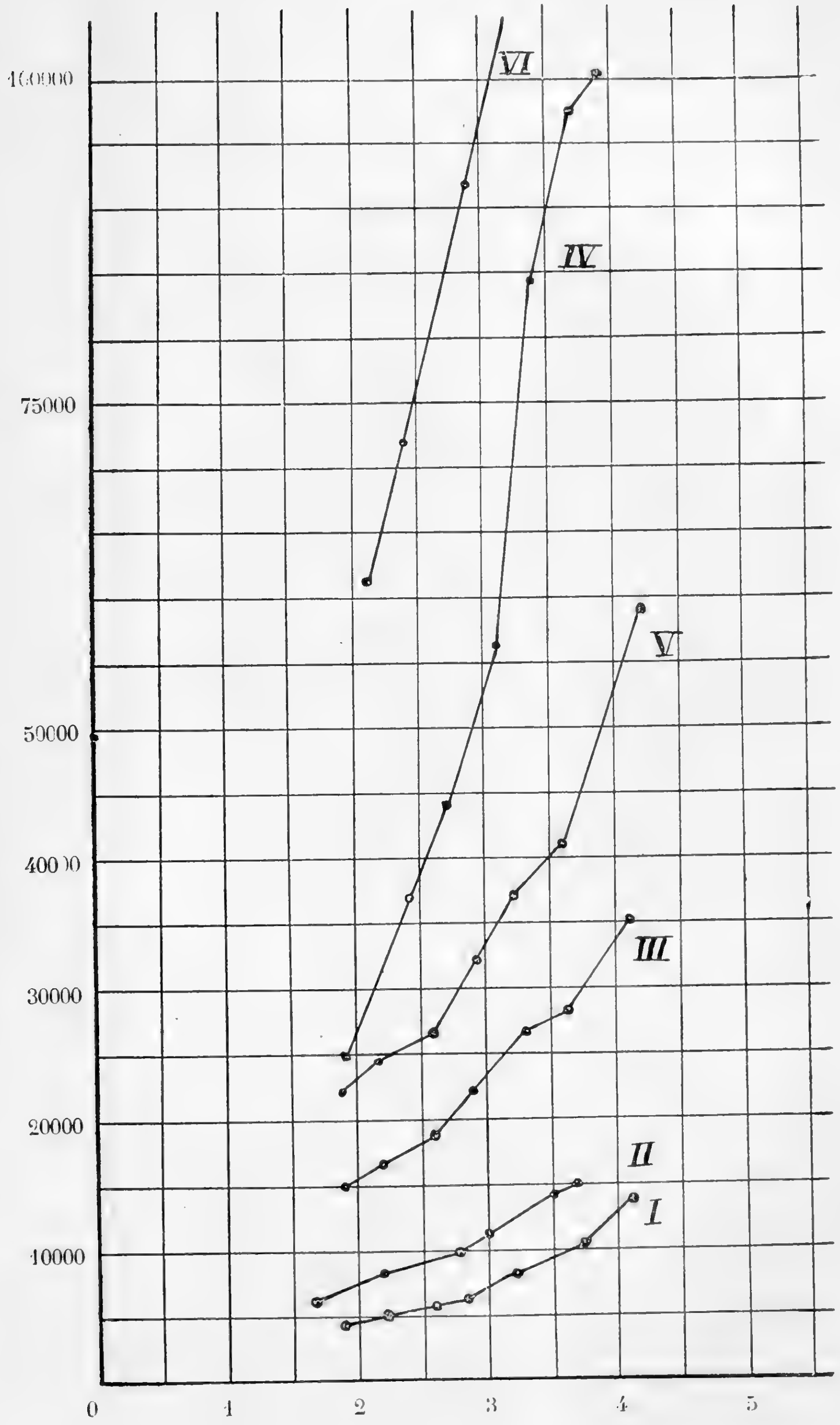
I have also tried a quadratic expression connecting the steadying resistance with the frequency, but this did not give satisfaction.

At last I found as the most simple formula and agreeing best with the observed results:

$$\log p = a + b\,I,$$

in which a and b are constants, p the frequency and I the constant current intensity.

I found for series 1:


100000
75000
50000
40000
30000
20000
10000
0
1
2
3
4
5
VI
IV
V
III
II
I

$$\log p = 3.23522 + 0.2165\, I.$$

I	$\log p$ (calc.)	$\log p$ (obs.)	ϱ	p (calc.)	p (obs.)
1.9	3.64757	3 65514	+ 0.00857	4432	4520
2.2	3.71152	3.71850	+ 0.00698	5147	5230
2.6	3.79812	3.77525	— 0.02287	6282	5960
2.8	3.84142	3.80956	— 0.03186	6941	6450
3.2	3.92802	3.90309	— 0.02493	8473	8000
3.7	4.03627	4.01662	— 0.01965	10871	10390
4.1	4.12287	4.14364	+ 0.02077	13270	13920

The mean error of $\log p$ being: $\sqrt{\frac{1}{6} \Sigma (\varrho)^2} = 0{,}02272$ the error-factor of p is 1.053 and the mean error of p is 5.3 %.

Considering that 3 galvanometer readings are necessary which individually ought to have errors of much less than 0.5 %, but which are to be taken all at the same time and therefore are more inaccurate, a mean error of 5.3 % in the result, representing an interval of less than a tone may not be called extravagant.

For series 2. I find: $\log p = 3.47786 + 0.18453\ I.$

I	$\log p$ (calc.)	$\log p$ (obs.)	ϱ	p (calc.)	p (obs.)
1.7	3.79156	3.79239	+ 0.00083	6189	6200
2.4	3.92073	3.91009	— 0.01064	8332	8130
2.8	3.99454	3.99211	— 0.00243	9875	9820
3 0	4.03145	4.04922	+ 0.01777	10751	11200
3.5	4.12371	4.13322	+ 0.00951	13296	13590
3.7	4.16062	4.14551	— 0.01511	14475	13980

$$\varrho\, m = \sqrt{\frac{1}{5} \Sigma (\varrho)^2} = 0.01228$$

the mean error of one observation being 2.867 %.

Series 3. $\log p = 3.84563 + 0.17062\ I.$

I	$\log p$ (calc.)	$\log p$ (obs.)	ρ	p (calc.)	p (obs.)
1.9	4.16981	4.17464	0.00483	14785	14950
2.3	4.23806	4.23654	0.00152	17300	17240
2.6	4.28927	4.27462	0.01465	19466	18820
2.9	4.34043	4.34635	0.00592	21900	22200
3.3	4.40868	4.42488	0.01620	25626	26600
3.6	4.45986	4.44963	0.01023	28831	28160
4.1	4.54517	4.54531	0.00014	35089	35100

$$\rho\, m = \sqrt{\frac{1}{6} \Sigma (\rho)^2} = 0.01035$$

mean error of one observation 2.412 %.

Series 4. $\log p = 3.80102 + 0.31641\ I.$

I	$\log p$ (calc.)	$\log p$ (obs.)	ρ	p (calc.)	p (obs.)
1.9	4.40220	4.40140	− 0.00080	25247	25200
2.4	4.56280	4.56585	+ 0.00305	36542	36800
2.7	4.65532	4.64640	− 0.00892	45219	44300
3.1	4.78189	4.74468	− 0.03721	60519	55550
3.4	4.87681	4.92788	+ 0.05107	75303	84700
3.7	4.97174	4.98989	+ 0.01815	93700	97700
3.9	5.03502	5.00217	− 0.03285	108400	100500

$$\rho\, m = \sqrt{\frac{1}{6} \Sigma (\rho)^2} = 0.02994$$

mean error of one observation 7.14 %.

Series 5. $\log p = 3.98960 + 0.17902\, I.$

I	$\log p$ (calc.)	$\log p$ (obs.)	ρ	p (calc.)	p (obs.)
1.9	4.32974	4.35025	+ 0.02051	21367	22400
2.2	4.38344	4.39270	+ 0.00926	24179	24700
2.6	4.45505	4.42651	— 0.02854	28513	26700
2.9	4.50876	4.50243	— 0.00633	32267	31800
3.2	4.56246	4.56820	+ 0.00574	36514	37000
3.6	4.63407	4.61490	— 0.01917	43060	41200
3.7	4.65197	4.63949	— 0.01248	44871	43600
4.2	4.74148	4.77232	+ 0.03084	55141	59200

$$\varrho\, m = \sqrt{\frac{1}{7}\,\Sigma\,(\varrho)^2} = 0.02024$$

mean error of one observation 4.77 %.

Series 6. $\log p = 4.31949 + 0.22466\, I.$

I	$\log p$ (calc.)	$\log p$ (obs.)	ρ	p (calc.)	p (obs.)
2.1	4.79128	4.78746	— 0.00382	61841	61300
2.4	4.85867	4.85673	— 0.00194	72222	71900
2.9	4.97100	4.96190	— 0.00910	93540	91600
3.6	5.12827	5.11394	— 0.01433	134360	130000
4.2	5.26306	5.29226	+ 0.02920	183257	196000

$$\varrho\, m = \sqrt{\frac{1}{4}\,\Sigma\,(\varrho)^2} = 0.01702$$

mean error of one observation 4.00 %.

The empirical formula represents fairly well the observed results in the range of the experiment. But it does not give more than that, I do not think that it may be used for extrapolating. This will be directly seen, when we extrapolate for the intensity = 0. We calculate for the frequency at the intensity = 0 in the 4th series: 6324 d. v. and in the 3rd series: 7009 d. v. Theoretically the frequency in series 4 should be exactly $\sqrt{2}$ times higher than in series 3.

A more exact method may perhaps give numbers from which a better formula might be deduced, and which at the same time might give us some insight in the phenomenon.

I have tried to get more exact numbers by means of the KUNDT dust-figures but I did not succeed, though others might. Yet the oscillatory discharge of a Leyden jar through an inductive resistance easily gave regular dust-figures. The reason why the KUNDT-method proved refractory with the singing arc, is not easy to be understood: I can only suppose that the intensity of the sound is not large enough.

Physics. — Dr. J. E. VERSCHAFFELT. "*Contributions to the knowledge of* VAN DER WAALS' *ψ-surface. VII. The equation of state and the ψ-surface in the immediate neighbourhood of the critical state for binary mixtures with a small proportion of one of the components*". Communication n°. 81 from the Physical Laboratory at Leiden, by Prof. H. KAMERLINGH ONNES. [1])

(Communicated in the meeting of June 28, 1902).

Introduction.

In Communication n°. 65 from the Physical Laboratory at Leiden [2]) I have given the first results of a treatment of my measurements on mixtures of carbon dioxide and hydrogen [3]) by the method which KAMERLINGH ONNES [4]) alone and with REINGANUM [5]) used for the measurements of KUENEN on mixtures of carbon dioxide and methyl chloride [6]). They confirm KAMERLINGH ONNES' opinion that the isothermals of mixtures of normal substances may be derived, by means of the law of corresponding states, from the general empirical reduced equation of statefor which he has given in communications nrs. 71 [7]) and 74 [8]) a development in series indicated in communication 59*a*. In this empirical reduced equation of state

$$\mathfrak{p} = \frac{\mathfrak{A}}{\lambda\mathfrak{v}} + \frac{\mathfrak{B}}{\lambda^2\mathfrak{v}^2} + \ldots. ,$$

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[1]) The translation of the first and second part of this article are treated as a whole, hence some minor changes in text will be found.

[2]) Arch. Néerl., (2), 5, 644, 1900; Comm. phys. lab. Leiden, n⁰. 65.

[3]) Thesis for the doctorate, Leiden, 1899.

[4]) Proc. Royal Acad., 29 Sept. 1900, p. 275; Comm. 59*a*.

[5]) Ibid. p. 289; Comm., n⁰. 59*b*.

[6]) Thesis for the doctorate, Leiden, 1892.

[7]) Proc. Royal Acad., June 1901; Comm., n⁰. 71.

[8]) Arch. Néerl., (2), 6, 874, 1901; Comm., n⁰. 74.

where $\mathfrak{A}$, $\mathfrak{B}$ etc. represent series of the powers of the reduced absolute temperature $\mathfrak{t}$, with co-efficients which like λ are the same for all substances, we then put:

$$\mathfrak{t} = \frac{T}{T_{xk}}, \qquad \mathfrak{p} = \frac{p}{p_{xk}}, \qquad \mathfrak{v} = \frac{v}{v_{xk}},$$

T_{xk}, p_{xk} and v_{xk} standing for the critical elements of the mixture with molecular composition x, if it remained homogeneous, while $\lambda = \frac{p_{xk}\, v_{xk}}{T_{xk}}$.

It must therefore also be possible to find expressions for the critical quantities of a mixture — these are the elements p_{xpl}, v_{xpl}, T_{xpl} of the plaitpoint and p_{xr}, v_{xr}, T_{xr} of the critical point of contact — in which only the co-efficients of the general empirical reduced equation of state and further the quantities characteristic of the mixture viz. T_{xk}, p_{xk}, v_{xk}, occur, or the co-efficients of the developments in series of these quantities in powers of x. In the case of mixtures with small values of x, it may, exclusive of exceptional cases, suffice, to a first approximation, to introduce the co-efficients:

$$\alpha = \frac{1}{T_k}\,\frac{dT_{xk}}{dx} \text{ and } \beta = \frac{1}{p_k}\,\frac{dp_{xk}}{dx}.$$

A first step towards realizing this idea of KAMERLINGH ONNES has been made by KEESOM [1]) who took for his basis the general equations by which VAN DER WAALS in his Théorie moléculaire and following papers has expressed the relation of the critical quantities and the composition; he has found what these equations would become for infinitely small x-values and has introduced into them the co-efficients α and β mentioned above, besides others which might be derived from the co-efficients of the general empirical equation of state. I have now tried to work out this idea in a method which is more closely connected to the treatment of the ψ-surface, namely by developing the co-efficients of the equation of state and the equation of the ψ-surface in the powers of x. On account of the great complication involved by the introduction of the higher co-efficients into the calculation, I have confined myself to the lower powers of x. However, the method followed by me can also be used to find the co-efficients of higher powers.

As I have confined myself to states in the neighbourhood of the critical point I could use instead of KAMERLINGH ONNES' empirical reduced equation of state the more simple one which it becomes within narrow limits of temperature and volume on developing the different

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[1]) Proc. Royal. Acad., 28 Dec. 1901, p. 293; Comm., n°. 75.

terms in powers of the small quantities $\mathfrak{v}-1$ and $\mathfrak{t}-1$. According to Van der Waals' method 1) I wrote this new equation:

$$\mathfrak{p} = 1 + \frac{\partial\mathfrak{p}}{\partial\mathfrak{t}}(\mathfrak{t}-1) + \ldots\ldots \qquad + \frac{\partial^2\mathfrak{p}}{\partial\mathfrak{v}\partial\mathfrak{t}}(\mathfrak{v}-1)(\mathfrak{t}-1) + \ . \ . \ . \quad (1)$$

where the co-efficients $\frac{\partial\mathfrak{p}}{\partial\mathfrak{t}}, \frac{\partial^2\mathfrak{p}}{\partial\mathfrak{v}\partial\mathfrak{t}}$ etc. can be immediately derived from those of the above mentioned empirical reduced equation of state.

1. *The p, v, T diagram for a simple substance in the neighbourhood of the critical point.*

In order to limit the number of the continually re-occurring factors as much as possible, I shall not write the equation of state of the pure substance in a reduced form, but thus:

$$p = k_0 + k_1(v-v_k) + k_2(v-v_k)^2 + k_3(v-v_k)^3 + \ldots\ldots = f(v) \ . \ . \quad (2)$$

where k_0, k_1, k_2 etc. are temperature functions which can be developed in powers of $T-T_k$; as for instance:

$$k_0 = k_{00} + k_{01}(T-T_k) + k_{02}(T-T_k)^2 + \ . \ . \ . \ . \quad (2')$$

and it is evident that $k_{00} = p_k$ while k_{10} and k_{20} are zero.

We might clearly find the equations of several curves in this diagram, such as: the border curve, the curve of the maximum or minimum pressures, the curve of the points of inflection etc. I shall derive the former only, chiefly in order to apply to a simple case the method of calculation to be used afterwards for finding the pressure, volume and composition of the co-existing phases with mixtures.

If v_2 and v_1 represent the molecular volumes of the vapour and of the liquid, co-existing at the temperature T under the pressure p_1, then these 3 unknown quantities will be determined by the equations:

$$p_1 = f(v_1), \qquad p_1 = f(v_2) \ . \ . \ . \ . \ . \ . \ . \ . \quad (3)$$

and by Maxwell's criterium

$$p_1(v_2-v_1) = \int_{v_1}^{v_2} p\,dv \ . \ . \ . \ . \ . \ . \ . \ . \ . \quad (4)$$

The two unknown quantities v_2 and v_1 I shall, however, replace by the two infinitely small quantities $\frac{1}{2}(v_2+v_1)-v_k=\Phi$ and $\frac{1}{2}(v_2-v_1)=\varphi$; Φ is therefore the abscissa of the diameter of the border curve for chords parallel with the v-axis, and φ is the half chord.

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1) Zeitschr. f. physik. Chem., 13, 694, 1894.

Equation (4) after division by 2 φ yields:

$$p_1=k_0+k_1\,\Phi+k_2(\Phi^2+\frac{1}{3}\varphi^2)+k_3\,\Phi(\Phi^2+\varphi^2)+k_4(\Phi^4+2\Phi^2\varphi^2+\frac{1}{5}\varphi^4)+\ldots(5)$$

where for completeness I have not regarded the order of the different terms. Also taking equation (3) once for v_1 and once for v_2 and adding together, yields:

$$p_1=k_0+k_1\Phi+k_2(\Phi^2+\varphi^2)+k_3\Phi(\Phi^2+3\varphi^2)+k_4(\Phi^4+6\Phi^2\varphi^2+\varphi^4)+\ldots(6)$$

and subtracting and dividing bij 2 φ gives

$$0=k_1+2k_2\Phi+k_3(3\,\Phi^2+\varphi^2)+4\,k_4\Phi(\Phi^2+\varphi^2)+\quad\ldots\quad(7)$$

while the, at least to a first approximation simpler equation:

$$0=\frac{2}{3}k_2+2k_3\,\Phi+4k_4\left(\Phi^2+\frac{1}{5}\varphi^2\right)+\quad\ldots\ldots\quad(8)$$

follows from (5) and (6).

The equations (6), (7) and (8) now determine the quantities Φ, φ and p_1-p_k; for we find:

$$\varphi^2=-\frac{k_{11}}{k_{30}}(T-T_k)-\quad\ldots\ldots\ldots\quad(9)$$

$$\Phi=-\frac{1}{k_{30}}\left(\frac{1}{3}k_{21}-\frac{2}{5}\frac{k_{11}\,k_{40}}{k_{30}}\right)(T-T_k)-{}^{1})\quad\ldots\quad(10)$$

$$p_1-p_k=k_{01}\,(T-T_k)+\quad\ldots\ldots\ldots\quad(11)$$

Along the border curve $v=v_k+\Phi\pm\varphi$, so that we may write the equation of the border curve:

$$0=(v-v_k)^2-2\,(v-v_k)\;\Phi+\Phi^2-\varphi^2,\;\ldots\ldots\quad(12)$$

and to the first approximation this represents a parabola [2]).

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[1]) Just as v. d. Waals (Arch. Néerl. (1), 28, 171) from the reduced equation of state $\mathfrak{p}=\dfrac{8\,\mathfrak{t}}{3\,\mathfrak{v}-1}-\dfrac{3\,e^{1-\mathfrak{t}}}{\mathfrak{v}^2}$ has derived $\frac{1}{2}(\mathfrak{v}_2-\mathfrak{v}_1)=2\sqrt{2}\,(1-\mathfrak{t})$, I have also derived $\frac{1}{2}(\mathfrak{v}_2+\mathfrak{v}_1)$ from the same equation by means of the reduced formula (10) and have found for it:

$$\tfrac{1}{2}(\mathfrak{v}_2+\mathfrak{v}_1)=1+7{,}2\,(1-\mathfrak{t}),$$

whence, if ρ_1 and ρ_2 stand for the liquid and vapour densities:

$$\tfrac{1}{2}(\rho_2+\rho_1)=\rho_k\,[1+0{,}8\,(1-\mathfrak{t})]$$

From Amagat's data for carbon dioxide I find:

$$\Delta=\tfrac{1}{2}(\rho_2+\rho_1)=0{,}464+0{,}001181\,(T_k-T),$$

or reduced $1+0{,}775\,(1-\mathfrak{t})$, and for isopentane (S. Young's data)

$$\Delta=\rho_k\,[1+0{,}881\,(1-\mathfrak{t})].$$

The above equation of state, therefore, represents the diameter numerically in a satisfactory manner.

[2]) The same problem with regard to φ has been treated by v. d. Waals (loc. cit.) in a somewhat different way; only φ is determined accurately by his method and the border curve can be derived from his formulae only to a first approximation.

2. *The p, v, T diagram of a mixture with a small value of x near the critical point of the homogeneous mixture.*

From the consideration we have started from it follows immediately that we obtain the system of isothermals of the mixture by moving that of the pure substance to an infinitely small amount parallel to itself so that the critical point (p_k, v_k) is brought on to the critical point of the homogeneous mixture (p_{xk}, v_{xk}), and at the same time by expanding it infinitely little parallel to its co-ordinates in multiplying the ordinates by $\frac{p_{xk}}{p_k}$ and the abscissae by $\frac{v_{xk}}{v_k}$. Moreover an isothermal, belonging to the temperature T in the first system will belong to the temperature $\frac{T_{xk}}{T_k} T$ after we have moved and magnified the system.

We put again:

$$p = l_0 + l_1 (v - v_{xk}) + l_2 (v - v_{xk})^2 + l_3 (v - v_{xk})^3 + \quad . \quad . \quad (13)$$

where l_0, l_1, l_2 etc. are once more functions of the temperature, thus:

$$l_0 = l_{00} + l_{01} (T - T_{xk}) + l_{02} (T - T_{xk})^2 + \quad . \quad . \quad . \quad . \quad (13')$$

According to the derivation from the reduced equation of state by means of T_{xk}, p_{xk}, v_{xk} the co-efficients l_{00}, $l_{01} \ldots . l_{10}$, l_{11} etc. are only functions of x. Putting:

$$\begin{aligned} T_{xk} &= T_k (1 + \alpha x + \alpha' x^2 + \ldots .) \\ p_{xk} &= p_k (1 + \beta x + \beta' x^2 + \ldots .) \quad . \quad . \quad . \quad . \quad . \quad (14) \\ v_{xk} &= v_k (1 + \gamma x + \gamma' x^2 + \ldots .) \end{aligned}$$

where

$$\gamma = \alpha - \beta, \quad \gamma' = \alpha' - \beta' - \alpha\beta + \beta^2 \text{ etc.}, \quad . \quad . \quad . \quad . \quad (14')$$

we find

$$\begin{aligned} &l_{00} = p_k[1 + \beta x + \ldots], \; l_{01} = k_{01}[1 - (\alpha - \beta) x + \ldots], \; l_{02} = k_{02}[1 - (2\alpha - \beta) x + \ldots], \ldots \\ &l_{10} = 0 \qquad\qquad\quad , \; l_{11} = k_{11}[1 - 2(\alpha - \beta) x + \ldots], \; l_{12} = k_{12}[1 - (3\alpha - 2\beta) x + \ldots], \ldots \\ &l_{20} = 0 \qquad\qquad\quad , \; l_{21} = k_{21}[1 - 3(\alpha - \beta) x + \ldots], \ldots \\ &l_{30} = k_{30}[1 - (3\alpha - 4\beta) x + \ldots .], \ldots . \\ &l_{40} = k_{40}[1 - (4\alpha - 5\beta) x + \ldots .], \ldots . ; \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (15) \end{aligned}$$

where all co-efficients l are expressed in co-efficients k as well as in KAMERLINGH ONNES' α's and β's.

From the values of T_{xk}, p_{xk}, v_{vk}, with mixtures of carbon dioxide with small quantities of hydrogen for $x = 0$, $x = 0{,}05$ and $x = 0{,}1$, [1] I find:

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[1] Comm., n⁰. 65.

$$\begin{aligned} T_{xk} &= T_k\,(1 - 1{,}17\,x + 1{,}58\,x^2) \\ p_{xk} &= p_k\,(1 - 1{,}62\,x + 2{,}45\,x^2)\,.\;.\;.\;.\;.\quad (16) \\ v_{xk} &= v_k\,(1 + 0{,}62\,x - 0{,}95\,x^2),\ ^{1)} \end{aligned}$$

while from (14′) would follow:

$$v_{xk} = v_k\,(1 + 0{,}45\,x + 0{,}08\,x^2).$$

Although the agreement between the two expressions for v_{xk} is not quite satisfactory, it yet by no means indicates that the law of corresponding states does not hold; it may very well be a result of the uncertainty of the critical data of the homogeneous mixtures, chiefly of the v_{xk}'s. Besides from the second formula for v_{xk} I find:

for $x = 0{,}05$ $v_{xk} = 0{,}00432$ and for $x = 0{,}1$ $v_{xk} = 0{,}00441$,

and these values deviate from those determined directly (0,00434 and 0,00444) not more than the amount of the error that can be made in these determinations. Besides, since the law of corresponding states does not hold entirely with pure substances, it is not likely to do so for mixtures.

3. *The p, v, x, diagram for mixtures with a small value of x, at a temperature differing little from T_k.*

We shall now consider different mixtures at the same temperature T; the system of isothermals in the p, v, x diagram, at that temperature is represented by the equation of state (13), where, however, T must now be taken as constant and x as variable. We will now put this equation in another and more suitable form.

Among all the mixtures there is one for which the critical temperature would be T if this mixture remained homogeneous; the composition x_{Tk} of this mixture, and also the critical elements p_{Tk} and v_{Tk} are determined by equation (14). (In this equation we must put: $T_{xk} = T$, $x = x_{Tk}$, $p_{xk} = p_{Tk}$ and $v_{xk} = v_{Tk}$).

Hence we find to a first approximation

$$x_{Tk} = \frac{T - T_k}{\alpha\,T_k},\quad p_{Tk} = p_k + \frac{p_k\beta}{\alpha\,T_k}\,(T - T_k),\quad v_{Tk} = v_k + \frac{v_k(\alpha - \beta)}{\alpha\,T_k}\,(T - T_k).\ (17)$$

It will be seen that to a first approximation the value x_{Tk} is either positive or negative according as $T - T_k$ and α have the same or opposite signs, that is to say

	$\alpha > 0$	$\alpha < 0$
$T > T_k$	$x_{Tk} > 0$; figs. 1 and 7	$x_{Tk} < 0$; figs. 3, 5, 9 and 11
$T < T_k$	$x_{Tk} < 0$; figs. 2 and 8	$x_{Tk} > 0$; figs. 4, 6, 10 and 12

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[2]) Comp. also KEESOM, *loc. cit.*, p. 12.

Although from a physical point of view x can only take positive values, in these considerations even the case $x_{Tk} < 0$ is not impossible; for the point p_{Tk}, v_{Tk} has only a mathematical meaning.

In general, equation (13) may now be written thus:

$$p = m_0 + m_1 (v - v_{Tk}) + m_2 (v - v_{Tk})^2 + m_3 (v - v_{Tk})^3 + \ldots, \quad . \quad (18)$$

where m_0, m_1 etc. are functions of x which can be developed in powers of $x - x_{Tk}$; for instance:

$$m_0 = m_{00} + m_{01} (x - x_{Tk}) + m_{02} (x - x_{Tk})^2 + \ldots \quad . \quad . \quad (18')$$

The co-efficients m are functions of the temperature which is here considered constant; it will be obvious that $m_{00} = p_{Tk}$, while m_{10} and $m_{20} = 0$. By equalization of (18) with (13) we can express all the m's in the k's, and in Kamerlingh Onnes' α's and β's; for we find:

$$m_{n0} = k_{n0} - \frac{k_{n0}}{T_k \alpha} [n\alpha - (n+1)\beta] (T - T_k) + \ldots .$$

$$m_{n1} = -k_{n0} [n\alpha - (n+1)\beta] - k_{n1} T_k \alpha - (n+1) k_{(n+1)0} (\alpha - \beta) v_k + \ldots, \text{etc.} \quad (19)$$

so that to a first approximation:

$$m_{30} = k_{30}, \quad m_{40} = k_{40}, \ldots .$$

$$m_{01} = p_k \beta - k_{01} T_k \alpha, \; m_{11} = - k_{11} T_k \alpha, \; m_{21} = - k_{21} T_k \alpha - 3 k_{30} v_k (\alpha - \beta), \; \text{etc.} \quad (19')$$

Hartman [1]) has given a diagrammatical representation of the p, v, x diagram. This representation completely resembles a p, v, T diagram; but this resemblance is not necessary. It follows directly from the p, v, T diagram that k_{01} is positive, while k_{11} and k_{30} are negative; in the p, v, x diagram m_{30} is negative, but according to (19), m_{01} and m_{11} may be either positive or negative. The circumstance $m_{01} < 0$ does not indeed influence the general shape of the diagram; it indicates that the isothermals of the mixtures lie below those of the pure substance as is the case at the upper limit ($x = 1$) of Hartman's representation [2]). But while in the p, v, T diagram the isothermals with maximum and minimum pressure occur under the critical, the opposite may be the case in the p, v, x diagram, if m_{01} and m_{11} have the same sign. The four cases which may now present themselves, leaving out very particular values of the coefficients, are given in the following table:

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[1]) Thesis for the doctorate, Leiden 1899, p. 6; Journ. of Phys. Chem., 5, 425, 1901.

[2]) From a mathematical point of view we may imagine the p, v, x diagram to be continued outside the limits $x = 0$ and $x = 1$. It is also obvious that x, if differing little from 1, means the same as x infinitely small and that $x > 1$ means the same as $x < 0$.

	$m_{01} > 0$ or $\frac{\beta}{\alpha} > \frac{T_k}{p_k} k_{01}$	$m_{01} < 0$ or $\frac{\beta}{\alpha} < \frac{T_k}{p_k} k_{01}$
$m_{11} > 0$ or $\alpha > 0$	figs. 1 and 2 [1]	figs. 7 and 8
$m_{11} < 0$ or $\alpha < 0$	figs. 3, 4, 5 and 6	figs. 9, 10, 11 and 12.

HARTMAN's diagram represents at the lower limit the case $m_{01} > 0$ and $m_{11} < 0$, at the superior $m_{01} < 0$ and $m_{11} > 0$. The case $\alpha > 0$ will in general occur when the second is less volatile than the first substance; this for instance is the case when methyl chloride is added to carbon dioxide [2]. On the other hand we shall find the case $\alpha < 0$ when the second substance is the more volatile, when for instance hydrogen is added to carbon dioxide (comp. formulae 16) or carbon dioxide to methyl chloride [3].

A p, v, x diagram based on observations has, so far as I know, not yet been published. A diagram of this kind which I have drawn from my measurements on mixtures of carbon dioxide and hydrogen perfectly resembles the p, v, T diagram after HARTMAN, so that in the neighbourhood of pure carbon dioxide we must have $m_{01} > 0$ and $m_{11} < 0$; according to formula (16) α is really negative, while with $k_{01} = 1{,}61$ (comp. KEESOM *loc. cit.*, p. 14) I find $m_{01} = 454$, and positive. For carbon dioxide with a small quantity of methyl chloride [4] $\alpha = 0{,}378$ and $\beta = 0{,}088$, and hence $m_{01} < 0$ and $m_{11} > 0$; and for methyl chloride with a small quantity of carbon dioxide, $\alpha = -\ 0{,}221$ and $\beta = 0{,}281$ so that $m_{01} > 0$ and $m_{11} < 0$. At temperatures between the critical temperatures of the two pure substances, the p, v, x diagram for mixtures of carbon dioxide and methyl chloride will probably correspond to HARTMAN's drawing.

While two neighbouring isothermals (T, $T + dT$) never intersect in the p, v, T diagram (the $\left(\frac{\partial p}{\partial T}\right)_v$ never being zero) this may be the case in the p, v, x diagram for two neighbouring mixtures

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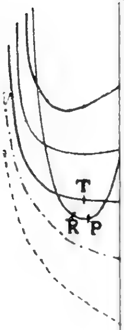
[1] Figs. 1—13 represent diagrammatically p, v, x curves for infinitely small values of x and $T—T_k$, such as they appear in reality for finite values of x and $T—T_k$. They are moreover theoretically extended into the imaginary region $x < 0$. All lines lying within the region of negative x are dotted; the isothermal $x = 0$ is represented by a dot-dash line. The line $x = x_{Tk}$ (erroneously marked x_T in figs. 1—12) would be the critical isotherm of the homogeneous mixture.

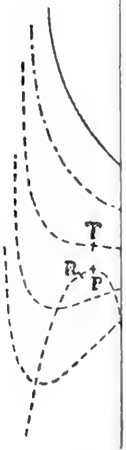
[2] Comp. KAMERLINGH ONNES and REINGANUM, *loc. cit.*, p. 35.

[3] *Ibidem.*

[4] Comp. KEESOM, Comm. n⁰. 79, p. 8.



$m_{01} > 0 \quad > 0.\ R$



$m_{01} > 0,\ \alpha < 0,$

J. E. VERSCHAFFELT. "Contributions to the knowledge of van der Waals' ψ-surface. VII. The equation of state and the ψ-surface in the immediate neighbourhood of the critical state for binary mixtures with a small proportion of one of the components."

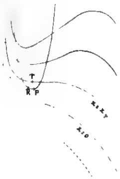


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Fig. 1

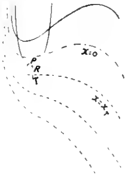

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Fig. 2

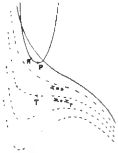

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Fig. 3

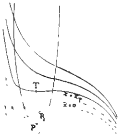

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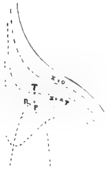
Fig. 4



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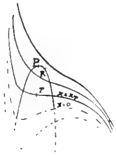

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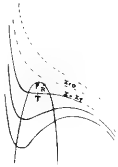

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Fig. 7

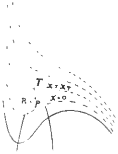

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Fig. 8

[illegible]

Fig. 9

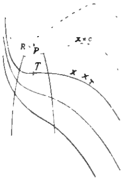

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Fig. 10

[illegible]

Fig. 11

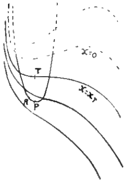

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Fig. 12

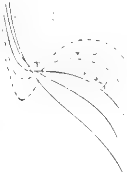

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Fig. 13

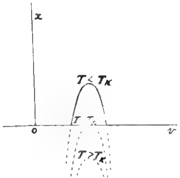

Fig. 14

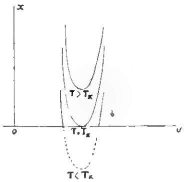

Fig. 15

(x and $x+dx$). If this point of intersection is situated at a finite distance from the point p_{Tk}, v_{Tk}, it lies outside the limits we are considering; but if it lies infinitely near this point, then it practically co-incides with it; then $m_{01}=0$ and all the isothermals in the neighbourhood will intersect each other approximately at the point p_{Tk}, v_{Tk}. This case is shown in fig. 13, where I have also supposed $a<0$ and $T<T_k$. The isothermals intersect in pairs, and the curve formed by all the points of intersection of two consecutive isothermals, also passes through the critical point (p_{Tk}, v_{Tk}); this is represented in fig. 13. The connecting line of the points of contact envelops the isothermals; its equation is found by eliminating x from equation (18) and from $\frac{\partial p}{\partial x}=0$, where we also put $m_{01}=0$; hence we find to the first approximation:

$$p-p_{Tk}=-\frac{1}{4}\frac{m^2_{11}}{m_{02}}(v-v_{Tk})^2.$$

This parabola is turned upwards (as in fig. 13) if m_{02} is negative.

4. *The ψ-surface.*

In order to find from equation (18) the phases co-existing at the temperature T, I shall make use of the properties of the ψ-surface of VAN DER WAALS. The equation of that surface is:

$$\psi=-\int pdv+RT\,[\,x\,log\,x+(1-x)\,log\,(1-x)\,]\,,$$

where R is the gas constant for a gramme molecule, hence the same quantity for all substances. Neglecting the linear functions of x, we may write:

$$\psi=-m_0\,(v-v_{Tk})-\frac{1}{2}m_1\,(v-v_{Tk})^2-\frac{1}{3}m_2\,(v-v_{Tk})^3-\frac{1}{4}m_3\,(v-v_{Tk})^4+\dots$$

$$+RT\,[x\,log\,x+\frac{1}{2}x^2+\frac{1}{6}x^3+\dots] \quad . \quad . \quad , \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (20)$$

5. *The co-existing phases.*

The co-existing phases are now determined by the co-existence conditions:

$$\left(\frac{\partial\psi}{\partial v}\right)_2=\left(\frac{\partial\psi}{\partial v}\right)_1\,,\quad\left(\frac{\partial\psi}{\partial x}\right)_2=\left(\frac{\partial\psi}{\partial x}\right)_1\quad\text{and}\quad\mu_2=\mu_1\quad . \quad . \qquad (21)$$

if μ represents the thermodynamic potential:

$$\mu=\psi-v\frac{\partial\psi}{\partial v}-x\frac{\partial\psi}{\partial x}\,.$$

Instead of the third condition I find it however better to use another which follows from all three, viz.

$$M_2 = M_1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (21')$$

where

$$M = \psi - (v - v_{Tk}) \frac{\partial \psi}{\partial v} - (x - x_{Tk}) \frac{\partial \psi}{\partial x} .$$

Corresponding to a former transformation now I write

$$\tfrac{1}{2}(v_2 + v_1) - v_{Tk} = \Phi \quad \text{and} \quad \tfrac{1}{2}(v_2 - v_1) = \varphi$$

and equally

$$\tfrac{1}{2}(x_2 + x_1) - x_{Tk} = \Xi \quad \text{and} \quad \tfrac{1}{2}(x_2 - x_1) = \xi,$$

and I consider the infinitely small quantities Φ, φ, Ξ and ξ as functions of the same variable, viz. $p_1 - p_{Tk}$. Thus I find to the first approximation [1])

$$\Phi = -\frac{1}{2m_{30}} \left[\frac{1}{3} \frac{m^3_{01}}{R^2 T^2} + \frac{m_{01} m_{11}}{RT} + \frac{2}{3} m_{21} - \frac{4}{5} \frac{m_{40}}{m_{30}} \left(\frac{m^2_{01}}{RT} + m_{11} \right) \right] \frac{p_1 - p_{Tk}}{m_{01}}$$

$$- \frac{m_{01}}{2RTm_{30}} \left[\frac{1}{3} \frac{m^2_{01}}{RT} + m_{11} - \frac{4}{5} \frac{m_{01} m_{40}}{m_{30}} \right] x_{Tk} \quad . \quad . \quad . \quad . \quad (22)$$

$$\varphi^2 = -\frac{1}{m_{30}} \left[\frac{m^2_{01}}{RT} + m_{11} \right] \frac{p_1 - p_{Tk}}{m_{01}} - \frac{m^2_{01}}{RTm_{30}} x_{Tk}, \quad . \quad . \quad (23)$$

$$\Xi = \frac{p_1 - p_{Tk}}{m_{01}}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (24)$$

and

$$\xi = \frac{m_{01}}{RT} \varphi \left[\frac{p_1 - p_{Tk}}{m_{01}} + x_{Tk} \right]; \quad . \quad . \quad . \quad . \quad . \quad . \quad (25)$$

where x_{Tk} and p_{Tk} may be replaced by their expression (17).

6. *The plaitpoint.*

In the plaitpoint the co-existing phases become identical. If we represent the elements of the plaitpoint by x_{Tpl}, p_{Tpl} and v_{Tpl} then

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[1]) The four equations from which I derive the relations (22)—(25) are:

$$\left(\frac{\partial \psi}{\partial x}\right)_2 = \left(\frac{\partial \psi}{\partial x}\right)_1, \; M_2 = M_1, \; \left(\frac{\partial \psi}{\partial v}\right)_2 = \left(\frac{\partial \psi}{\partial v}\right)_1 \text{ and } p_1 \doteq -\tfrac{1}{2} \left[\left(\frac{\partial \psi}{\partial v}\right)_2 + \left(\frac{\partial \psi}{\partial v}\right)_1 \right].$$

The two first equations contain the expression $log \frac{x_2}{x_1}$; as all the other terms are infinitely small, this must also be the case with $log \frac{x_2}{x_1}$, in other words, the ratio $\frac{x_2}{x_1}$ can differ only infinitely little from 1; ξ must therefore be of a higher order than Ξ, so that also $log \frac{x_2}{x_1}$ may be developed in a series in powers of $\frac{\xi}{\Xi + x_{Tk}}$.

at that point $\Phi = v_{Tpl} - v_{Tk}$, $\varphi = 0$, $\Xi = x_{Tpl} - x_{Tk}$ and $\xi = 0$, while $p_1 = p_{Tpl}$; thus we obtain, from the equations (22), (23) and (24),

$$x_{Tpl} = \frac{RTm_{11}}{m^2_{01} + RTm_{11}} x_{Tk}\,, \quad . \quad . \quad . \quad . \quad . \quad . \quad (26)$$

$$p_{Tpl} = p_{Tk} - \frac{m^3_{01}}{m^2_{01} + RTm_{11}} x_{Tk}\,, \quad . \quad . \quad . \quad . \quad (27)$$

and

$$v_{Tpl} = v_{Tk} + \frac{m_{01}}{2m_{30}(m^2_{01} + RTm_{11})}\left[\frac{2}{3} m_{01} m_{21} - \frac{1}{3} \frac{m^2_{01} m_{11}}{RT} - m^2_{11}\right] x_{Tk}. \text{ [1]} (28)$$

If x_{Tk}, p_{Tk}, and v_{Tk} are replaced by their expressions (17), the elements of the plaitpoint are thereby determined to the first approximation as functions of the temperature T; RTm_{11} may then be replaced by $RT_k m_{11}$.

From equations (26) and (27) follows immediately :

$$\frac{p_{Tpl} - p_{Tk}}{x_{Tpl} - x_{Tk}} = m_{01} \quad . \quad . \quad , \quad . \quad . \quad . \quad . \quad (29)$$

In order to see how this relation holds for mixtures of carbon dioxide and hydrogen I consider the temperature 27,10° C. at which the mixture $x = 0{,}05$ has its plaitpoint ($p_{Tpl} = 91{,}85$ atm.); at that temperature $x_{Tk} = 0{,}011$ and $p_{Tk} = 72{,}4$ atm. so that $\dfrac{p_{Tpl} - p_{Tk}}{x_{Tpl} - x_{Tk}} = 500$, in good agreement with the value 454 which I have found for m_{01}.

It follows from equation (26) that x_{Tpl} can be positive or negative. As $x_{Tk} < 0$ is not impossible, this is equally the case with x_{Tpl}. It is true that from a purely physical point of view the ψ-surface, only exists between the limits $x = 0$ and $x = 1$ (in our case $x > 0$), but from a mathematical point of view we can imagine this surface to extend also beyond those limits [2]. If we consider a temperature lying above the critical temperatures of the two components of a mixture, then there are, exceptional cases excluded (HARTMAN's 3d type), no co-existing phases, that is to say the real ψ-surface does not show a plait, although formula 26 shows that there is a plait-

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[1] If we take the value of x_{Tk} from the equation (26), insert it in (27) and (28), and finally introduce the k's, α's and β's, the formulae (27) and (28) become KEESOM's formulae (2*b*) and (2*c*) (Comm. n⁰. 75), while (26) corresponds to KEESOM's formula (2*a*).

[2] Outside the limits $x = 0$ and $x = 1$ ψ is imaginary owing to the presence of terms with *log* x and *log* $(1-x)$. Although this is the case the co-existing phases beyond those limits are real, as the co-existence conditions contain the necessarily real expressions $\log \dfrac{x_2}{x_1}$ and $\log \dfrac{1-x_2}{1-x_1}$.

point on the imaginary part of it. If the temperature is lower than the critical temperatures of the two components the plait occurs between the limits $x = 0$ and $x = 1$, but, except for mixtures of the second type, according to formula 26 the plaitpoint lies outside these limits. Hence the case is physically not without significance, but the plaitpoint cannot be observed.

Equation (26) may be written:

$$x_{Tpl} = \frac{RT_k k_{11}}{RT^2_k k_{11} a - m^2_{01}} (T - T_k) , \quad . \quad . \quad . \quad . \quad (26')$$

and this form shows that x_{Tpl} will be positive or negative as $T - T_k$ and $RT^2_k k_{11} a - m^2_{01}$ have different or the same signs. $RT^2_k k_{11} a > m^2_{01}$ is only possible if $a < 0$; $RT^2_k k_{11} a < m^2_{01}$ will always be the case if $a > 0$, but may occur with $a < 0$. The different cases that may occur are shown in the following table.

	$RT^2_k k_{11} a > m^2_{01}$	$RT^2_k k_{11} a < m^2_{01}$	
		$a > 0$	$a < 0$
$T > T_k$	$0 > x_{Tk} > x_{Tpl}$ figs. 5 and 11	$x_{Tk} > x_{Tpl} > 0$ figs. 1 and 7	$x_{Tpl} > 0 > x_{Tk}$ figs. 3 and 9
$T < T_k$	$x_{Tpl} > x_{Tk} > 0$ figs. 6 and 12	$0 > x_{Tpl} > x_{Tk}$ figs. 2 and 8	$x_{Tk} > 0 > x_{Tpl}$ figs. 4 and 10

7. *The border curve in the p, v, x diagram at the temperature T.*

Along the border curve $v = v_{Tk} + \Phi \pm \varphi$, so that the equation of the border curve may be written

$$0 = (v - v_{Tk})^2 - 2\,\Phi\,(v - v_{Tk}) + \Phi^2 - \varphi^2 \quad . \quad . \quad . \quad . \quad (30)$$

where Φ and φ must be replaced by the expressions as functions of p_1. To the first approximation we can take therefor the expressions (22) and (23) and neglect Φ^2; the equation (30) then represents a parabola of the second degree. The apex of this parabola does not, as in the p, v, diagram of a simple substance co-incide with the critical point (p_{Tk}, v_{Tk}), but with the plaitpoint.

Along that parabola

$$\frac{d^2p}{dv^2} = - \frac{2\, m_{01}\, m_{30} RT_k}{m^2_{01} + RT_k m_{11}} = \frac{2\, m_{01}\, k_{30}\, RT_k}{RT^2_k k_{11} a - m^2_{01}} \quad . \quad . \quad . \quad (31)$$

This expression is either positive or negative; that is to say that the border curve may be turned with its convex side towards the v-axis, while in the p, v, diagram for a simple substance the border curve is always concave to the v-axis. $\frac{d^2p}{dv^2}$ will be positive if m and $RT^2{}_k k_{11} \alpha - m^2{}_{01}$ have different signs, and will be negative in the other case:

	$RT^2{}_k\, k_{11}\, \alpha > m^2{}_{01}$	$RT^2{}_k\, k_{11}\, \alpha < m^2{}_{01}$
$m > 0$	figs. 5 and 6	figs. 1—4
$m_{01} < 0$	figs. 11 and 12	figs. 7—10

8. *The projection of the connodal line on the x, v plane.*

The equation of this curve has been given by KORTEWEG 1). In connection with our preceding formulae it is most easily derived from equation (30) by expressing p in terms of x and v by means of the equation of state (18). I shall now bring it in a form analogous to (30).

The border curve intersects the isothermal of the mixture x at two points (p'_1, v'_1), and (p'_2, v'_2) which indicate the phases where the condensation begins and ends. I again make:

$$\tfrac{1}{2}(v'_2 + v'_1) - v_{Tk} = \Phi',\ \tfrac{1}{2}(v'_2 - v'_1) = \varphi'$$

$$\tfrac{1}{2}(p'_2 + p'_1) - p_{Tk} = \Pi' \text{ and } \tfrac{1}{2}(p'_2 - p'_1) = \pi',$$

and consider the four infinitely small quantities Φ', φ', Π' and π' as functions of x.

By expressing that the two points are situated on the isothermal (18) and on the border curve (30), I obtain four equations from which the relations we want can be derived. In this way I obtain to the first approximation,

$$\Phi' = -\frac{1}{2m_{30}}\left[\frac{1}{m_{01}}\left(\frac{m^2{}_{01}}{RT} + m_{11}\right)^2 - \frac{2}{3}\frac{m^3{}_{01}}{R^2T^2} + \frac{2}{3}m_{21} - \frac{4m_{40}}{5m_{30}}\left(\frac{m^2{}_{01}}{RT} + m_{11}\right)\right]x +$$
$$+ \frac{1}{2m_{30}}\left[\frac{m_{11}}{m_{01}}\left(\frac{m^2{}_{01}}{RT} + m_{11}\right) + \frac{2}{3}m_{21} - \frac{4}{5}\frac{m_{11}m_{40}}{m_{30}}\right]x_{Tk} \quad . \; . \; . \; . \; . \; . \quad (32)$$

$$\varphi'^2 = -\frac{1}{m_{30}}\left[\frac{m^2{}_{01}}{RT} + m_{11}\right]x + \frac{m_{11}}{m_{30}}x_{Tk}, \quad . \; . \; . \; . \quad (33)$$

$$\Pi' = m_{01}(x - x_{Tk}), \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (34)$$

and

$$\pi' = m_{11}(x - x_{Tk})\,\varphi'. \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (35)$$

---

1) Wien. Ber. 98, 1159, 1889.

Now we may again write for the equation of the connodal line

$$0 = (v - v_{Tk})^2 - 2\,\Phi'\,(v - v_{Tk}) + \Phi'^2 - \varphi'^2. \quad . \quad . \quad . \quad (36)$$

To the first approximation along this curve

$$\frac{d^2x}{dv^2} = -\frac{2m_{30}\,RT_k}{m^2_{01} + RT_k\,m_{11}} = \frac{2k_{30}\,RT_k}{RT^2_k\,k_{11}a - m^2_{01}} \quad . \quad . \quad . \quad (37)$$

and this expression has the opposite sign to $RT^2_k\,k_{11}\,a - m^2_{01}$. Here therefore we distinguish only two cases.

1. $RT^2_k\ k_{11}\ a > m^2_{01}$; $\frac{d^2x}{dv^2} < 0$, i. e. the connodal line turns its concave side towards the v-axis (fig. 14);

2. $RT^2_k\ k_{11}\ a < m^2_{01}$; $\frac{d^2x}{dv^2} > 0$ and the connodal line is convex to the v-axis (fig. 15).

9. *The critical point of contact.*

The characteristic of the critical point of contact is that there the two phases with which the condensation begins and ends coincide. If x_{Tr}, p_{Tr} and v_{Tr} represent the elements of that point we have there

$$\Phi' = v_{Tr} - v_{Tk},\ \varphi' = 0,\ \Pi' = p_{Tr} - p_{Tk},\ \pi' = 0 \text{ and } x = x_{Tr}.$$

and from (33) it follows that

$$x_{Tr} = \frac{RT_k\,m_{11}}{m^2_{01} + RT_k\,m_{11}}\,x_{Tk}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (38)$$

that is to say to the first approximation the composition at the critical point of contact is the same as at the plaitpoint (cf. 26). The different cases which may occur now follow.

1. $RT^2_k\,k_{11}\,a > m^2_{01}$ (fig. 14).

a). $T > T_k$; x_{Tr} is negative and there is no connodal line inside the region that can be observed. This corresponds to the position of the border curve in figs. 5 and 11.

b) $T = T_k$; $x_{Tr} = 0$ and the formula (30) represents a connodal line which touches the v-axis.

c) $T < T_k$; $x_{Tr} > 0$ and there is a connodal line in the region of positive x, (see also figs. 6 and 12).

2. $RT^2_k\,k_{11}\,a < m^2_{01}$ (fig. 15).

a) $T > T_k$; $x_{Tr} > 0$ and the connodal line lies entirely within the region that can be observed; (figs. 1, 3. 7 and 9).

b) $T = T_k$; $x_{Tr} = 0$ and the connodal line touches the v-axis;

c) $T < T_k$; $x_{Tr} > 0$ and the connodal line can only be completed by prolonging it in the region of the negative x (fig. 2, 4, 8 and 10).

Equation (34) gives :

$$p_{Tr} = p_{Tk} + m_{01}\,(x_{Tr} - x_{Tk}) = p_{Tk} - \frac{m^3_{01}}{m^2_{01} + RT_k m_{11}}\,x_{Tk}\,, \quad . \quad (39)$$

so that also to the first approximation $p_{Tr} = p_{Tpl}$ (comp. equation 27). And from the equation (32) we derive in connection with (38):

$$v_{Tr} = v_{Tk} + \frac{1}{3}\,\frac{m^2_{01}}{m_{30}(m^2_{01} + RT_k m_{11})}\left(m_{21} + \frac{m_{01} m_{11}}{RT_k}\right) x_{Tk}\,, \quad . \quad . \quad (40)$$

from which by comparison with (28) we find

$$v_{Tr} - v_{Tpl} = \frac{1}{2}\,\frac{m_{01} m_{11}}{RT_k m_{30}}\,x_{Tk} = -\frac{1}{2}\,\frac{k_{11}\,m_{01}}{RT_k k_{30}}\,(T - T_k) \quad . \quad . \quad (41)$$

The difference $v_{Tr} - v_{Tpl}$ may be positive or negative, that is to say the critical point of contact may be situated on the vapour or on the liquid branch of the border curve (or of the connodal line). In the first case, as it is well-known, we have retrograde condensation of the first type for all mixtures comprised between x_{Tr} and x_{Tpl}, in the second case retrograde condensation of the second type :

$T > T_k$	$v_{Tr} < v_{Tpl}$; r. c. II; figs. 1,3 and5	$v_{Tr} > v_{Tpl}$; r. c. I; figs. 7,9 and11
$T < T_k$	$v_{Tr} > v_{Tpl}$; r. c. I; figs. 2, 4and6	$v_{Tr} < v_{Tpl}$;r.c.II;figs.8,10and12

Expressing that the plaitpoint and the critical point of contact lie on the connodal line and subtracting the equations thus obtained we find to the second approximation :

$$x_{Tr} - x_{Tpl} = \frac{1}{4}\,\frac{m^2_{01}\,m^2_{11}}{RT_k\,m_{30}\,(m^2_{01} + RT_k\,m_{11})}\,x^2_{Tk}\,; \quad . \quad . \quad (42)$$

this expression is positive if $RT^2_k\,k_{11}\,a > m^2_{01}$ (fig. 14), and negative if $RT^2_k\,k_{11}\,a < m^2_{01}$ (fig. 15). In the same way we find by means of the border curve

$$p_{Tr} - p_{Tpl} = -\frac{1}{4}\,\frac{m^3_{01}\,m^3_{11}}{RT_k\,m_{30}\,(m^2_{01} + RT_k\,m_{11})}\,x^2_{Tk} \quad . \quad . \quad (43)$$

so that

	$m_{01} > 0$	$m_{01} < 0$
$RT^2_k\,k_{11}\,a > m^2_{01}$	$p_{Tr} < p_{Tpl}$; figs. 5 and 6	$p_{Tr} > p_{Tpl}$; figs. 11 and 12
$RT^2_k\,k_{11}\,a < m^2_{01}$	$p_{Tr} > p_{Tpl}$; figs. 1—4	$p_{Tr} < p_{Tpl}$; figs. 7—10

(To be continued).

Physics. — Dr. J. E. VERSCHAFFELT: "*Contributions to the knowledge of* VAN DER WAALS' *ψ-surface. VII. The equation of state and the ψ-surface in the immediate neighbourhood of the critical state for binary mixtures with a small proportion of one of the components.*" (Continued). Communication n°. 81 from the physical Laboratory at Leiden, by Prof. H. KAMERLINGH ONNES. [1])

(Communicated in the meeting of Sept. 27, 1902).

10. *The border curve and the connodal line in special cases.*

1. When $m_{01}=0$, i. e. $p_k\beta = k_{01}\, T_k\, \alpha$, all isotherms intersect one another nearly at the critical point (p_{Tk}, v_{Tk}) as we have seen in § 3; according to the equations (26), (27) and (28) the plaitpoint coincides in that case with this critical point. Besides from (31) it follows that $\frac{d^2p}{dv^2}=0$; this value however belongs to $\frac{d^2p}{dv^2}$ only to the first approximation (i. e. at the critical point itself), or the border curve is a parabola of a higher degree than the second. In fact we find in this case:

$$\Phi = -\frac{1}{2m_{30}}\left(\frac{2}{3}m_{21}-\frac{4}{5}\frac{m_{11}\,m_{40}}{m_{30}}\right)\Xi, \quad \varphi^2=-\frac{m_{11}}{m_{30}}\,\Xi, \text{ and}$$

$$p_1-p_{Tk}=\left(m_{02}-\frac{1}{3}\frac{m_{11}\,m_{21}}{m_{30}}\right)\Xi^2;$$

and therefore the border curve to the first approximation becomes a parabola of the fourth degree; the equation of that parabola is:

$$p-p_{Tk}=\frac{m^2_{30}}{m^2_{11}}\left(m_{02}-\frac{1}{3}\frac{m_{11}\,m_{21}}{m_{30}}\right)(v-v_{Tk})^4.$$

The connodal line, however, remains a parabola of the second degree, on which $\frac{d^2x}{dv^2}=\frac{2k_{30}}{T_k\,k_{11}\,\alpha}$.

2. A second remarkable case is that where $RT_km_{11}+m^2_{01}=0$; for then the term p_1-p_{Tk} disappears from the expression for φ^2 (equation 23), so that φ becomes of the first order with respect to p_1-p_{Tk}. We then find:

$$\Phi=-\frac{1}{3m_{30}}\left(\frac{m_{01}\,m_{11}}{RT_k}+m_{21}\right)\frac{p_1-p_{Tk}}{m_{01}}-\frac{m_{01}}{RT_km_{30}}\left(\frac{1}{3}m_{11}-\frac{2}{5}\frac{m_{01}\,m_{40}}{m_{30}}\right)x_{Tk}$$

and

$$\varphi^2=\frac{m_{11}}{m_{30}}x_{Tk}-\frac{1}{m_{30}}\left(\frac{5}{2}\frac{m_{01}m_{02}}{RT_k}-\frac{1}{3}\frac{m^2_{01}m^2_{11}}{R^2T_k^2m_{30}}+\right.$$
$$\left.+\,m_{11}+m_{12}-\frac{2}{3}\frac{m_{01}m_{11}m_{21}}{RT_km_{30}}-\frac{1}{3}\frac{m^2_{21}}{m_{30}}\right)\left(\frac{p_1-p_{Tk}}{m_{01}}\right)^2;$$

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[1]) Comp. Proceedings Royal Acad. of Sciences Sept. 1902.

in the last term I shall express the co-efficient of $(p_1 - p_{Tk})^2$ for convenience by K.

Substituting this in equation (30) we obtain to the first approximation an equation of the second degree, which now no longer represents a parabola but an ellipse or a hyperbola. The coordinates of the centre are:

$$p_c = p_{Tk} \quad \text{and} \quad v_c = v_{Tk} - \frac{m_{01}}{RT_k m_{30}}\left(\frac{1}{3} m_{11} - \frac{2}{5} \frac{m_{01} m_{40}}{m_{30}}\right) x_{Tk},$$

while the straight lines

$$p = p_{Tk} \quad \text{and} \quad v = v_{Tk} + \Phi$$

are conjugate axes. With respect to these axes the coordinates of the border curve are φ and $p_1 - p_{Tk}$, so that the equation of the border curve with respect to those axes is:

$$\varphi^2 - K(p - p_{Tk})^2 = \frac{m_{11}}{m_{30}} x_{Tk} = -\frac{k_{11}}{k_{30}} (T - T_k).$$

In the same case the equation of the connodal line is:

$$\varphi'_2 - K m^2_{01} (x - x_{Tk})^2 = -\frac{k_{11}}{k_{30}} (T - T_k),$$

with respect to the conjugate axes:

$$x = x_{Tk} \quad \text{and} \quad v = v_{Tk} + \Phi';$$

where Φ' is obtained through substituting $x - x_{Tk}$ for $\dfrac{p_1 - p_{Tk}}{m_{01}}$ in Φ.

We must now distinguish two cases.

a. $K < 0$; the equations of the border curve and the connodal line represent ellipses. Provided $k_{11} < 0$ and $k_{30} < 0$ these ellipses are real when $T < T_k$; they lie only partially — to the first approximation half — in the real part $(x > 0)$ of the ψ-surface. We find two plaitpoints of which only one is in the real ψ-surface and two critical points of contact co-inciding with the plaitpoints (at least to the degree of approximation considered here, i. e. to the order $\sqrt{(T - T_k)}$; the coordinates of these points are:

$$x_{T_{pl}} = x_{T_r} = x_{Tk} \pm \frac{1}{m_{01}} \sqrt{\frac{k_{11}}{K k_{30}} (T - T_k)}$$

$$p_{T_{pl}} = p_{T_r} = p_{Tk} \pm \sqrt{\frac{k_{11}}{K k_{30}} (T - T_k)}$$

$$v_{T_{pl}} = v_{T_r} = v_c \mp \frac{1}{3 m_{01} m_{30}} \left(\frac{m_{01} m_{11}}{RT_k} + m_{21}\right) \sqrt{\frac{k_{11}}{K k_{30}} (T - T_k)}.$$

If $T = T_k$, the border curve and the connodal line shrink to one point, the critical point of the pure substance; and if $T > T_k$, there is no longer a border curve nor a connodal line.

b. $K > 0$; the border curve and the connodal line are hyperbolae; the asymptotes are:

$\varphi = \pm (p - p_{Tk}) \sqrt{K}$ (border curve) and $\varphi' = \pm m_{01} (x - x_{Tk}) \sqrt{K}$ (connodal line).

If $T > T_k$, φ (or φ') is the real axis; only that branch of the hyperbola which lies above the axis $p = p_{Tk}$ can be observed as border curve; in the case of the connodal line it is only the branch lying above the axis $x = x_{Tk}$ which can be observed; again two plaitpoints are found of which only one can be observed, and the coordinates of which can be expressed by the same terms as used for the ellipse. If $T = T_k$, the border curve and the connodal line consist of two straight branches meeting at the critical point of the pure substance, which is therefore a double plaitpoint. Lastly, if $T < T_k$ there is no longer a plaitpoint; we observe two branches of the border curve and the connodal line lying to the right and the left of the point p_{Tk}, v_{Tk}; each phase on one branch co-exists with a phase on the other.

11. *The border curve in the p, v, T diagram for a mixture of composition x.*

In equation (36) of the projection of the connodal line on the x, v-plane, if we consider x as constant and T as variable, that equation will express how the volumes of the phases, where the condensation begins and ends depend for the same mixture on the temperature. It therefore may be considered as the projection on the v, T-plane of the border curve on the p, v, T-surface for the mixture of composition x.

This projection, can be written in the following form, corresponds to (36)

$$0 = (v - v_{xk})^2 - 2\,\Phi''\,(v - v_{xk}) + \Phi''^2 - \varphi''^2, \quad . \quad . \quad . \quad (44)$$

where

$$\Phi'' = \frac{1}{2}(v'_2 + v'_1) - v_{xk} = \Phi' + v_{Tk} - v_{xk} = \text{(to a first approximation)}$$

$$= -\frac{1}{2m_{30}}\left[\frac{m_{01}}{RT_k}\left(\frac{m^2_{01}}{RT_k} + m_{11}\right) - \frac{2}{3}\,\frac{m^3_{01}}{R^2T_k^2} - \frac{4m_{40}}{5m_{30}}\cdot\frac{m^2_{01}}{RT_k}\right]x +$$

$$+ \frac{v_k(\alpha - \beta)}{\alpha T_k}(T - T_{xk}) + \frac{1}{2m_{30}}\left[\frac{m_{11}}{m_{01}}\left(\frac{m^2_{01}}{RT_k} + m_{11}\right) + \frac{2}{3}\,m_{21} -\right.$$

$$\left. - \frac{4}{5}\,\frac{m_{11}m_{40}}{m_{30}}\right]\frac{T - T_{xk}}{\alpha T_k} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (45)$$

and

$$\varphi''^2 = \frac{1}{4}(v'_2 - v'_1)^2 = \varphi'^2 = -\frac{m^2_{01}}{RT_k m_{30}}\,x + \frac{m_{11}}{m_{30}}\,\frac{T - T_{xk}}{\alpha T_k} \quad . \quad . \quad (46)$$

To this can be added

$$\Pi'' = \frac{1}{2}(p'_2 + p'_1) - p_{xk} = k_{01}(T - T_{xk}) \quad . \quad . \quad . \quad . \quad (47)$$

and

$$\pi'' = -\frac{m_{11}}{aT_k}(T - T_{xk})\,\varphi'' \quad . \quad . \quad\quad . \quad (48)$$

To the first approximation equation (44) represents a parabola, of which the apex determines the elements of the critical point of contact for the mixture x. For we know that in the case of the critical point of contact $v'_2 = v'_1 = v_{xr}$, so that $\varphi'' = 0$ and $\Phi'' = v_{xr} - v_{xk}$. Hence it follows that[1]):

$$T_{xr} = T_{xk} - \frac{m^2_{01}}{RT_k\,k_{11}}\,x \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (49)$$

$$p_{xr} = p_{xk} - \frac{k_{01}m^2_{01}}{RT_k\,k_{11}}\,x \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (50)$$

$$v_{xr} = v_{xk} + \left[m^2_{01}\,v_k(\alpha - \beta) + \frac{1}{3}\frac{m^2_{01}}{m_{30}}\left(\frac{m_{01}m_{11}}{RT_k} + m_{21}\right)\right]\frac{x}{RT_k\,m_{11}} \quad . \quad (51)$$

In order to derive from this the equation of the border curve in the p, v, T-diagram, we must express T in terms of p and v by means of equation (13).

Then we find:

$$0 = (v - v_{xk})^2 - 2\,\Phi'''(v - v_{xk}) + \Phi'''^2 - \varphi'''^2 \quad . \quad . \quad . \quad (52)$$

where

$$\Phi''' = -\frac{1}{2m_{30}}\left[\frac{m_{01}}{RT_k}\left(\frac{m^2_{01}}{RT_k} + m_{11}\right) - \frac{2}{3}\frac{m^3_{01}}{R^2T_k^2} - \frac{4}{5}\frac{m_{40}}{m_{30}}\frac{m^2_{01}}{RT_k}\right]x +$$
$$+ \frac{v_k(\alpha - \beta)}{k_{01}aT_k}(p - p_{xk}) + \frac{1}{2k_{01}m_{30}}\left[\frac{m_{11}}{m_{01}}\left(\frac{m^2_{01}}{RT_k} + m_{11}\right) + \frac{2}{3}m_{21} - \frac{4}{5}\frac{m_{11}m_{40}}{m_{30}} -\right.$$
$$\left. - \frac{k_{11}m_{11}}{k_{01}}\right]\frac{p - p_{xk}}{aT_k} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (53)$$

and

$$\varphi'''^2 = -\frac{m^2_{01}}{RT_k\,m_{30}}\,x + \frac{m_{11}}{k_{01}m_{30}}\frac{p - p_{xk}}{aT_k} \quad . \quad . \quad . \quad . \quad . \quad . \quad (54)$$

To a first approximation (52) is a parabola on which

$$\frac{d^2p}{dv^2} = 2\frac{k_{01}m_{30}}{m_{11}}\,aT_k = -2\frac{k_{01}k_{30}}{k_{11}}$$

as in the case of the border curve of the pure substance.

The apex of the border curve is the point of the maximum co-existence

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[1]) We obtain the same formulae if we replace in equation (26) x_{Tk} by its value (17), put $T = T_{xr}$ and $x_{Tr} = x$, solve T_{xr} and substitute it in (39) and (40).

pressure [1]). Let p_{xm}, v_{xm}, T_{xm}, be its coordinates, then we find by putting $\varphi''' = 0$ and $\Phi''' = v_{xm} - v_{xk}$

$$p_{xm} = p_{xk} - \frac{k_{01} m^2_{01}}{RT_k k_{11}} x \;.\;.\;.\;.\;.\;.\;.\;.\;. \quad (55)$$

$$v_{xm} = v_{xk} + \left[m^2_{01} v_k (\alpha - \beta) + \frac{1}{3} \frac{m^2_{01}}{m_{30}} \left(m_{21} + \frac{m_{01} m_{11}}{RT_k} - \frac{3}{2} \frac{k_{11} m_{11}}{k_{01}} \right) \right] \frac{x}{RT_k m_{11}} \quad (56)$$

$$T_{xm} = T_{xk} - \frac{m^2_{01}}{RT_k k_{11}} x \;.\;.\;.\;.\;.\;.\;.\;.\;. \quad (57)$$

Hence to the first approximation $p_{xm} = p_{xr}$ and $T_{xm} = T_{xr}$, but

$$v_{xm} - v_{xr} = - \frac{1}{2} \frac{m^2_{01} k_{11}}{RT_k k_{01} k_{30}} x \;;\;.\;.\;.\;.\;.\;. \quad (58)$$

for real mixtures, that is to say $x > 0$, the latter expression is necessarily negative, so that the critical point of contact is always situated on the descending (right) branch of the border curve. We cannot call it the vapour branch, because here the apex of the border curve is not the plaitpoint as in the p, v, x-diagram. The critical point of contact is situated thus, because the critical isothermal touches the border curve at that point, and because on that isothermal and hence also at the critical point of contact $T_{xr} > T_{xk}$ (at least for real mixtures), therefore $\frac{\partial p}{\partial v} < 0$ for the border curve. This corresponds to a diagrammatical representation of a p, v, T-diagram for a mixture given by KUENEN [2]) and also with the experimental diagram for the mixture: 0.95 carbon dioxide, 0.05 hydrogen which I have given in my thesis for the doctorate. In spite of the small value of x, terms of higher order appear to have such a great influence in the case of this mixture that the apex of the border curve lies far outside the area investigated, and the border curve at the critical point of contact is no longer concave towards the v-axis but convex.

The plaitpoint elements for the mixture of composition x are found by substituting T_{xpl} for T and x for x_{Tpl} in equation (26), by solving T_{xpl} and substituting that value in (27) and (28). Then we find

$$T_{xpl} = T_k \left[1 + \frac{m^2_{01} + RT_k m_{11}}{RT_k m_{11}} \alpha x \right] = T_{xk} - \frac{m^2_{01}}{RT_k k_{11}} x \;.\;\;. \quad (59)$$

$$p_{xpl} = p_k + \left[p_k \beta + \frac{k_{01} m^2_{01}}{R m_{11}} \alpha \right] x = p_{xk} - \frac{k_{01} m^2_{01}}{RT_k k_{11}} x \;\;.\;\;. \quad (60)$$

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[1]) Comp. HARTMAN, *Journ. Phys. Chem.*, 5, 437, 1901. Communications Leiden Suppl. N⁰ 3 p. 14.

[2]) *Zeitschr. f. physik. Chem.*, XXIV, 672, 1897.

$$v_{xpl} = v_{xk} + \left[m^2_{01} v_k(\alpha - \beta) + \frac{m_{01}}{2m_{30}} \left(\frac{2}{3} m_{01} m_{21} - \frac{1}{3} \frac{m^2_{01} m_{11}}{RT_k} - m^2_{11} \right) \right] \frac{x}{RT_k m_{11}}, \quad (61)$$

which formulae, after some reductions, can be put in the form in which KEESOM has given them (*Comm.*, n°. 75). Also the following well known equation [1]) results directly from equations (59) and (60)

$$p_{xpl} - p_{xk} = k_{01} (T_{xpl} - T_{xk}) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (62)$$

which also according to equations (49), (50), (55) and (57) holds for the coordinates of the critical point of contact and for the apex of the border curve.

From the coordinates of the plaitpoint of mixtures of carbon dioxide with a small proportion of hydrogen [2]) ($x = 0$, 0,05 and 0,1) I derive the following formulae

$$\left. \begin{aligned} T_{xpl} &= T_k\,(1 - 0{,}30\,x + x^2) \\ p_{xpl} &= p_k\,(1 + 4{,}4\,x + 11\,x^2) \\ v_{xpl} &= v_k\,(1 - 0{,}40\,x - 8\,x^2) \end{aligned} \right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad (63)$$

In connection with the formulae (16) I obtain directly from these:

$$\frac{p_{xpl} - p_{xk}}{T_{xpl} - T_{xk}} = 1{,}66\,(1 + 2x),$$

in good harmony with equation (62) ($k_{01} = 1{,}61$) [3]). Using the value $k = -513$ [4]), I moreover find that the formulae (59) and (60) applied to mixtures of carbon dioxide and hydrogen become:

$$T_{xpl} = T_k\,(1 + 0{,}03\,x) \quad \text{and} \quad p_{xpl} = p_k\,(1 + 6{,}4\,x); \quad . \quad (63')$$

hence the agreement with the formulae (63) is decidedly bad, as has also been remarked by KEESOM (*loc. cit.*, p. 13). We cannot, however, draw any conclusions from this; it is improbable that the inaccuracy of the data should cause this great deviation; but from the fact that terms of higher order produce such a great influence in the mixture $x = 0{,}05$, we see that quadratic formulae are very unfit for this comparison [5]), the more so as it appears from

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[1]) Comp. V. D. WAALS, *Versl. Kon. Akad.*, Nov. 1897. It also follows directly from the equation of state (13) in connection with (15), by expressing that the elements of the plaitpoint satisfy this equation and by neglecting terms of a higher order than the first.

[2]) VERSCHAFFELT, Thesis for the doctorate, Leiden 1899.

[3]) Comp. also KEESOM, *loc. cit.*, p. 14.

[4]) Derived from $\dfrac{RT_k}{p_k v_k} \dfrac{\partial^2 \pi}{\partial \omega \partial \tau} = -32{,}2$ (KEESOM, p. 12).

[5]) By introducing the values for $x = 0{,}2$ (comp. VERSCHAFFELT, *Arch. Néerl.*, (2), 5, 649 etc., 1900, Comm. n°. 65, and KEESOM, *loc. cit.* p. 12) they certainly will not become better.

Keesom's calculations (p. 13) that tolerably small variations in the values of α and β greatly influence the values of $\frac{dT_{xpl}}{dx}$ and $\frac{dp_{xpl}}{dx}$. Accurate observations for mixtures with still smaller compositions are therefore highly desirable. As the v_{xpl}, and also the coordinates of the critical plaitpoint, are known with less certainty than the T_{xpl} and p_{xpl}, a comparison of the theoretical and the experimental values for these quantities is practically useless.

Again from the preceding equations $p_{xpl} = p_{xr}$, $T_{xpl} = T_{xr}$ to a first approximation, and

$$v_{xpl} - v_{xr} = -\frac{1}{2}\frac{m_{01}}{RT_k m_{30}}\left(\frac{m^2_{01}}{RT_k} + m_{11}\right)x \quad . \quad . \quad . \quad . \quad (64)$$

Hence the plaitpoint may lie either to the right or to the left of the critical point of contact; for positive x we have

	$m_{01} > 0$	$m_{01} < 0$
$RT^2_k\, k_{11}\, \alpha > m^2_{01}$	$v_{xpl} < v_{xr}$; r. c. I	$v_{xpl} > v_{xr}$; r. c. II
$RT^2_k\, k_{11}\, \alpha < m^2_{01}$	$v_{xpl} > v_{xr}$; r. c. II	$v_{xpl} < v_{xr}$; r. c. I

If the plaitpoint lies to the left of the critical point of contact, it may still lie either to the right or to the left of the apex, that is to say either on the descending or on the ascending branch of the border curve. In fact, according to (58) and (64) it lies:

1. to the right of the critical point of contact when m_{01} and $\frac{m^2_{01}}{RT_k} + m_{11}$ have the same signs,

2. between the critical point of contact and the apex when

$$\frac{k_{01}}{k_{11}}\left(\frac{m^2_{01}}{RT_k} + m_{11}\right) > m_{01} > 0 \quad \text{or} \quad 0 > m_{01} > \frac{k_{01}}{k_{11}}\left(\frac{m^2_{01}}{RT_k} + m_{11}\right), \text{ and}$$

3. to the left of the apex when

$$m_{01} > \frac{k_{01}}{k_{11}}\left(\frac{m^2_{01}}{RT_k} + m_{11}\right) > 0 \quad \text{or} \quad 0 > \frac{k_{01}}{k_{11}}\left(\frac{m^2_{01}}{RT_k} + m_{11}\right) > m_{01}.$$

In the p, v, T-diagram the plaitpoint has no geometrical meaning.

The expression that the coordinates of the critical point of contact and the plaitpoint satisfy the equation (44) gives, to the second approximation:

$$T_{xpl} - T_{xr} = -\frac{1}{4}\frac{m^2_{01}}{RT_k k_{30} k_{11}}\left(\frac{m^2_{01}}{RT_k} + m_{11}\right)^2 x^2 \quad . \quad . \quad . \quad (65)$$

The right side is necessarily negative and therefore we always have $T_{xr} > T_{xpl}$, which also necessarily follows from the meaning of the critical point of contact. In the same way we find by means of equation (52):

$$p_{xpl} - p_{xr} = \frac{1}{2}\frac{k_{01}}{k_{11}}\frac{m^2_{01}}{RT_k k_{30}}\left(\frac{m^2_{01}}{RT_k} + m_{11}\right)\left[\frac{m_{01}k_{11}}{k_{01}} - \frac{1}{2}\left(\frac{m^2_{01}}{RT_k} + m_{11}\right)\right]x^2 \,. \quad (66)$$

12. *The condensation.*

The line which indicates the relation between the pressure and the volume during the condensation, the so-called experimental isothermal, extends between the two points p'_1, v'_1 and p'_2, v'_2 (the points where the condensation begins and ends) but we can also imagine it to extend beyond those two points, although there it has only a mathematical meaning; for beyond those two points the quantity of one of the phases would be negative. In order to find the equation of the experimental isothermal we must seek at each volume for the pressure at which the two phases into which the mixture splits, can co-exist. For this purpose I return to the projection on the x, v-plane (§ 8) of the ψ-surface belonging to the temperature T. If v_1, x_1 and v_2, x_2 are the phases into which the mixture x splits when the volume v is reached ($v_2 > v > v_1$), the point v, x lies on the straight line connecting the points v_1, x_1 and v_2, x_2 and hence we have this relation:

$$\frac{v - v_{Tk} - \Phi}{x - x_{Tk} - \Xi} = \frac{\varphi}{\xi} \quad , \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (67)$$

where Φ, Ξ, φ and ξ have the same meaning as in § 5. If p_1 is the pressure at which the two phases x_1 and x_2 co-exist then we obtain the equation of the experimental isothermal by expressing the quantities Φ, Ξ, φ and ξ of equation (67) in p_1 by means of the equations (22), (23), (24) and (25).

That this experimental isothermal passes through the two points v'_1, x and v'_2, x follows directly from the way in which its equation has been derived; we also obtain it from the substitution of v'_1, x'_1 — or v'_2, x'_2 — for v, x, which involves the substitution of v'_1, x'_1 for v_1, x_1, — or of v'_2, x'_2 for v_2, x_2.

By successive approximations (67) is brought to the form:

$$p_1 = p_{Tk} + m_{01}(x - x_{Tk}) - \frac{m^2_{01}}{RT_k}(v - v_{Tk})\,x + \ldots\,; \quad . \quad . \quad (68)$$

if we consider only the three first terms, this is the equation of a straight line, hence of that connecting the two phases where the condensation begins and ends. In connection with (18) we find, neglecting terms of higher order,

$$p-p_1 = m_{11}\,(v-v_{Tk})\,(x-x_{Tk}) + \frac{m^2_{01}}{RT_k}\,(v-v_{Tk})\,x + m_{30}\,(v-v_{Tk})^3,$$

and according to (33) this may be written

$$p-p_1 = k_{30}\,(v-v_{Tk})\,[(v-v_{Tk})^2 - \varphi'^2].$$

We see that in this form the experimental isothermal intersects the theoretical at three points [1]), viz. $v = v_{Tk} + \varphi'$, $v = v_{Tk} - \varphi'$ and $v = v_{Tk}$ (all to the first approximation); the two first points are the points at which condensation begins and ends (Φ' has been neglected as being of higher order than φ'), the third lies between the two first.

When $v_{Tk} + \varphi' > v > v_{Tk}$, that is to say at the beginning of the condensation, $p > p_1$ and the theoretical isothermal lies above the experimental; when $v_{Tk} > v > v_{Tk} - \varphi'$, i.e. at the end of the condensation, $p > p_1$ and the experimental isothermal is the higher [2]); this, indeed, follows necessarily from the *s*-shape of the theoretical isothermal, and the approximate straightness of the experimental.

According to thermodynamics the two areas enclosed by the theoretical and the experimental isothermal must be equivalent [3]), that is to say:

$$\int_{v'_1}^{v'_2} (p-p_1)\,dv = 0.$$

or

$$\int_{-\varphi'}^{+\varphi'} (p-p_1)\,d\,(v-v_{Tk}) = 0,$$

and this actually follows from the form, found just now for $p-p_1$. This has only been proved for the terms considered here; but obviously it must also be possible to prove this for terms of higher order.

13. *The p, T diagram.*

a. The vapour pressure curve of the pure substance. We have found to a first approximation:

$$p_1 = p_k + k_{01}\,(T-T_k).$$

As k_{01} is positive, this straight line rises and terminates at the

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[1]) Comp. for this HARTMAN, Comm., n⁰. 56 and Suppl. n⁰. 3 p. 25; Journ. Phys. Chem., 5, 450, 1901.

[2]) Here the proof is only given for mixtures with small composition. For a general proof comp. KUENEN, Zeitschr. f. Physik. Chem., XLI, 46, 1902.

[3]) It has escaped BLÜMCKE's notice, who mentions this theorem in 1890 (Zeitschr. f. physik. Chem., VI, p. 157) that it occurs already in a treatise of VAN DER WAALS of 1880 (Verh. Kon. Akad., Bd. 20, p. 23).

point p_k, T_k. T_k is a maximum temperature, so that this curve lies in the third quadrant ($S'O$, fig. 16.)

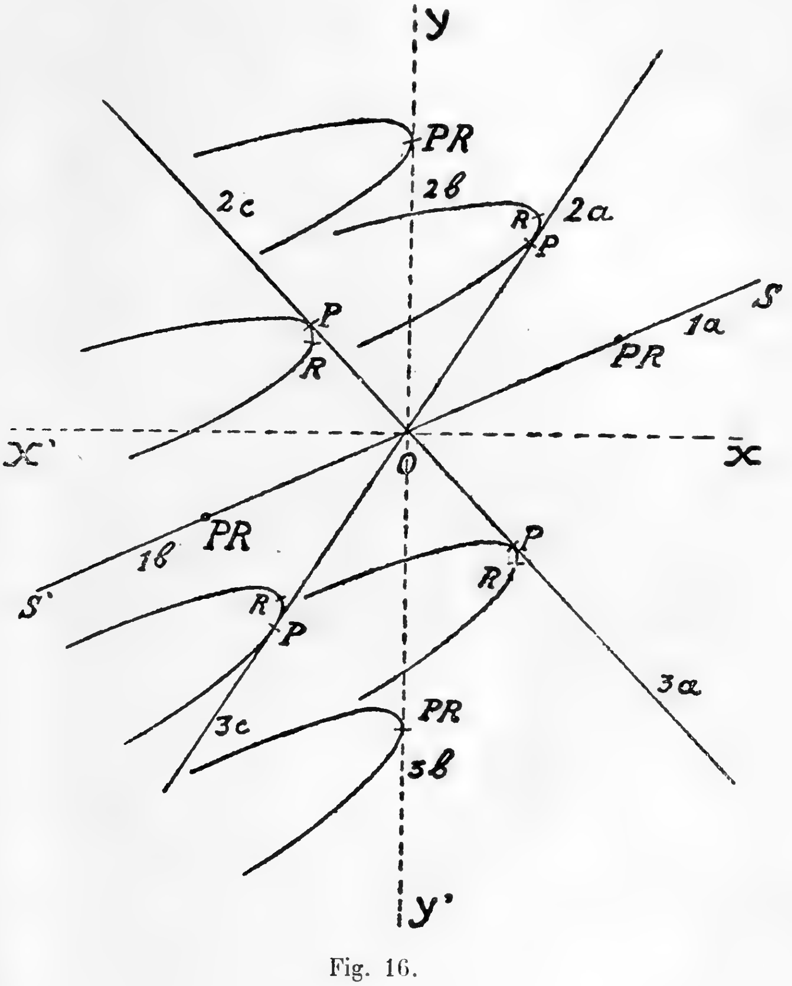

Fig. 16.

b. The plaitpoint curve. According to equation (27)

$$p_{T_{pl}}=p_k+\left[p_k\beta-\frac{m^3_{01}}{m^2_{01}+RT_k m_{11}}\right]\frac{T-T_k}{aT_k}=p_k+\left(k_{01}-\frac{RT_k k_{11} m_{01}}{m^2_{01}+RT_k m_{11}}\right)(T-T_k)$$

This curve may have all possible directions. If we consider only real mixtures ($x>0$), it extends only on one side of the point p_k, T_k, namely that corresponding to such values that $T-T_k$ and $m^2_{01}+RT_k m_{11}$ have the same signs (according to equation 26').

With regard to the position of the plaitpoint curve we distinguish the following cases:

1. $m_{01}=0$. $p_{T_{pl}}=p_k+k_{01}(T-T_k)$, hence the beginning of the plaitpoint curve will lie either in the direction of the vapour pressure

curve of the pure substance or will co-incide with it as $T > T_k$ or $T < T_k$, that is to say, according to (26′), as α is positive or negative. In the first case (1*a*), therefore, the plaitpoint curve will lie in the first quadrant (OS fig. 16), in the second case (1*b*) in the third quadrant (OS'). We have noted that then the plaitpoint elements of a mixture co-incide with the critical elements which the mixture would have, if it remained homogeneous, hence the mixture behaves like a pure substance. This is the case $\frac{\partial^2 \psi}{\partial x \, \partial v} = 0$ already discussed by VAN DER WAALS [1]); in this case there is a mixture — here it must be the pure substance itself — for which the vapour tension is a maximum or a minimum, and indeed it follows from the expression for $p_1 - p_{Tk}$ in this case [2]) that $\left(\frac{\partial p_1}{\partial x_1}\right)_{x_1=0} = 0$.

2*a*. $m_{01} > 0$ and $m^2_{01} + RT_k \, m_{11} > 0$. $\frac{dp_{Tpl}}{dT} > k_{01}$ so that the plaitpoint curve lies in the angle SOY because $T - T_k$ must be also positive.

2*b*. $m_{01} > 0$ and $m^2_{01} + RT_k \, m_{11} = 0$, $\frac{dp_{Tpl}}{dT} = \pm \infty$, and the beginning of the plaitpoint curve co-incides with OY [3]).

Thus we have here the second special case of the shape of the plaitpoint curve investigated by VAN DER WAALS, i. e. where there is a maximum or minimum temperature, here the critical temperature of the pure substance. Really in this case (§ 10,2), as $p_{Tk} - p_k$ is of higher order than $p_{Tpl} - p_k$,

$$T - T_k = \frac{Kk_{30}}{k_{11}} (p_{Tpl} - p_k)^2$$

hence $\left(\frac{dT_{pl}}{dp_{Tpl}}\right)_k = 0$. $T > T_k$, that is to say T_k is the minimum plaitpoint temperature, when $K > 0$; this is the case where the border curve and the connodal line are hyperbolae (mixtures of HARTMAN's third type). And $T < T_k$, that is so say T_k is a maximum, when $K < 0$; in this case the border curve and the connodal line are ellipses (mixtures of the second type).

2*c*. $m_{01} > 0$ and $m^2_{01} + RT_k \, m_{11} < 0$. $\frac{dp_{Tpl}}{dT} < k_{01}$, and because

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[1]) Arch. Néerl., (1), 30, 266, 1896.

[2]) Comp. preceding communication, p. 267; to the first approximation $\Xi = x_1$.

[3]) Not with OY', for, as in this case $p_{Tk} - p_k$ and x_{Tk} are infinitely small with respect to $p_{Tpl} - p_k$ and x_{Tpl} (§ 10,2), according to (29) $p_{Tpl} - p_k = m_{01} \, x$, so that for $x > 0$, $p_{Tpl} > p_k$.

$T - T_k$ must also be negative the plaitpoint curve lies in the angle $S'OY$.

3*a*. $m_{01} < 0$ and $m^2_{01} + RT_k m_{11} > 0$, $\frac{dp_{T_{pl}}}{dT} < k_{01}$, but $T - T_k > 0$, and hence in the angle SOY'.

3*b*. $m_{01} < 0$ and $m^2_{01} + RT_k m_{11} = 0$. The plaitpoint curve touches OY' [1]). Compare moreover 2*b*.

3*c*. $m_{01} < 0$ and $m^2_{01} + RT_k m_{11} < 0$. $\frac{dp_{T_{pl}}}{dT} > k_{01}$, but $T - T_k > 0$, hence in the angle $S'OY'$.

From this it appears that $\frac{dp_{T_{pl}}}{dT}$ can take all possible values. According to VAN DER WAALS [2]), however, this is not true and the case $\frac{dp_{T_{pl}}}{dT} = \frac{pk}{T_k}$ for instance could never occur. But it should be borne in mind that this rule of VAN DER WAALS does not rest on an exclusively thermodynamic reasoning, but also on special suppositions about the form of the equation of state, which naturally corresponds to special relations between the co-efficients introduced here, and as a matter of course it is always possible that the numerical values of the coefficients are such, that one or more of the cases considered are excluded.

c. *The critical point of contact curve.* To the first approximation $p_{T_r} = p_{T_{pl}}$, so that the critical point of contact curve to a first approximation co-incides with the plaitpoint curve and the considerations in *b* hold also for this line. Equation (43) shows moreover that to a second approximation:

$$p_{T_r} - p_{T_{pl}} = -\frac{1}{4}\,\frac{m^3_{01}k^2_{11}}{RT_k m_{30}(m^2_{01} + RT_k m_{11})}(T - T_k)^2,$$

from which it follows that the critical point of contact curve lies above the plaitpoint curve when m_{01} and $m^2_{01} + RT_k m_{11}$ have the same signs; this occurs in the cases 2*a* and 3*c* just mentioned, hence in the angles SOY and $S'OY'$. In the other cases the point of contact curve is the lower. Moreover the two curves also co-incide to a second approximation if $m_{01} = 0$ and even if $m^2_{01} + RT_k m_{11} = 0$. $\left(\frac{dp_{T_{pl}}}{dT} = \frac{dp_{T_r}}{dT} = \pm \infty\right)$ although in that case $p_{T_r} - p_{T_{pl}}$ is not zero to the second approximation.

d. *The border curves.* This position of the critical point of con-

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[1]) $p_{T_{pl}} < p_k$ for $x > 0$; comp. preceding note.

[2]) Arch. Néerl., (2), 2, 79, 1898.

tact curve with respect to the plaitpoint curve corresponds to the position of the critical point of contact with respect to the plaitpoint on the border curves, represented in an exaggerated way in fig. 16. To the second approximation those border curves are parabolae which touch the plaitpoint curve and have a vertical tangent at the critical point of contact, but to the first approximation they co-incide with the axis which is conjugate to the vertical chords and the equation of which according to (47), is:

$$p = p_{xk} + k_{01}(T - T_{xk}) = p_{xpl} + k_{01}(T - T_{xpl}).$$

Hence these straight lines are parallel with the vapour pressure curve of the pure substance and terminate, on the plaitpoint curve, in the plaitpoint of the mixture to which they belong.

14. *Continuation of § 9: the critical point of contact.*

Mr. KEESOM kindly informs me that the method given by him in Comm. N°. 75 and which leads very easily to the constants of the plaitpoint presents difficulties when applied to determine the constants of the critical point of contact.

He however succeeded, by means of the method used by me in § 9, in deriving the constants of the critical point of contact from the formulae [1]), given by KORTEWEG in his paper "Ueber Faltenpunkte", Wien. Sitz. Ber. Bd. 98, p. 1154, 1889, and proceeded thus.

It has been shown in Comm. N°. 59^b, p. 36 [2]) that instead of deducing the coexistence-conditions by rolling the tangent-plane over the ψ-surface, we can also obtain them by rolling the tangent-plane over a ψ'-surface, the latter being deduced from the ψ-surface by making the distance, measured in the direction of the ψ-axis, between this surface and a fixed tangent-plane the third coordinate perpendicular to x and v. We can go a step further in this direction by deducing a ψ''-surface by means of KORTEWEG's projective transformation [3])

$$\psi'' = \psi' - v'\left(\frac{\partial\psi'}{\partial v'}\right)_{pl} - x'\left(\frac{\partial\psi'}{\partial x'}\right)_{pl}$$

$$x'' = x' - m\,v'$$

$$v'' = v'$$

Here

$$\psi' = \psi - \psi_{Tpl}$$

$$x' = x - x_{Tpl}$$

$$v' = v - v_{Tpl}$$

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[1]) The simplest way of proving that the case $c_1 = \infty$ in KORTEWEG's formula (4) does not influence the present deduction, is by noting that the area over which the development is applied is infinitely small in comparison with xT_{pl}.

[2]) Proceedings Sept. 1900, p. 296.

[3]) See KORTEWEG l. c. equation 38.

As
$$\left(\frac{\partial\psi''}{\partial x''}\right)_1=\left(\frac{\partial\psi''}{\partial x''}\right)_2$$
$$\left(\frac{\partial\psi''}{\partial v''}\right)_1=\left(\frac{\partial\psi''}{\partial v''}\right)_2$$
$$\psi_1''-x_1''\left(\frac{\partial\psi''}{\partial x''}\right)_1-v_1''\left(\frac{\partial\psi''}{\partial v''}\right)_1=\psi_2''-x_2''\left(\frac{\partial\psi''}{\partial x''}\right)_2-v_2''\left(\frac{\partial\psi''}{\partial v''}\right)_2$$
when
$$\left(\frac{\partial\psi'}{\partial x'}\right)_1=\left(\frac{\partial\psi'}{\partial x'}\right)_2,\ \text{etc.}$$
it is also possible to obtain the coexisting phases by rolling a tangent-plane over this ψ''-surface. ψ'' as function of x' and v'' presents the form
$$\psi''=c_1\,x''^2+d_3\,x''\,v''^2+e^5\,v''^4 \qquad (\text{Korteweg's equation 4}).$$

Hence for the connodal curve Korteweg's deduction may be applied, and we find for the equation of that curve
$$x''=-2\frac{e_5}{d_3}v''^2 \qquad (\text{equation 8 l. c.}).$$
m is now found from
$$m\left(\frac{\partial^2\psi}{\partial x^2}\right)_{vT}+\left(\frac{\partial^2\psi}{\partial x\partial v}\right)_T=0 \qquad (\text{equation 34}),$$
where the differential quotients are taken for the plaitpoint, so that for a substance with a small proportion of one component, to the first approximation
$$m=\frac{1}{MRT_k}\left(\frac{\partial p}{\partial x}\right)_{vT}x_{T_{pl}}\,.$$

Further we may put, leaving out terms of higher order, according to equation (39)
$$d_3=-\frac{1}{2MRT_k}\left\{\left(\frac{\partial p}{\partial x}\right)^2_{vT}+MRT_k\left(\frac{\partial^2 p}{\partial x\partial v}\right)_T\right\}$$
$$e_5=-\frac{1}{24}\left(\frac{\partial^3 p}{\partial v^3}\right)_{xT}.$$

Using the property that for the point of contact $\frac{dx}{dv}=0$, this yields:
$$v_{T_r}-v_{T_{pl}}=3\frac{\left(\frac{\partial p}{\partial x}\right)_{vT}}{(MRT_k)^2.\left(\frac{\partial^3 p}{\partial v^3}\right)}\left\{\left(\frac{\partial p}{\partial x}\right)^2_{vT}+MRT_k\left(\frac{\partial^2 p}{\partial x\partial v}\right)_T\right\}x_{T_{pl}}$$

and

$$x_{Tr} - x_{Tpl} = \frac{3}{2} \frac{\left(\frac{\partial p}{\partial x}\right)^2_{vT}}{(MRT_k)^3 . \frac{\partial^3 p}{\partial v^3}} \left\{ \left(\frac{\partial p}{\partial x}\right)^2_{vT} + MRT_k \left(\frac{\partial^2 p}{\partial x \partial v}\right) \right\} x^2{}_{Tpl} .$$

So that for $x = 0$: $\frac{dx_{Tr}}{dT} = \frac{dx_{Tpl}}{dT}$, or $\frac{dT_{xr}}{dx} = \frac{dT_{xpl}}{dx}$, from which we easily derive that also $\frac{dp_{xr}}{dx} = \frac{dp_{xpl}}{dx}$ so that in the pT-diagram the point of contact curve and the plaitpoint curve touch at the ends. We find further that with the same x:

$$T_{xr} - T_{xpl} = \frac{3}{2} \frac{\left(\frac{\partial p}{\partial x}\right)^2_{vT}}{(MRT_k)^4 . \left(\frac{\partial^3 p}{\partial v^3}\right) \left(\frac{\partial^2 p}{\partial v \partial T}\right)} \left\{ \left(\frac{\partial p}{\partial x}\right)^2_{vT} + MRT_k \left(\frac{\partial^2 p}{\partial x \partial v}\right)_T \right\}^2 x^2 .$$

from which $p_{xr} - p_{xpl}$ can be easily found.

If, as in Communication N°. 75 (Proceedings Nov. 1901), we introduce the law of corresponding states, we find:

$$v_{Tr} - v_{Tpl} = 3\, C_4\, v_k \frac{\beta - \alpha \left(\frac{\partial \pi}{\partial \tau}\right)}{C^3{}_4 \left(\frac{\partial^3 \pi}{\partial \omega^3}\right)} \left[\left\{ \beta - \alpha \left(\frac{\partial \pi}{\partial \tau}\right) \right\}^2 - C_4\, \alpha \left(\frac{\partial^2 \pi}{\partial \omega \partial \tau}\right) \right] x$$

$$T_{xr} - T_{xpl} = \frac{3}{2} \frac{\left\{ \beta - \alpha \left(\frac{\partial \pi}{\partial \tau}\right) \right\}^2}{C^3{}_4 \left(\frac{\partial^3 \pi}{\partial \omega^3}\right) . C_4 \left(\frac{\partial^2 \pi}{\partial \omega \partial \tau}\right)} \left[\left\{ \beta - \alpha \left(\frac{\partial \pi}{\partial \tau}\right) \right\}^2 - C_4 \alpha \left(\frac{\partial^2 \pi}{\partial \omega \partial \tau}\right) \right]^2 x^2 .$$

Physiology. — *"On the structure of the light-percepting cells in the spinal cord, on the neurofibrillae in the ganglioncells and on the innervation of the striped muscles in amphioxus lanceolatus."* By Dr. J. BOEKE. (Communicated by Prof. T. PLACE).

In connection with a former note[1] I mean to describe here some points of the histology of the central and peripheral nervous system of amphioxus lanceolatus, especially to follow the neurofibrillae in their arrangement and distribution in the cells and in the muscle-plates.

This paper is the outcome of observations begun in 1900 in the Stazione Zoologica at Naples, but then not carried any farther, to study the structure of the pigmented cells of the spinal cord. During

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[1] Proceedings of the Royal Academy of Amsterdam. Meeting of April 19, 1902.

a stay at the Zoological Laboratory of Prof. St. Apáthy in Kolozsvár once again I took up the theme, with some excellently fixed material I got through Prof. Apáthy's kindness. Finally the researches were carried on in the Histological Laboratory of Amsterdam.

A. The structure of the light-percepting cells (eye-cells).

In 1898 Hesse [1]) showed, that the peculiar pigmented cells, which are found in the spinal cord grouped round the ventral wall of the central canal, and which after beginning at the third segment, are arranged segmentally through the whole medulla, are each of them composed of two cells, one of them a big ganglioncell without pigment, the other a cupshaped cell, filled up entirely with dark brown pigmentgrains; the last cell covering the greater part of the firstnamed cell and hiding it from view.

The big unpigmented cells Hesse called eye-cells, light-percepting cells, the cupshaped pigmented cells he called the pigmentcup (Pigmentbecher), and the whole complex he compared with the cupshaped eyes of the Planarians, that are equally composed of two cells, and attributed to it the function of light-perception.

The arrangement of these two-celled eyes in the spinal cord is strictly segmental. They begin in the fourth segment, with two eyes; from there each segment is furnished with about 25 eyes. In the region of the tail the number lessens, until a segment has only one eye or none at all.

The eyes lying ventrally of the central canal are always looking down, their line of vision, if we may call it so, being directed to the ventral side of the animal, those at the left side of the central canal look upward and to the right, those at the right side look down and to the right.

The pigmentcup consists of one cell, the nucleus, when distinguishable, lying at the concave side of the cup.

The eye-cell is coneshaped, the base being covered by the pigmentcup, the top being drawn out into a thin process. At the basal side (turned towards the pigmentcup) the protoplasm is differentiated into a layer of fine small rods, placed at right angles to the cell-periphery, and continuing in the protoplasm as a network of very thin fibres. Another layer of minute rods may be seen close against the pigmentcup. Between those two layers a clear space is formed, which is not caused by a shrinking of the cell.

W. Krause [1]) did not agree with the results of Hesse. He still maintained that the pigmented cells in the spinal cord consisted

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[1]) Zeitschr. f. Wiss. Zoologie. Bd. 63. 1898. p. 456.

[1]) Anat. Anzeiger. Bd. 14. Pag. 470. Zoöl. Anzeiger. Bd. 21. p. 481.

each of them of only one cell with the pigmentgrains lying only at the periphery, just as HEIJMANS and V. D. STRICHT [1]) had said in 1898; by BEER [2]) and SCHNEIDER [3]) the description given by HESSE was taken for right and confirmed.

As to the arrangement of the pigmentcells in the spinal cord in the first place, the observations of HESSE are not complete. They do not simply lessen in number going from before backwards. In young pelagic larvae there are to be seen very distinctly two groups of pigmentcells, one in the cranial part of the body, the other in the caudal half. Between those groups there are much less pigment-cells in each segment. In later stages however these two groups become fused, and then the arrangement is in the main as it is described by HESSE.

As regards the position occupied by the pigmentcap on the eye-cell, I can in the main confirm the observations of HESSE. The eyes at the ventral side of the central canal are always looking down, those at the left are mostly looking upwards and to the right, those at the right mostly downwards and to the right.

The histological structure of the eyes seems to me to be slightly different from the one described by HESSE and SCHNEIDER.

The nucleus of the pigment-cell is never lying at the concave, but mostly at the convex side of the cupshaped cell; sometimes the nucleus is found in the middle of the pigment-cell, where often a clear pigmentfree zone of protoplasm may be distinguished. According to HESSE the pigment-cup consists always of only one cell. Now sometimes in young animals, where the pigment is of a light-brown colour and the nucleus may therefore be seen very clearly, I found two nuclei in the pigment-cap, and so it seems to me that there are sometimes two pigment-cells with one eye-cell. So the form of the pigment-cap in fig. 3 seems also to point to the pigment-cap being composed of two cells. As a rule, however, there is only one pigment-cell in each eye.

In the eye-cell, lying under the pigment-cell, HESSE describes a double row of small rods, lying close to the pigment-cell. This double row of small rods exists, but the two parts of it are not separate, but continuous at both ends, in whatever direction the cell is cut through. So a flat oval body is formed, with a striated wall, lying close to the pigment-cap (fig. 1. *a*), and following in its shape the form of the cap. This body seems to me to be homologous with

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[1]) Mém. couronn. de l'Acad. roy. de Belgique T. LVI 1898.

[2]) Wiener med. Wochenschrift 1900.

[3]) Lehrb. der vergl. Histologie der Tiere 1902.

J. BOEKE. **On the structure of the light percepting cells in the spinal cord, on the neurofibrillae in the ganglioncells and on the innervation of the striped muscles in amphioxus lanceolatus.**

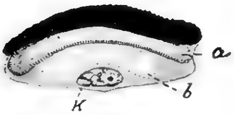


Fig. 1.
Pigment-cup and eye-cel with vitreous bodies.

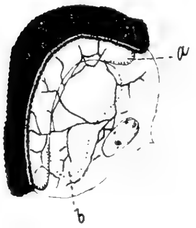


Fig. 2.
Pigment-cup and eye-cell with the network of neurofibrillae
Enlarg : 800.

Fig. 3.
Pigment-cup and eye-cell with network of neurofibrillae.
Enlarg : 1200.

Fig. 4.

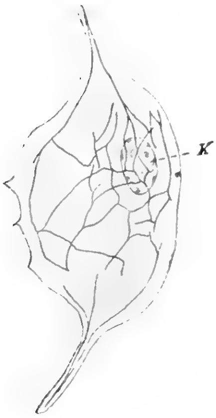
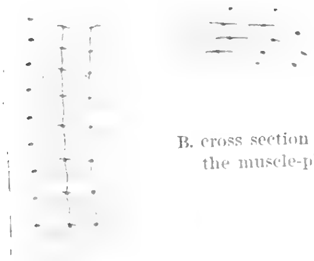


Fig. 5. Arrangement of the neurofibrillae in a section through a ganglioncell from the dorsal part of the medulla. Fibrillae drawn with the drawing apparatus in different optical sections.



B. cross section through the muscle-plates.

Fig. 6.
A. longitudinal section.

the "Glaskörper" with a striated wall, as it is found in the eye-cells of the Hirudines. As is the case with those eye-cells, here in Amphioxus too the vitreous body seems to be filled with a granular-looking substance (coagulation?) but this was not always clearly to be seen.

Between this body (*a*), that lies close to the pigmented cap, and the nucleus (fig. 1 *k*) lying at the other side of the eye-cell, there is in most cases to be seen another beanshaped body, that does not possess a striated wall, but by a clearer tinction with protoplasmic dyes and a more homogeneous substance may be distinguished from the darker and more granular-looking protoplasm of the cell (fig. 1*b*). This body seems to be connected with the perception of light by the eye-cell in the same way as the vitreous body described above. The arrangement of the neurofibrillae in the eye-cells seems to point to this conclusion. Entering the cell at the ventral side of the nucleus, there, where according to HESSE the eye-cell is drawn out to a point, the neurofibril forms a loosely built network round the nucleus. From this network large neurofibrils ascend through the cell and take the beanshaped body (*b*) between them (fig. 2, fig. 3). Between this body and the pigment-cap these neurofibrils anastomose again and form a second net, which seems to enclose the vitreous body (*a*) with the striated wall. How the further course of these fibrils is between the vitreous body (*a*) and the pigment-cap I could not determine with any accuracy.

To obtain good results with the chlorid of gold-method of APÁTHY the sections may not be very much thinner than 10 μ. Now for the study of the eye-cells it is necessary to make sections of about 6 to 7 μ, because in thicker sections the black pigment of the capshaped cell embraces the greater part of the eye-cell and shuts it out from view. It is therefore not possible to get those deep black neurofibrillae, which may be seen so distinctly in the preparations of APATHY (the more so as the neurofibrillae of Amphioxus are thinner than those of Hirudines); and even in sections of 6 to 7 μ that part of the neurofibrillae-network, which is lying beneath the pigment-cap is entirely concealed by the pigment-grains. Probably the network is continuous and anastomoses at the other side with the more ventrally lying network.

In what manner the neurofibrillae leave the eye-cell I could see only in a few cases. The fibril seemed then to proceed horizontally for some time but could not be followed any farther.

B. The neurofibrillae in the ganglion-cells.

On the neurofibrillae in the ganglioncells I 'll say only a few words.

It would lead us too far to go into details about the arrangement of the neurofibrillae in all the different types of ganglioncells, and besides, that would not be possible without many plates and drawings. I will therefore confine myself here to the following statements:

According to BETHE [1]) in most of the ganglioncells of the vertebrates the neurofibrillae pass through the cellbody without branching or breaking up into a network. Only in the spinal-ganglioncells and in the cells of the lobus electricus of Torpedo marmorata BETHE observed networks of the neurofibrillae, and according to this author networks possibly occur in the basal part of the cells of PURKINJE in the cerebellum and in the cells of the cornu Ammonis.

According to BOCHENEK [2]) it is on the other hand probable, that in the vertebrate ganglioncells the neurofibrillae form a very fine network with small meshes. The very dense reticulum of neurofibrillae, he was able to demonstrate in the ganglioncells of HELIX, forms according to BOCHENEK an intermediate stage between the coarse network in the cells of Hirudines and Lumbricus, and the very fine network in the vertebrate ganglioncells.

In accordance with the statements by these two authors, we should expect to find in the ganglioncells of Amphioxus either a dense reticulum or a mass of disconnected interwoven very fine threads, passing from one process through the cell-body into another process without branching. This is not the case. In most of the ganglioncells the arrangement and distribution of the neurofibrillae in the ganglioncells resembles very much that which is described by APÁTHY in the ganglioncells of Hirudines and Lumbricus.

Sometimes we find cells as the one shown in fig. 4, where the neurofibrillae pass through the cell-body without interruption, but this is only to be found in a few cases.

In the bigger ganglioncells, which are lying in the dorsal part of the spinal cord and in the dorsal group of ganglioncells behind the brain-ventricle, there is always a network of neurofibrillae branching and anastomosing with each other. After having entered the cell in most cases the neurofibrillae form a network round the nucleus (partially distinguishable in fig. 5). From out this reticulum radial fibrillae go through the cell body to the periphery (often branching on their way) where they form a second network. With this network are connected fibrillae, which pass through one of the processes of the cell (out of the cell or into it?) — in short, a distribution of

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[1]) Arch. f. Mikrosk. Anatomie, Bd. 55. 1900. P. 513.

[2]) Le Névraxe. Vol. III. Fasc. I, 1901. P. 85.

the neurofibrillae very much like that described by APÁTHY in the smaller ganglioncells of Lumbricus. The fibrillae however in Amphioxus are thinner, and the reticulum finer.

In other ganglioncells there are not two networks (one round the nucleus and one more at the periphery), connected with each other by means of the radial fibrillae, but the neurofibrillae enter the cell, form a network round the nucleus and leave the cell at the other side, without there being any trace of a more peripheral network to be seen.

A connection between different ganglioncells by means of the neurofibrillae, I could not yet state with a sufficient amount of certainty.

In the colossal ganglioncells the "Kolossalzellen", lying just in the middle of the spinal cord, the arrangement of the neurofibrillae is very peculiar. From out the colossal nerve-fibres, the axons of these cells, a thick bundle of very thin neurofibrillae, arranged very regularly and equally in the whole axis cylinder, enter the ganglioncell; in the cell-body they pursue their way as a thick bundle that passes round the nucleus, turns upon itself, forms a sort of vortex and then seems to condense itself into a few thick (composed of a great number of elementary fibrillae) fibrillae. Where these fibrils go to, I could not state accurately. In the axons the extremely thin neurofibrillae are closely set and parallel to each other, and so a striking resemblance is formed with the "sensorische Schläuche" of Hirudines and Astacus. During the course of these nerve-fibres through the spinal cord the neurofibrillae are seen to pass one by one every now and then in an oblique direction through the wall of these nerve-fibres; then they are lost in the nervous network without, and could not be followed any farther. Perhaps they are connected there with other ganglioncells, which should be in concordance with the character of the colossal ganglioncells as connecting cells ("Schaltzellen").

C. The innervation of the striped muscular tissue.

According to ROHDE [1]) the motor nerves simply enter the muscle-plates there where these end, and there is no trace of a motor nerve endplate; according to HEYMANS and VAN DER STRICHT [2]) however the motor nerves of Amphioxus terminate each in a shovelshaped endplate, that lies itself against the muscle-plate just as the motor nerve endplates of the higher vertebrates do. According to their descriptions and drawings the endplates of Amphioxus are thick shovel-shaped plates without branchings, without further differentiations (Golgi method).

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[1]) SCHNEIDER's Zoologische Beiträge. Bd. II, 1888.

[2]) Mém. couronn. par l'Acad. roy. de Belgique 1898.

Now Apáthy and Ruffini [1]) were able to demonstrate in homo the existance of "ultraterminal" nerve-fibres, that is to say nerve-fibres which grow out from the branching and thickening of the motor nerve known as "endplate", and enter the muscle-fibre (this could not be made out with absolute certainty) pass through it and in many cases are connected with other endplates. Only a few cases are described but they are sufficient to show that the so-called nerve end-plate is not always to be considered as the real termination of the motor nerves.

The following observations seem to point to the same conclusion.

The thin muscle-plates of Amphioxus (fig. 6*a*) present in longitudinal sections a beautiful cross striation. Each isotropous disc (*i*) is divided into two discs by a delicate, but distinct membrane of Krause; each anisotropous disc (*q*) is composed of two discs, separated by a thin layer, that takes but a faint stain with chloride of gold, the median disc of Hensen. In the middle of this transparent portion there is sometimes to be seen an extremely delicate line, the membrane of Hensen.

The membranes of Krause form, as is known, crossnets, which bring the fibrillae of the entire muscle-plate in connection with each other. In the adult animal real muscle-cells are not to be distinguished, there are only the thin flattened muscle-plates to be found, which however in hardened specimens sometime appear to be broken up into rows of flat bundles of fibrillae. This is nothing but an artefact.

In longitudinal sections of Amphioxus in which therefore the muscle-plates are cut in the same direction, but mostly appear not as plates but cut obliquely as bundles of muscle-fibres (fig. 6*a*), there are to be found, in case the sections are coloured after the chloride of gold method, in many places just there were the anisotropous and isotropous discs meet, minute black dots, or small corpuscles; seen under a microscope of the highest magnifying power these dots appear as very delicate cross lines, thickened in the middle, running just between *q* and *i*. In these discs belonging to the same muscle-plate these dots are lying in adjoining discs one just beneath the other, so that rows of black dots running parallel to the myofibrillae are formed. In each muscle-plate such longitudinal rows seem to be distributed with some regularity. These black dots were always found only at one side of the anisotropous disc, and, so it seems, always at the same side of *q*, viz. at that turned caudal. The black dots lying in the same muscle-plate in the same longitudinal row, are often

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[1]) Rivista di Patologia nervosa e mentale. Vol. V fasc. 10. 1900.

found to be connected with each other by means of very delicate fibrillae, which are running parallel to the myofibrillae. This could be stated in many cases with great clearness. In some cases these fibrillae were straight, in other cases more or less undulating. In fig. 6 *a* a longitudinal section through the muscular plates (cut obliquely) is drawn greatly enlarged. The small dots and fibrillae are easily to be seen.

In transverse sections the same rows of fibrillae and black dots were also to be seen, and here they are seen to be distributed more or less regularly on the muscle-plates (fig. 6*b*). At both ends of the black dot here too a delicate black line may be seen, extending for some way along the muscle-plates but then being lost to view. By playing up and down by means of the micrometer screw of the microscope in cross sections too a longitudinal fibril may be made out extending upwards and downwards from the black corpuscle; this fibril is identical with that, which in longitudinal sections was seen to run parallel to the myofibrillae and to connect the black dots of a longitudinal row with each other.

So we find here in the muscle-plates of Amphioxus an apparatus, which brings the anisotropous discs of the same muscle-plate in connection with each other, which seems to be distributed with some regularity over the whole muscle-plate, and which gives the staining reaction of the neurofibrillae. Although I could not find the connection of these fibrillae with the motor nerves, still these facts seem to point to the conclusion, that we may regard these fibrillae and their knobshaped thickenings at one side of the anisotropous discs as representing the real innervation-apparatus of the striped muscle-fibres. Sometimes I saw one of the longitudinal fibrillae near the place of attachment of the myofibrillae to the myosepts bend off from the muscle-plate; but it was lost almost immediately between the myofibrillae in the neighbourhood and could not be traced any farther. When we consider however the constant position of the small knobshaped thickenings at one side of the anisotropous disc, the fine often undulated connecting fibrillae, the dark-purple tinction with chloride of gold (Nachvergoldung APÁTHY) so characteristic for neurofibrillae, then, I think, it is difficult to avoid the conclusion that they are neurofibrillae.

This seems to me to be important from a general point of view. Although the structure of the striped muscular tissue of Amphioxus differs largely from that of the higher Vertebrates, yet the same type of cross striation, that is, the same structure of the myofibrillae, is present in all.

Where now HEYMANS and VAN DER STRICHT found a motor nerve endplate identical with those of the higher Vertebrates and at the side of this structure can be seen an innervation of each anisotropous disc, as I have attempted to show, there is room for the conclusion that in other vertebrates too the so-called motor nerve endplate is not the ending of the motor nerve, but that from here neurofibrillae enter the muscle-fibre, and that every anisotropous disc is innervated. The truth of this surmise, however, must be tested by further study.

Amsterdam, October 1902.

(November 20, 1902).

KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN
TE AMSTERDAM.

PROCEEDINGS OF THE MEETING
of Saturday November 29, 1902.

(Translated from: Verslag van de gewone vergadering der Wis- en Natuurkundige Afdeeling van Zaterdag 29 November 1902, Dl. XI).

CONTENTS.

The following papers were read:

Chemistry. — „*The intramolecular rearrangement of atoms in halogen acetanilides and its velocity,*" II. By Dr. J. J. Blanksma. (Communicated by Prof. C. A. Lobry de Bruyn).

(Communicated in the meeting of October 25, 1902).

In a former communication [1]) it was shown that the conversion of acetylchloranilide in acetic acid solution under the influence of hydrochloric acid proceeds like a monomolecular reaction. In continuing this research the object was to study the influence of:

1st. The dilution of the acetic acid with water.
2nd. The quantity of added hydrochloric acid.
3rd. The solvent (besides acetic acid, alcohols etc.).
4th. Different catalysers (H Cl, H Br, H_2SO_4).
5th. Different groups in the nucleus and their relative positions.
6th. The temperature.

First of all the influence of the dilution of the acetic acid was studied, varying proportions of hydrochloric acid being also added. afterwards a few experiments were made in alcoholic solution.

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[1]) Proc. Royal Acad. Amsterdam. June 29, 1902.

The *modus operandi* was as follows:

A definite quantity (3 to 4 grams) of acetylchloranilide was dissolved in respectively 100, 150, 200 and 250 c.c. of 100 °/₀ acetic acid; to this were added 10, 15, 20 or 25 c.c. of 28,67 °/₀ hydrochloric acid and the mixture was finally diluted with water to 500 c.c. The experiments were then conducted as described in the previous communication; by applying the formula $k = \frac{1}{t}\, l\, \frac{A}{A-x}$ the k's were calculated; t is expressed in minutes.

The following results have been obtained:

c.c. acetic acid. in 500 of solution.	10	15	20	25 c.c. hydrochloric acid.
100	0.00506	0.00973	0.0189	0.0241
150	0.00846	0.0186	0.0318	0.0460
200	0.0157	0.0335	0.0588	
250	0.0359	0.0719		
300	0.0836			

c.c. alcohol. in 500 of solution.	10	15	20 c.c. hydrochloric acid.
200	0.00883	0.0201	0.0341
250	0.0158	0.0358	0.0591

By means of these figures curves may be constructed either by taking the figures from a horizontal row or those from a column. The first row for instance shows how the velocity of reaction (constant) increases in 20 °/₀ acetic acid in the presence of a varying amount of hydrochloric acid (10, 15, 20, 25 c.c.) etc.

In this manner the different series may be represented by the lines *A*, *B*, *C* and *D*.

The first column shows how the velocity of reaction changes with different concentrations of the acetic acid if the amount of the catalyser is constant. These columns are represented by the lines *E*, *F*, *G* and *H*. The alcoholic solution has been represented in the same manner (A', B' ; C', D', E').

These curves show:

1st. That the velocity of reaction, both in acetic and alcoholic solution, is decreased by addition of water.

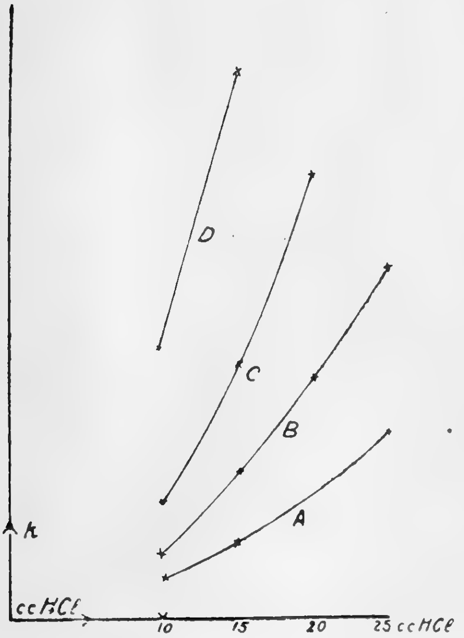
2nd. That the velocity of reaction is much accelerated by increasing the catalyser.

3rd. That the curves all end in the origin of the co-ordinates which means that the velocity of change in water without hydrochloric acid is zero so that the substance is stable therein. [Always on condition that light is excluded, (compare first communication)].

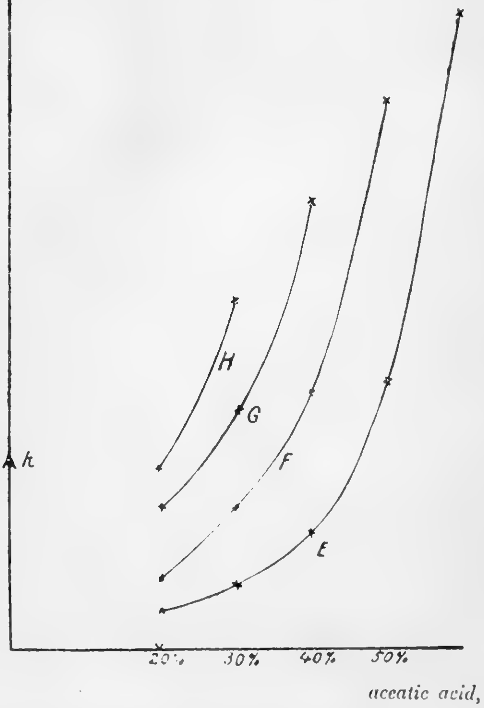
On comparing the two tables it will be also noticed that the velocity of reaction is greater in acetic acid than in alcohol; for instance, in a mixture of 200 c.c. of acetic acid and 15 c.c. of hydrochloric acid, k = 0.0335; when using 200 c.c. of alcohol and 15 c.c. hydrochloric acid k = 0.0201 1).

If we compare the curves *E*, *F*, *G* and *H* we notice that on decreasing the concentration of the catalyser, the curves begin to approach the abscissa axis which again shows that, in the absence of hydrochloric acid, the velocity of change in acetic acid or alcohol is zero or in any case very small, which may also be seen from the curves *A*, *B*, *C* and *D*.

A 100c.c. acet.acid with water to 500c.c.
B 150 » » » » » » »
C 200 » » » » » » »
D 250 » » » » » » »



E 10 c.c. HCl in 500 c.c. solution.
F 15 » » » » » »
G 20 » » » » » »
H 25 » » » » » »



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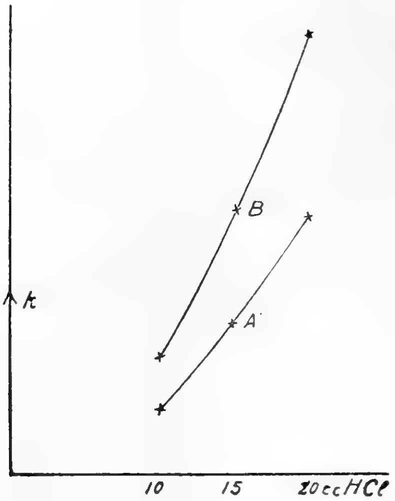
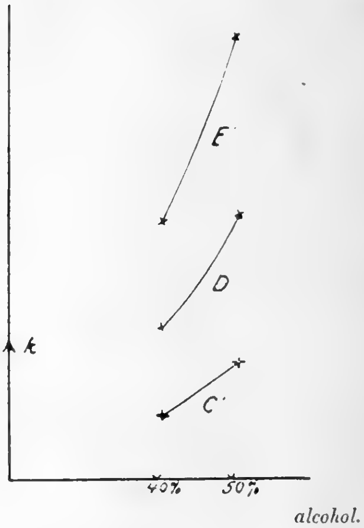
1) If we calculate number of mols. of alcohol or acetic acid to a given number of mols. of water we see that this difference in velocity of reaction is still greater.

A′ 200 c.c. alcohol + water to 500 c.c.
B′ 250 » » + » » 500 »



C′ 10 c.c. HCl in 500 c.c. solution.
D′ 15 » » » » » »
E′ 20 » » » » » »



Mathematics. — "*Five rotations in S_4 in equilibrium.*" By Dr. S. L. van Oss, Zaltbommel. (Communicated by Prof. P. H. Schoute).

In a previous paper (these *Proceedings*, Vol. IV, p. 218) the investigation of the elementary motion in S_4 was reduced to the consideration of the elementary motion in S_3 by making use of a principle to be read as follows: A system of rotations about planes *all passing through one and the same point* is in equilibrium when their intersections with an arbitrary S_3 are in equilibrium. Here we mean by section of a rotation with any S_3 the rotation of the intersecting space caused by its component about the plane orthogonally cutting this S_3 in the intersection of the plane of rotation.

As an immediate result of this principle we can state the conditions under which three to seven planes through *one* point can be the planes of a system of rotations in equilibrium. Thus i. a. the condition for four planes, that they must belong to a hyperboloidic pencil, etc. etc.

We now wish to extend this principle in order to arrive by investigation also at the case, that the planes do not pass any longer through one and the same point.

It goes without saying, that if a system of rotations is in equilibrium, its section with every S_3 must be in equilibrium. The question here, however, is to find out how many of those intersections will have to be examined before we can conclude about the system being in equilibrium or not.

To this end we direct our attention in the first place to the case, that a system Ω has two sections in equilibrium, namely with the spaces A and B.

If the section Ω/A is in equilibrium, then Ω must necessarily be reducible to a single rotation about a plane in A; likewise, if Ω/B is in equilibrium, then Ω can be reduced to a single rotation about a plane in the space B.

So from the equilibrium of the sections it does not yet follow that the system itself is in equilibrium, for the possibility remains that it may be reducible to a rotation about the plane common to the two spaces of intersection.

If, however, we can point out three spaces S_3 not passing through the same point, their sections being in equilibrium, then the equilibrium of the system itself is guaranteed. Let us now apply this result to determine five planes which can be the bearers of a system of rotations in equilibrium.

The neccessary condition which these planes must satisfy is that they be intersected by three spaces S_3, not passing through one and the same point, in rays of a linear congruence. In other words: They must intersect three pairs of straight lines, the director lines of these congruences.

Now we know that in S_4 there are just 5 planes intersecting 6 given lines. They are the five "associated planes" of SEGRE (*Rend. di circ. math. di Palermo*, t. II, 1888).

Now we have the necessary condition; we shall show, that it is also sufficient.

Let Ω be a system of rotations about 5 associated planes, A an S_3 so that Ω/A is in equilibrium. If Ω were not in equilibrium itself, this system would have to be equivalent to a rotation ω about a plane α in A. If we reverse the direction of the rotation about this plane, then the combination (Ω—ω) is in equilibrium. If we now consider a second intersecting space B, not through α, then the planes of Ω are intersected in 5 rays of a congruence and the plane of ω in a line not belonging to this congruence. The section of B with the combined system Ω—ω would, however, have to be in equilibrium. This is impossible, unless ω is equal to naught, i. e. unless Ω is in equilibrium.

Nothing remains but to determine the ratios of the intensities of the rotations of Ω. This should be done as follows:

We consider an arbitrary S_3 which intersects the planes of Ω in the axes of rotation of the section; the determination of the ratios of the intensities belonging to them is a well known problem.

If, finally, we notice that between the intensities ω and ω' of a rotation in S_4 and its intersection with a space A the relation $\omega' = \omega \sin (A\omega)$ exists, then in this way the intensities of the rotations about the five associated planes have become known quantities.

Mathematics. — "*On interpolation based on a supposed condition of minimum.*" By J. Weeder. (Communicated by Prof. H. G. van de Sande Bakhuyzen.)

For the reduction of the daily rates of the standard clock in the Leyden Observatory I have developed a method of interpolation, which may perhaps also be profitably used for other investigations.

The following is the problem we have to deal with: a variable quantity, here the correction of the clock, is given for a series of instants, during a long period, with unequal intervals; how can we find an intermediate value of that correction at any moment.

First I tried to solve this problem with the limiting condition that for all the intervals of time which enter into the calculation there is a smallest common divisor, which we take as unit of time.

1. Let S (clock correction) be the variable quantity, and g (rate) the amount by which it increases during a unit of time. Let S_p and S_q, be two successively determined values of S separated by m units of time, then $\frac{S_q - S_p}{m}$ is the average increase per unit; that increase is represented by Q_m. Hence the m quantities $g_1\, g_2 \ldots g_i \ldots g_m$ of the interval considered depend on the relation $\sum\limits_{i=1}^{i=m} g_i = S_q - S_p = m\, Q_m$ and a similar relation exists for each interval between two consecutive determinations of S.

In order to determine the quantities g, I put the condition that the sum of the squares of the differences of the first order for the whole period of observation should be a minimum. This condition of minimum was selected with a view to the special case where we have to interpolate between the clock corrections, but I doubt whether in all cases these interpolated values will be the most probable ones. Leaving aside for the moment these considerations, I go on developing the problem in hand. The quantities which correspond to an interval of m units occur only in the following terms of the sum which according to this condition must be a minimum:

$$(g_1-g_p)^2+(g_2-g_1)^2\dots\dots+(g_m-g_{m-1})^2+(g_q-g_m)^2,$$

g_p represents the rate preceding S_p and g_q the rate following S_q.

If to this quantity we add:

$$2k_m\,(g_1+g_2\dots\dots+g_i\dots\dots+g_{m-1}+g_m)$$

their sum U will also be a minimum for the same values g_1 to g_m, because $\sum\limits_{i=1}^{i=m} g_i=S_q-S_p=mQ_m$ is constant.

These values $g_1\dots g_m$ are found by means of the condition that each derivative of U taken with reference to each variable shall be zero. At the same time we must assign a definite value to k_m in order to satisfy the equation $\sum\limits_{i=1}^{i=m} g_i=mQ_m$.

Thus we obtain the following equations:

$$\left.\begin{array}{lllll}
-g_p & +2g_1 & -g_2 & +k_m & =0\\
-g_1 & +2g_2 & -g_3 & +k_m & =0\\
\dots & \dots & \dots & \dots & \dots\\
-g_{i-1} & +2g_i & -g_{i+1} & +k_m & =0\\
\dots & \dots & \dots & \dots & \dots\\
-g_{m-2} & +2g_{m-1} & -g_m & +k_m & =0\\
-g_{m-1} & +2g_m & -g_q & +k_m & =0
\end{array}\right\}\quad\dots\dots\quad(A)$$

Bij taking the sum of these m equations, each multiplied by $i\,(m-i)$, we eliminate g_1, g_i, g_m, the coefficient of each g_i of that sum being equal to 2; hence the sum of the terms is $2\sum\limits_{i=1}^{i=m} g_i=2\,mQ_m$.

The coefficient of k_m is:

$$\sum_{i=1}^{i=m} i\,(m-i)=\frac{m\,(m+1)\,(m+2)}{1\,.\,2\,.\,3}.$$

Hence the sum of the multiplied equations is:

$$-m\,g_p+2\,m\,Q_m-m\,g_q+k_m\,\frac{m\,(m+1)\,(m+2)}{6}=0$$

whence

$$k_m=\frac{6\,(g_p+g_q-2\,Q_m)}{(m+1)\,(m+2)}.$$

Then we determine the values of g_i by multiplying the m equations by the terms of the following series:

$1(m-i+1)$, $2(m-i+1)$,...$(i-1)(m-i+1)$, $i(m-i+1)$, $i(m-i)$,...., $i.2$, $i.1$

and taking their sum; in the resulting equation all unknown quantities $g_1 \dots g_m$ except g_i are eliminated. That equation got by summation is:

$$-g_p(m-i+1)+(m+1)g_i-i\,g_q+\frac{1}{2}\,i\,(m-i+1)\,(m+1)\,k_m=0$$

which yields:

$$g_i=\frac{m-i+1}{m+1}\,g_p+\frac{i}{m+1}\,g_q-\frac{i\,(m-i+1)}{2}\,k_m$$

hence $$g_1=\frac{m}{m+1}\,g_p+\frac{1}{m+1}\,g_q-\frac{1}{2}\,m\,k_m$$

and $$g_m=\frac{1}{m+1}\,g_p+\frac{m}{m+1}\,g_q-\frac{1}{2}\,m\,k_m\,.$$

The quantities g_p and g_q are still unknown and depend on the quantities Q of the neighbouring intervals; they may be derived from them by means of successive approximation.

It gives some advantage to determine $\frac{1}{2}(g_p+g_1)$ and $\frac{1}{2}(g_m+g_q)$ by approximations, because then we shall have to approximate only one quantity for each S. The approximation may be made in the following way: we put $\frac{1}{2}(g_p+g_1)=c_p$ and $\frac{1}{2}(g_m+g_q)=c_q$, then we obtain:

$$k_m=\frac{6}{m^2+2}\,(c_p+c_q-2\,Q_m)$$

$$g_p=-\frac{3m}{m^2+2}\,Q_m+\left(1+\frac{2m^2+1}{m(m^2+2)}\right)c_p+\frac{m^2-1}{m(m^2+2)}\,c_q$$

$$g_q=-\frac{3m}{m^2+2}\,Q_m+\frac{m^2-1}{m(m^2+2)}\,c_p+\left(1+\frac{2m^2+1}{m(m^2+2)}\right)c_q\,.$$

For the next interval of n units of time between the determinations S_q and S_r we have the following equation:

$$g_m=-\frac{3n}{n^2+2}\,Q_n+\left(1+\frac{2n^2+1}{n(n^2+2)}\right)c_q+\frac{n^2-1}{n(n^2+2)}\,c_r\,.$$

As $g_q+g_m=2\,c_q$ we obtain when finding the summation of the two last equations a recurrent equation containing 3 consecutive quantities c, so that c_q can be expressed in c_p and c_r. This equation can also be written thus:

$$\left\{\frac{2m^2+1}{m(m^2+2)}+\frac{2n^2+1}{n(n^2+2)}\right\} c_q = -\frac{m^2-1}{m(m^2+2)}\, c_p + \frac{3m}{m^2+2}\, Q_m +$$

$$+\frac{3n}{n^2+2}\, Q_n - \frac{n^2-1}{n(n^2+2)}\, c_r\,. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (B)$$

For the first interval considered here the first of the equations (A) is $g_1-g_2+k_m=0$. This equation may also be written in the general form by putting $-g_1+2\,g_1-g_2+k_m=0$, thus assuming that the value of g preceding g_1 and c belonging to the first observation are both equal to g_1. In the same way c belonging to the last observation is equal to the last g of the last interval. Between each three consecutive quantities c, therefore, a relation exists of the form (B) and two other equations are added to the beginning and to the end of this series, each containing only two values c derived from the formulae for g_p and g_q. Let c_a and c_b be the first two and c_y and c_z the last two quantities c, then we obtain by substituting c_a for $g_p=c_p$ and c_b for c_q the first condition, and by substituting c_z for $g_q=c_q$ and c_y for c_p the last condition of the series which determine the values c.

If the lengths of the limiting intervals are represented by μ and ν these equations are:

$$(2\mu^2+1)\, c_a = +\, 3\mu^2 Q_\mu - (\mu^2-1)\, c_b$$
$$(2\nu^2+1)\, c_z = +\, 3\nu^2 Q_\nu - (\nu^2-1)\, c_y$$

The series (B) and these two equations determine all the quantities c. If we solve them by approximation our purpose is soon gained; we assume to the first approximation $c_q=\dfrac{nQ_m+mQ_n}{m+n}$ and c_a and c_z equal to the values of Q of the first and the last interval respectively. From the equations (B) we derive the first corrections $\Delta_1 c_p$, $\Delta_1 c_q$, etc. and $\Delta_2 c_q$ is derived from the formula:

$$\left\{\frac{2m^2+1}{m(m^2+2)}+\frac{2n^2+1}{n(n^2+2)}\right\} \Delta_2 c_q = -\frac{m^2-1}{m(m^2+2)}\, \Delta_1 c_p - \frac{n^2-1}{n(n^2+2)}\, \Delta_1 c_r\,.$$

In this interpolation we determine g_i and S_i of an interval of m units according to the formulae:

$$g_i = \left(\frac{1}{4}\, m\, k_m + c_p + \frac{c_p-c_q}{2m}\right) - \left(\frac{m+1}{2}\, k_m + \frac{c_p-c_q}{m}\right) i + \frac{1}{2}\, k_m\, i^2$$

$$S_i = S_p + \left(c_p - \frac{1}{6}\, k_m\right) i - \left(\frac{m}{4}\, k_m + \frac{c_p-c_q}{2m}\right) i^2 + \frac{1}{6}\, k_m\, i^3.$$

2. In the previous section the observed and the interpolated quantities S, occurring in the problem discussed, form a series of discrete values corresponding to an arithmetical series of the argument; now I will remove the restriction of commensurable arguments and will make this mode of interpolation applicable to a continuous varying quantity and an arbitrary argument by putting for the ratio of that series the infinitely small value dt. The condition of minimum then becomes $\int_a^z \left(\frac{d^2S}{dt^2}\right)^2 dt = \text{min.}$

The formulae for this continuous interpolation may be derived independently, but it is shorter to derive them from the corresponding formulae of the discrete interpolation developed above. For the present I shall put for the lengths of the intervals between which we have to interpolate m' and n', for the derived values $\frac{dS}{dt}$ of the interpolated function g', to distinguish them from the letters we have used in the former problem.

Instead of m and n we have $\frac{m'}{dt}$ and $\frac{n'}{dt}$; for c_p, c_q, c_r we must substitute the quantities $g'_p\,dt$, $g'_q\,dt$, $g'_r\,dt$, and for Q_m and Q_n the quantities $\frac{S_q - S_p}{m'}\,dt$ and $\frac{S_r - S_q}{n'}\,dt$ or $Q_{m'}\,dt$ and $Q_{n'}\,dt$.

After dividing the relations (B) by dt^2 and omitting the infinitely small values we have:

$$\left(\frac{2}{m'} + \frac{2}{n'}\right) g'_q = -\frac{1}{m'} g'_p + \frac{3}{m'} Q_{m'} + \frac{3}{n'} Q_{n'} - \frac{1}{n'} g'_r$$

from which, after dropping the accents, we get:

$$g_q = \frac{nQ_m + mQ_n}{m + n} + \frac{n(Q_m - g_p)}{2\,(m + n)} + \frac{m(Q_n - g_r)}{2\,(m + n)} \quad . \quad . \quad . \quad (C)$$

to which we must add as first and last equations:

$$g_a = Q_\mu + \frac{Q_\mu - g_b}{2} \quad \text{and} \quad g_z = Q_\nu + \frac{Q_\nu - g_y}{2}$$

For k_m we substitute $\frac{6}{m'^2}(g'_p + g'_q - 2\,Q_{m'})\,(dt)^3$; for i we substitute $\frac{t}{dt}$, if t represents the time between the last preceding observation at the moment for which we interpolate. These substitutions in the formula for S_i yield a formula for S_t, which, after the omission of infinitely small values and accents, is:

$$S_t = S_p + g_p t - \left[\frac{3}{2m}(g_p + g_q - 2\,Q_m) + \frac{g_p - g_q}{2m}\right] t^2 + \frac{g_p + g_q - 2Q_m}{m^2}\, t^3$$

By substituting in the above formula $m - t'$ for t, we obtain for S_t a formula developed according to the ascending powers of t', the interval between the moment for which we interpolate and the moment of the next observation. It is simpler to find the same formula by imagining the interpolation to be made in the inverse direction, so that the quantities g and Q change signs and the indices p and q change places. Hence:

$$S_{m-t'} = S_t = S_q - g_q t' + \left[\frac{3}{2m}(g_p + g_q - 2Q_m) - \frac{g_p - g_q}{2m}\right] t'^2 - \frac{g_p + g_q - 2Q_m}{m^2}\, t'^3.$$

For S_t to be interpolated in the following interval we use:

$$S_t = S_q + g_q t - \left[\frac{3}{2n}(g_q + g_r - 2Q_n) + \frac{g_q - g_r}{2n}\right] t^2 + \frac{g_q + g_r - 2Q_n}{n^2}\, t^3.$$

Therefore the formulae on either side of each observation are different. If in the latter formula t is negative and $-t'$ is substituted for it, the resulting formula differs from the preceding one only in the coefficients of the terms of the 3rd degree. The coefficients of the terms of the 2nd degree have become equal by satisfying the relation (C).

Therefore we also obtain the interpolated function if, by starting from a value (S_q) derived from observation, we represent the values of S_{-t} and S_{+t} for the moments between that observation and the next preceding one and those between that observation and the next following one by the formulae:

$$S_{-t} = S_q - g_q t + c_q t^2 - e_m t^3 \quad \text{and} \quad S_{+t} = S_q + g_q t + c_q t^2 + e_n t^3.$$

Taking this as basis, we find:

$$c_q = \frac{+g_p - 3Q_m + 2g_q}{m} = \frac{-2g_q + 3Q_n - g_r}{n} \quad e_m = \frac{g_p + g_q - 2Q_m}{m^2} \quad e_n = \frac{g_q + g_r - 2Q_n}{n^2}$$

The integral $\int_a^z \left(\frac{d^2S}{dt^2}\right)^2 dt$, which becomes a minimum through this nterpolation, is equal to the sum of the integrals between two consecutive observations, and each of these integrals can be expressed in the coefficients of the interval in the following manner:

$$I_n = \int_q^r \left(\frac{d^2S}{dt^2}\right)^2 dt = \frac{3(g_q + g_r - 2Q_n)^2}{n} + \frac{(g_q - g_r)^2}{n} = 3\,n^3 e_n^2 + \frac{(g_q - g_r)^2}{n}$$

or:

$$I_n = \frac{4}{3} n\,(c_q^2 + c_q\, c_r + c_r^2).$$

For the total integral ΣI_n we can also derive a simple form by integrating partially:

$$\int_a^z \left(\frac{d^2S}{dt^2}\right)^2 dt = \left[\frac{dS}{dt}\frac{d^2S}{dt^2}\right]_a^z - \int_a^z \frac{dS}{dt}\frac{d^3S}{dt^3}\,dt.$$

For the first moment a and the last moment z, $\frac{d^2S}{dt^2} = 0$, as follows from the first and the last equations belonging to (C). For each interval between two observations $\frac{d^3S}{dt^3}$ is a constant quantity. Hence we find:

$$I = \Sigma\, 6\, e_n (S_q - S_r)$$

where the summation extends over all the intervals between the observations. We can easily find a simple expression for the differential quotient of I according to each of the observed values, which may be useful when we want not only to interpolate for an intermediate moment but when at the same time we have to determine the most probable values of the observed quantities. For then the difficulty presents itself how to find the best method for diminishing the amount of the minimum value I by applying corrections to the observations, of which corrections the mean value is known.

In doing so heed must be taken that these corrections, being errors of observation, shall satisfy the law which determines their probabilities as functions of their magnitudes.

I have not yet reached a satisfactory solution of this problem. The following remarks, however, on this subject seemed important enough to be communicated.

3. Let L_p, L_q, L_r be the observed quantities, free from errors of observation, and f_p, f_q, f_r the errors themselves.

If we have developed the interpolation by means of the quantities L and f separately, we obtain the formulae:

$$L_t = L_q + G_q\, t + C_q\, t^2 + E_n\, t^3$$
$$f_t = f_q + \beta_q\, t + \gamma_q\, t^2 + \varepsilon_n\, t^3\,.$$

By means of the summation of these two formulae we get:

$$S_t = S_q + g_q\, t + c_q\, t^2 + e_n\, t^3.$$

If we apply a partial integration to $\int_a^z \frac{d^2L}{dt^2}\cdot\frac{d^2f}{dt^2}\,dt$, we get:

$$\left[\frac{d^2L}{dt^2}\,\frac{df}{dt}\right]_a^z - \int_a^z \frac{d^3L}{dt^3}\,\frac{df}{dt}\,dt$$

or $$\left[\frac{dL}{dt}\,\frac{d^2f}{dt^2}\right]_a^z - \int_a^z \frac{dL}{dt}\,\frac{d^3f}{dt^3}\,dt$$

In either case the integrated parts are equal to 0, because at the beginning and end $\frac{d^2L}{dt^2}$ and $\frac{d^2f}{dt^2}$ are zero.

In this way we find the relation:

$$\Sigma\, E_n\,(f_q - f_r) = \Sigma\, \varepsilon_n\,(L_q - L_r).$$

In the same way we find the relation:

$$\Sigma\, e_n\,(f_q - f_r) = \Sigma\, \varepsilon_n\,(S_q - S_r).$$

By applying the corrections $-f$, the minimum I_S becomes the minimum $I_L = I_S - f$.

$$I_S - f = \Sigma\, 6\,(e_n - \varepsilon_n)\,(S_q - f_q - S_r + f_r) =$$
$$= \Sigma\, 6\, e_n\,(S_q - S_r) - \Sigma\, 6\, \varepsilon_n\,(S_q - S_r) - \Sigma\, 6\, e_n\,(f_q - f_r) + \Sigma\, 6\, \varepsilon_n\,(f_q - f_r)$$

which expression by means of the latter relation may be reduced to:

$$I_S - f = I_S - 12\, \Sigma\, e_n\,(f_q - f_r) + \Sigma\, 6\, \varepsilon_n\,(f_q - f_r).$$

For infinitely small values f, the last term in the expression given above becomes of the order f^2 so that we find $\frac{\partial I_S}{\partial S_q} = 12(e_n - e_m)$. This result enables us to determine the set of small corrections, which, when applied to the quantities S, diminish I_S by the greatest amount. These corrections will be proportional to the abrupt changes of $\frac{d^3S}{dt^3}$.

The variations in the interpolation coefficients g, c, e, resulting from these corrections are found by repeating the interpolation, with this sole difference that for the observed quantities S we substitute the abrupt changes of $\frac{d^3S}{dt^3}$.

As a rule a set of corrections of this kind will not show the character of the errors of observation and therefore be dissimilar to the set of errors which actually exist in the observed quantities S. We may also determine a limit which should not be passed in the rectification.

If the quantities f represent the real errors, we have:

$$I_S = I_L + \Sigma\, 12\, E_n\,(f_q - f_r) + \Sigma\, 6\, \varepsilon_n\,(f_q - f_r)$$

The coefficients E of the interpolation formula between the correct quantities S and the errors f being as a rule entirely independent, we must assume that in $\Sigma\, 12\, E_n\,(f_q - f_r)$ the positive and negative terms neutralize each other for the greater part. Hence the difference $I_S - I_L$ does not exceed $\Sigma\, 6\, \varepsilon_n\, (f_q - f_r)$, the value of which depends only on the errors and the lengths of the intervals; the mean value of this expression for every possible distribution of the errors of the observations may be derived from the mean error of those observations.

This is the utmost limit to which by means of corrections to the observed quantities S we can diminish I_S, lest the interpolation curve found should assume a less sinuous form than would be probable with regard to the results of the observations and their precision.

Here follows an example of the computation.

The annexed table contains the interpolation coefficients of a part (period 1882 June 8 to August 30), taken from a longer series of observed rates of the clock Hohwü 17. Therefore the coefficients at the limits of this period are not in accordance with the boundary-conditions supplying the formula (C).

We compute the interpolated clock corrections by means of the formula:

$$S_t = S_q + t\left(g_q + n\, c_q \frac{t}{n} + n^2\, e_n \frac{t^2}{n^2}\right)$$

S_q is the clock correction of the last preceding observation and the coefficients g_q, nc_q, n^2e_n are given in the columns 5, 6 and 7; they are expressed in the unit $0^s.001$. The values g_q and nc_q to be used are placed a little above the horizontal line corresponding to the length of the interval expressed in days, which interval contains the moment t for which we interpolate. Because of its connection with the constant derivative of the third order of the interpolation curve within each interval, the coefficient n^2e_n for each interval has been placed on the horizontal line of that interval.

The 8th column contains the coefficients e and the 9th their differences σ by passing from one interval to the other. For each of these differences I have calculated the variation $\Delta\sigma_q$ of a given σ_q, as the corresponding correction of the clock S_q increases by $+\,0^s.100$ while the other corrections remain unmodified; they are given in the 10th column. By the increase $\Delta S_q = -\dfrac{\sigma_q}{\Delta\sigma_q} \times 0^s.100$ the difference σ_q becomes zero, so that by means of this increase we obtain the same result as if in the determination of the interpolation curve we had omitted the observation S_q. Hence the correction of the clock S_q derived from this interpolation is equal to the observed

Duration of the intervals in days m, n.	Mean daily rates Q.	$\frac{mQ_n+nQ_m}{m+n}$	Correction term $\frac{m(Q_n-g_r)+n(Q_m-g_p)}{2(m+n)}$	g. coefficient of t.	nc. c = coefficient of t^2.	n^2e. e = coefficient of t^3.	e.	$\sigma = e_n - e_m$	$\Delta\sigma$ for a variation $\Delta S = +0^s.100$.	Obs.—Comp. = $\frac{\sigma}{\Delta\sigma} \times 0^s.100$.
										s
		118	−03	115	+ 63			− 7.0	+ 5.4	−0.13
4	135					−43	− 2.7			
		110	+02	112	− 62			+ 4.9	+ 4.0	+0.12
4	086					+36	+ 2.2			
		106	−10	096	+ 44			− 3.1	+ 3.9	−0.08
4	126					−14	− 0.9			
		126	+16	142	+ 04			− 0.3	+ 3.7	−0.01
4	126					−20	− 1.2			
		102	−12	090	− 68			+ 3.2	+ 3.0	+0.11
5	073					+51	+ 2.0			
		108	−01	107	+ 52			− 5.3	+ 4.1	−0.13
3	129					−30	− 3.3			
		122	−01	121	− 94			+ 4.9	+ 3.3	+0.15
7	104					+77	+ 1.6			
		156	+08	164	+ 18			−20.6	+ 26.0	−0.08
1	163					−19	−19.			
		143	00	143	−150			+23.4	+ 29.3	+0.08
4	064					+71	+ 4.4			
		081	−25	056	+ 46			− 5.3	+ 6.5	−0.08
3	094					−08	− 0.9			
		110	+14	124	+ 32			− 0.6	+ 5.6	−0.01
4	132					−24	− 1.5			
		113	+03	116	− 50			+ 2.5	+ 3.0	+0.08
5	090					+24	+ 1.0			
		089	−01	088	+ 14			− 2.4	+ 4.2	−0.06
3	089					−13	− 1.4			
		082	−05	077	− 45			+ 2.9	+ 4.3	+0.07
5	070					+38	+ 1.5			
		095	+06	101	+ 43			− 5.3	+ 4.6	−0.12
3	110					−34	− 3.8			
		093	−08	085	− 78			+ 7.7	+ 6.4	+0.12
4	070					+63	+ 3.9			
		113	+05	118	+ 28			−25.9	+ 57.0	−0.05
1	124					−22	−22.			
		106	+02	108	− 38			+39.	+167.	+0.02
1	087					+17	+17.			
		090	−07	083	+ 31			−21.2	+ 85.0	−0.03
2	097					−17	− 4.2			
		101	−07	094	− 28			+ 8.8	+ 21.9	+0.04
3	107					+41	+ 4.6			
		153	+08	161	+ 33			−29.6	+ 57.8	−0.05
1	169					−25	−25.			
		148	+04	152	− 84			+34.2	+114.	+0.03
2	105					+37	+ 9.2			
		106	−11	095	+ 81			−11.0	+ 10.6	−0.10
6	110					−66	− 1.8			
		054	+05	059	− 77			+ 3.9	+ 2.6	+0.15
4	016					+34	+ 2.1			
		021	−14	007	+ 25			− 2.5	+ 3.8	−0.07

S_q diminished by $\frac{\sigma_q}{\Delta\sigma_q} \times 0^s.100$. These differences Obs.—Comp. given in seconds of time, are contained in the 11th column.

From the developed formulae I derived for these 24 intervals the value $I_S = \Sigma \frac{4}{3} n (c_q^2 + c_q c_r + c_r^2) = 69500$, while for all the different manners of distribution of the errors of observation the mean of all the values $I_f = \Sigma\, 6\, \varepsilon_n (f_q - f_r)$, which values depend only on the magnitude of the errors and on their distribution is equal to 30500. In the computation the mean error of the observations has been put $0^s.028$, which value must be regarded as the smallest that can be assumed on the strength of other investigations. Therefore the sinuosity of the interpolation curve must be ascribed for a great part to errors of observation.

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