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Physics. — Communication N°. 59^b from the Physical Laboratory at Leiden, by Prof. H. KAMERLINGH ONNES and Dr. M. REINGANUM: "*Contributions to the knowledge of* VAN DER WAALS' *ψ-surface*". II. "*The part of the transverse plait in the neighbourhood of the plaitpoint in* KUENEN'*s experiments on retrograde condensation*".

(Read June 30, 1900.)

1. The most important part of a transverse plait in VAN DER WAALS' ψ-surface is no doubt that in the neighbourhood of the plaitpoint. For investigations of this part however a higher degree of accuracy is required than was sufficient for the construction of the model of the whole plait and of the constructions belonging to it, described in Communication N°. 59^a.

In the following pages we represent the part of the surface shown by a rectangle in figs. 3 and 4 of Pl. II, which representation is based on more accurate calculations of p (to 5 decimals) made for values of x and v in a smaller range by means of the same equation of state, from which we started for the construction of the general model. The principles on which the choice of this equation of state was based for the following illustration of VAN DER WAALS' theory have been laid down in § 4 of Comm. N°. 59^a; in the present paper we will consider the manner in which the constants occurring in that equation have been obtained, and in how far by this choice of constants the accepted equation of state can be made to harmonize with KUENEN's observations. As explained in § 2 Communication N°. 59^a two questions are specially prominent: 1st. in how far do the mixtures investigated by KUENEN agree with the law of corresponding states and 2nd. in how far can the critical constants of the homogeneous mixtures be represented by VAN DER WAALS' formulae of the second degree.

2. To obtain an opinion on this we cannot directly apply to KUENEN's observations the ordinary method of calculating the reduced values of the pressure, the volume and the temperature by means of the critical quantities. For the critical temperature of the homogeneous mixture (point K in fig. 3, Pl. IV) is situated according to VAN DER WAALS' theory in the unstable part and has therefore not been observed.

Neither are we assisted even to a moderate extent by RAVEAU's method of measuring off the logarithms of the pressure and the volumes as ordinates and abscissae and by then shifting the systems of isothermals of the two substances parallel to themselves until they cover one another. This is chiefly to be ascribed to the smallness of the range over which each of the isothermals extends. Those parts of the isothermals that can be drawn, show no striking curvatures and run almost parallel. Hence there is too much latitude in the adjustment, so that it is not possible to determine sharply enough the exact position in which the one system coincides with the other.

Therefore we can only very roughly consider the ratio of the absolute temperatures of two isothermals covering each other in the way mentioned, as being the ratio of the critical temperatures belonging to them; the same holds for the pressure and the volume.

It is obvious that we may use instead of the pressure itself, the product pv, which is moreover of so much importance for the investigation of the isothermals, draw for one temperature $\log pv$ as a function of $\log v$ and determine by shifting the curve $\log pv = f(\log v)$ on the one hand the ratios $\frac{p_{k1}v_{k1}}{p_{k2}v_{k2}}$ (or what comes to the same $\frac{T_{k1}}{T_{k2}}$) and on the other hand $\log \frac{v_{k1}}{v_{k2}}$. As this still implies shifting the system in the direction of both the axes of co-ordinates, it also still offers too great a latitude.

We may do without the displacement in the direction of one of the axes, when we measure off not $\log pv$ but $\frac{pv}{RT}$, which has the same value or molecular quantities in corresponding states. For large volumes this quantity has the value 1, for the critical state about 0.29.

In applying this method it appeared that it was not possible to completely cover the system of $\frac{pv}{RT}$ curves of the one substance by those of the other. Irregular deviations did show themselves, which may probably to a large extent be ascribed to errors of observation. The result was that a certain latitude still remained in the adjustments and the limits were sought within which the coincidence might be called satisfactory.

The ratio of the critical volumes follows immediately from the curves of $\log v$ covering each other, which ratio could then only be included within the limits just mentioned.

The ratio of the critical temperatures is given by the temperature to which two $\frac{pv}{RT}$ curves belong, covering each other, so that this also can only be included within limits, while the same holds for the critical pressures, obtained by means of $Cp_kv_k = T_k$. For C we took the value found by AMAGAT for carbon dioxide.

The following table gives the results of these processes starting from $p_{k2} = 72.9$, $v_{k2} = 0{,}00426$, $T_{k2} = 304.35$ for carbon dioxide.

Proportion of CH_3Cl.	V_{kx}.	V_{kx} mean	T_{kx}	T_{kx}. mean.	p_{kx}.
$x = 1\ 0$	0 00668 to 0 00728	0.00698	413 to 419	416	63.2 to 57.8
$x = 0.75$	633 to 588	610	382 to 391	386 5	mean value 64 7
$x = 0.50$	654 to 675	665	337 5 to 340	339	mean value 52.2
$x = 0.25$	501 to 562	531	indefinite	indefinite	

For the critical temperature of pure methylchloride we find the same value as found experimentally by KUENEN (416.0). The mean value of the critical pressure (60.5) however deviates much (7,5 pCt.) from the value found by KUENEN (64.98). The highest value is in better agreement (3 pCt.)

We will naturally next consider how *the critical temperatures of the homogeneous mixtures* T_{xk} found by us, are situated with respect to *the critical point of contact temperatures* T_{xR} found by KUENEN. This may be seen from the following table:

Mixture.	T_R	T_k
$x = {}^3/_4$	396	386 5
$x = {}^1/_2$	370.1	339
$x = {}^1/_4$	338.4	indefinite

In good agreement with the theory, the values of T_k are found to be lower than those of T_R, and one would be inclined to fill in for $x = {}^1/_4$, symmetrically with $x = {}^3/_4$, $T_k = 328$. Yet the difference of 31° found for $x = {}^1/_2$ gives rise to some objections against putting great trust in the determinations. If we also bear in mind the irregular deviations, remaining between the two systems covering each other, which leaves undecided whether the mixtures deviate from the law of corresponding states more than the simple substances, and also the large deviations found in determining the pressure of methylchloride, much uncertainty remains about the critical value itself.

Therefore it is desirable to try to deduce in a different way something about the critical temperatures and the pressures of the homogeneous mixtures from the whole of the observations for each mixture. We find a means for this in the equations given by KUENEN which express as well as possible the whole of the observations for each mixture, which equations we at first did not think it advisable to use in order that we should be as little biassed as possible in forming an opinion from the observations themselves about the problems in hand. But it is not to be expected that we can satisfactorily determine the critical quantities, firstly because KUENEN has not taken for all his mixtures the same temperature function for a, secondly as states situated far from the critical point, which have influenced the determination of the equations, can give rise to errors by the extrapolation with the defective equations of state.

However it may be considered as a confirmation of our conclusions from the adjustments when the former can also be derived from these equations.

With regard in the first place to the fulfillment of the law of corresponding states, we might conclude from the disagreement of the ratio $n_x = \frac{\beta_x}{b_x}$ given by KUENEN,

$x = 1 \qquad n_1 = 1,40$
$x = {}^3/_4 \qquad n_{3/4} = 1,26$
$x = {}^1/_2 \qquad n_{1/2} = 1,66$
$x = {}^1/_4 \qquad n_{1/4} = 1,38$
$x = 0 \qquad n_0 = 1,09$

that the mixtures investigated do not fulfill the law of corresponding states[1]. The value of this conclusion becomes smaller, when we consider that KUENEN has accepted b_x somewhat arbitrarily. Both this and the choice of different temperature functions for a must influence the values found for β, and although we may allow that the variation of the values of n indicates a peculiarity in the closely related quantities b and β, they can only support the conclusion but weakly, that the mixtures would satisfy the law of corresponding states to a smaller degree than the simple substances.

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[1] That n must have the same value for all substances that fulfill the law of corresponding states, has been demonstrated by KAMERLINGH ONNES, Verh. Kon. Akad. v. Wet. XXI, 1881, p. 20; Arch. Néerl. T. XXX, p. 112.

Let us consider now what follows from KUENEN's equations for the critical volumes and temperatures.

x	V_{xk}.	T_{kx}	T_{Rx}.
1	0.00725		
3/4	606	402 (397.5)	396
1/2	620	350	370.1
1/4	489	338 (332 5)	331.4
0	435	304	

It is remarkable that (as follows from the values of n and the linear variation of b just mentioned and the relation $v_k = 3\,b + 2\,\beta$) the critical volumes show the same course as that found by means of the method of coincidence. From KUENEN's combined experiments it would hence appear that for mixtures of methylchloride and carbon dioxide the critical volumes cannot be expressed as a function of the second degree of the composition, as it is accepted by VAN DER WAALS in his theory of ideal mixtures, but that at least a function of the third degree is required for it.

In fig. 5 the curve of v_k is represented by a dot-dash-line when resulting from the coincidence method, and by a dash-line when resulting from KUENEN's equation, and by a complete line that of the ideal mixture to be considered in the next section.

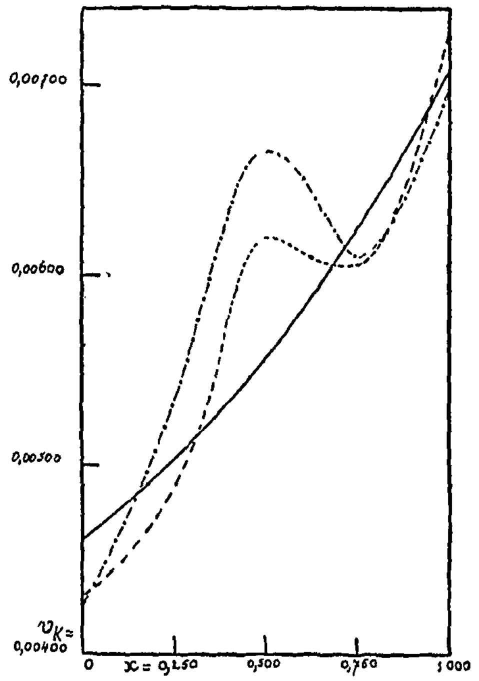

Fig. 5.

Concerning the critical temperatures, not much can be derived from KUENEN's equations. For the values between brackets in the table given above a has been calculated by means of $\frac{K}{T}$, in which we have used for K the numbers given in brackets by KUENEN. The temperature values without brackets in the same table have been calculated with values of a obtained by interpolation between the values of a given by KUENEN separately for different temperatures.

Only for the second mixture an acceptable value of $T_R - T_k$ is found, i. e. 20°, but it is obvious that this difference cannot be negative as with $x = {}^3/_4$ or zero as with $x = {}^1/_2$. And so the values from KUENEN's equations cannot be an argument either for or against the values found by means of the method of the coincident systems.

Therefore for the time being no arguments other than those derived from the deviations of the critical volume mentioned above, can be adduced to justify the doubt of the possibility of expressing the critical quantities of the homogeneous mixtures in the case of KUENEN's experiments by the formulae given by VAN DER WAALS for the critical quantities of homogeneous mixtures, together with KUENEN's, identity $T_{ax} = K_x$.

§ 3. In order to obtain for $K_{11}, K_{12}, K_{22}, b_{11}, b_{12}, b_{22}$ in the equation

$$p = \frac{R\,T}{v - b_x} - \frac{K_x}{T(v + n\,b_x)^2}$$

$$K_x = K_{11}\,x^2 + 2\,K_{12}\,x\,(1-x) + K_{22}\,(1-x)^2$$

$$b_x = b_{11}\,x^2 + 2\,b_{12}\,x\,(1-x) + b_{22}\,(1-x)^2$$

(p = pressure in atmospheres, v = volume expressed in terms of the theoretical normal volume, R=gasconstant, T=absolute temperature, x = molecular composition, while the value of 1.4610 was taken for n) values which agree as well as possible with KUENEN's experiments, a curve of the second degree was drawn almost corresponding with the critical volumes found from the coincident systems, from which b_{11}, b_{12} and b_{22} were found. The convexity was chosen towards the x-axis, because in that case a value for K_{12} could be found, for which K_x was obviously of the second degree. This is justified as the final equations represented KUENEN's isothermals still within 2 pCt.

Subsequently the observation of the critical temperature of the point of contact for the mixture $x = {}^1/_2$ was taken as a basis for the calculation of the a's.

Now that the difference $T_{xR} - T_{xk}$ could not be deduced with any certainty from the observations, we had to confine ourselves to an estimation of it.

According to the results of the graphical determination of the connodal curve on a plaster cast constructed previously (see HART-

MAN's figure derived from it, Communication N°. 59^a, § 3) the critical temperature of the homogeneous mixture is situated lower than the plaitpoint temperature and although the place remains very uncertain, we thought ourselves justified in searching it at double the distance.

For our purpose it seemed at any rate sufficient to subtract 7° from the temperature of the critical point of contact for the composition $^1/_2$. With $T_{R\frac{1}{2}} - 7° = T_{k\frac{1}{2}}$, T_{ko} and T_{k1} we could now calculate K_{11}, K_{12}, K_{22}.

When the plaster-cast of the part of the surface near the plaitpoint was ready, it appeared that for the ideal mixture supposed $T_{R\frac{1}{2}} - T_{K\frac{1}{2}}$ amounts to about 19° C. which deviates from the value first accepted in the sense of what had been derived from the observations of the mixture $^1/_2$ (i. e. 30° C. from the method of the coincident systems, 20° C. from KUENEN's equations.)

The following table gives the constants found and the critical quantities derived from their combination.

$K_{11} = 6.276$ $b_{11} = 0.001193$

$K_{12} = 3.314$ $b_{12} = 0.000893$

$K_{22} = 2.176$ $b_{22} = 0.000780$

	T_{kx}	p_{kx}	v_{kx}
$x = 1$	416	64.8	0.007065
$x = ^3/_4$	391	68.9	6249
$x = ^1/_2$	363	71.8	5568
$x = ^1/_4$	336	73.0	5022
$x = 0$	303	72.2	4620

The value of $\frac{p_k v_k}{RT_k}$ is thus found to be $= \frac{1}{3.33}$. The variation of p_k agrees with that of p_R (see the usual pT diagram).

§ 4. In the construction of the detailed plaster-cast it was important not only to profit by the opportunity of being able to choose a larger scale for v and x with almost unchanged dimensions of the whole model, but also to make the curvature of the ψ-surface near the plaitpoint as well defined as possible and thus to make the determination of the connodal curve and the tangent chords as accurate as possible. As now the surface near the plaitpoint is but little removed from its plane of contact, an enlargement of ψ, by which the differences $\psi'' = \psi - \psi_c$, where ψ_c is the value of ψ for points in the tangent plane lying at the same values of x and v, are enlarged in the same proportion, will cause the surface as a whole to become much more inclined with regard to the xv-plane, which again would cause the model to have only limited dimensions in the x- and v-directions with the same dimension in the ψ-direction, in order to make the curvature more prominent. We have avoided this difficulty by constructing a model in which the properly magnified values ψ'' of $\psi - \psi_c$ for x and of v as independent rectangular variables are measured perpendicularly to the xv-plane. In this way the general oblique position of the surface with regard to the vx-plane is eliminated, and $\psi - \psi_c$ can be enlarged as much as is allowed by the greatest dimension which we wish to give to the model in the ψ co-ordinate, through which the curvatures become prominent as desired. The plane of contact on this model if continued to $v = \infty$ would become for $x = {}^1/_2$ and for $v = \infty$ a-plane sloping to the xv-plane with the angular-tangents a and b, whereas in the case of the ψ-surface it would be parallel to the xv-plane.

ψ_c in $\psi'' = \psi - \psi_c$ is a linear function of x and v. VAN DER WAALS has already demonstrated that the addition of a linear function in x does not influence the properties which are of importance in the thermo-dynamical consideration of the ψ-surface. This holds good also for a linear function of v.

Putting $\psi' = \psi + av + bx$ we get

$$\frac{d\psi'}{dx} = \frac{d\psi}{dx} + b$$

$$\frac{d\psi'}{dx} = \frac{d\psi}{dv} + a$$

$$\mu_1' = \psi' - v\frac{d\psi'}{dv} - x\frac{d\psi'}{dx} = \psi - v\frac{d\psi}{dv} - x\frac{d\psi}{dx} = \mu_1$$

$$\mu_2' = \psi' - v\frac{d\psi'}{dv} + (1-x)\frac{d\psi'}{dx} = \psi - v\frac{d\psi}{dv} + (1-x)\frac{d\psi}{dx} = \mu_2 - b\,.$$

For the shape of the projection of the curves $\frac{d\psi''}{dx} =$ const. $\frac{d\psi''}{dv} =$ const. $\mu_1 =$ const. $\mu_2 =$ const. on the xv-surface it is of no consequence whether each is increased by a constant quantity, for in the case of μ_1 there is not even difference between the two values of the quantities μ_1 and μ_1'.

The values of ψ'' used for the construction of the model and the drawings are determined in connection with the absolute values of ψ used in the general model of the whole plait (comp. Communication 59^a) by means of the following equations.

$$\psi'' = -31786\ \psi - 0{,}25\, v + 48000\, x - 164780$$

$$-\psi = \int_{\infty}^{v} p\, dv - R\, T (x\, lg\, x + (1-x)\, lg\, 1-x) + 9.4383.$$

§ 5. Plate III is a photographic representation of the detailed model on which the connodal line and the tangent chords are shown, the depth of the plait is made clear by the shadow of the tangent lines. Fig. 1 and 2 Pl. IV shows the sections $\psi''_x = f(v)$ and $\psi''_x = f(x)$. Pl. IV fig. 3 shows the pressure-curves $\frac{d\psi''}{dv} =$ const. and the substitution-curves $\frac{d\psi''}{dx} =$ const., fig. 4 represents the pressure curves and the potential curves $\mu_1' = u_1 =$ const. (all this on the vx-surface). In the two last figures x is ordinate and v, in $\frac{1}{100000^{\text{th}}}$ parts of the theoretical normal volume, is abscissa.

In fig. 3 and 4 the connodal line has been shown as a dot-dash line, a shadow approximately indicates how great is the uncertainty of this line. The exact place of P (the plaitpoint) on the connodal line is still fairly uncertain. A detailed investigation like the foregoing would again be required with regard to a limited part round P. A similar investigation of the two parts round the two points of contact of a tangent-chord will give us greater certainty as to the exact situation of that tangent chord. So the point R (the critical point of contact) can also still be better fixed.

It may be assumed that we have nearly obtained the difference $x_{TR} - x_{TK}$ of the composition ratios of critical point of contact and of the plaitpoint at the temperature $T = 373°$ C. From this by a better estimation more suitable values can be derived for the difference $T_{R^1/_2} - T_{K^1/_2}$, from which we started for the deduction of a_{12} etc., through which again values for a_{12} etc. could be found, from which a better agreement with **Kuenen**'s experiments near the plaitpoint is to be expected.

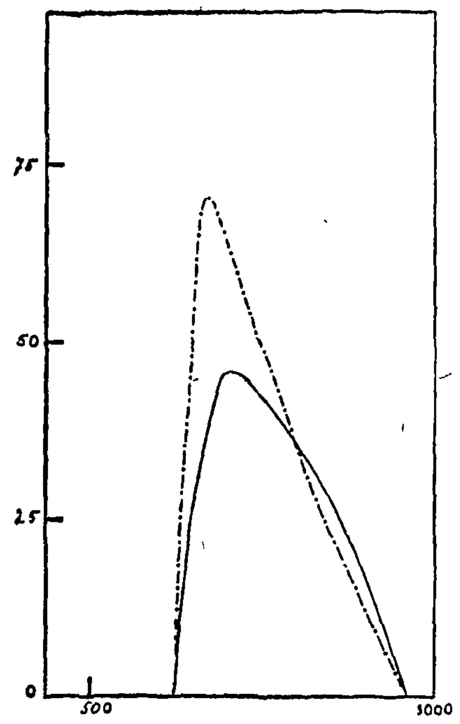

Fig. 6.

When we trace by means of the graphically found connodal line, the condensation phenomena for a mixture with composition x between the plaitpoint composition x_{PT} and the critical point of contact composition x_{RT} this will give us a representation of KUENEN's observations at 103° C. and the composition 0.41, which representation however will only be an approximation. Fig. 6 is obtained by reading on Fig. 4 Pl. IV for each a the relation of $\frac{S_{2a}}{S_{1a}+S_{2a}}$, the ratio to the whole tangent-chord of the piece from the intersection with the line which has the composition x (for which we want to investigate the condensation phenomena) to the contact on the vapour side — which ratio gives the number of molecules in the liquid state — and by determining from this the liquid volume at the tangent-chord a by multiplication with v_x. In the figure[1]) the liquid volume has been measured as ordinate of the curve and the total volume as abscissa.

The dotted line is KUENEN's curve. The composition for which the construction has been made has been chosen so, that the beginning and the end of the condensation are in the same ratio as in KUENEN's observations.

By reading the values of the pressure at the points of intersection of the tangent chords in fig. 4. Pl. IV, we find that the pressure during the condensation varies almost linearly with the total volume. This is also very nearly the case in KUENEN's experiments. Also the amount of the pressure is in fairly good agreement. While KUENEN found an increase of 73,5—83,8, we find from our figure one of 78,6—93,2.

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[1]) Compare also the figure for the retrograde condensation in mixtures of carbon dioxide and hydrogen. VERSCHAFFELT, Comm. 45, fig. 2 on the plate (Proc. Acad. Amst. Dec. '98.

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PLATE III.

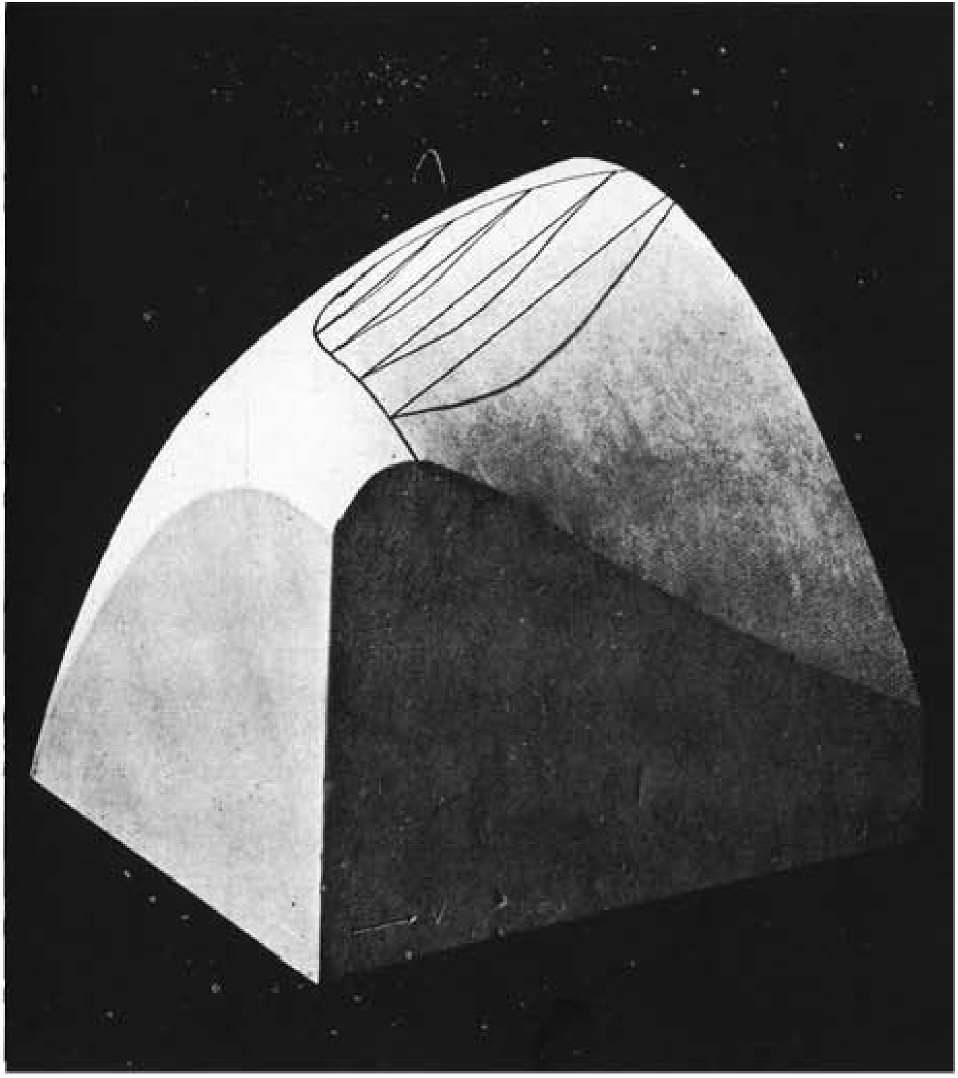

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PLATE IV.

Fig. 2

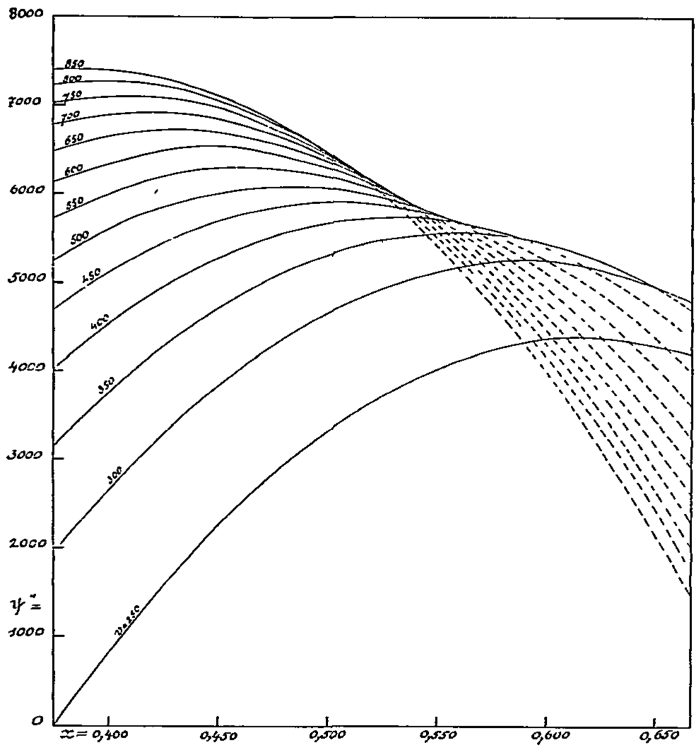

Fig 1.

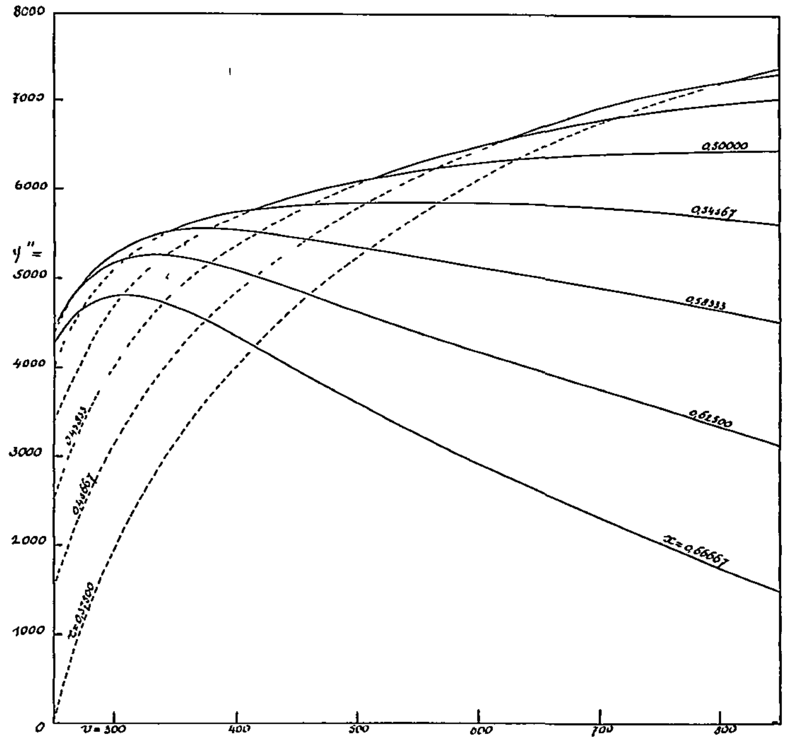

Fig. 4.

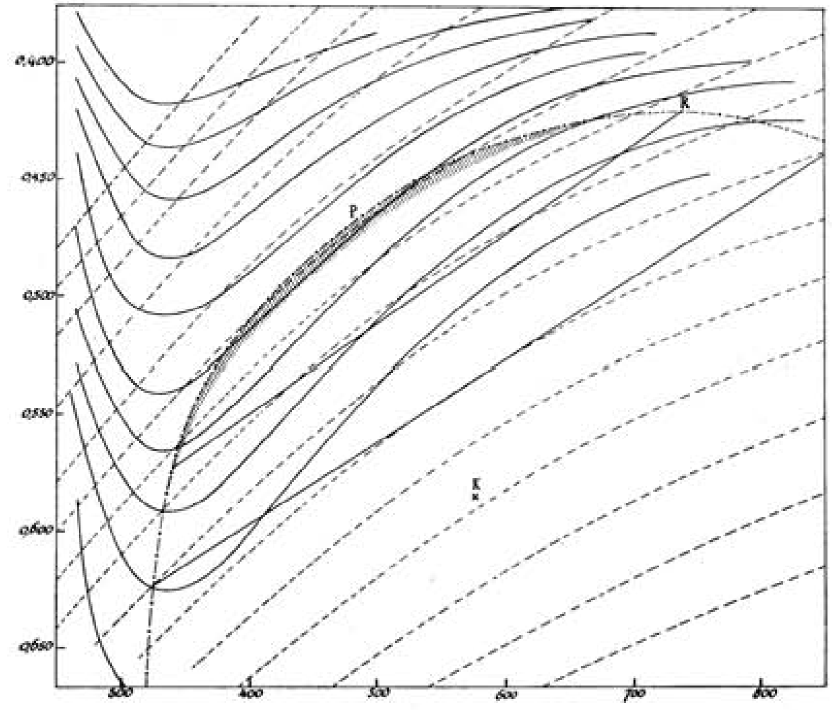
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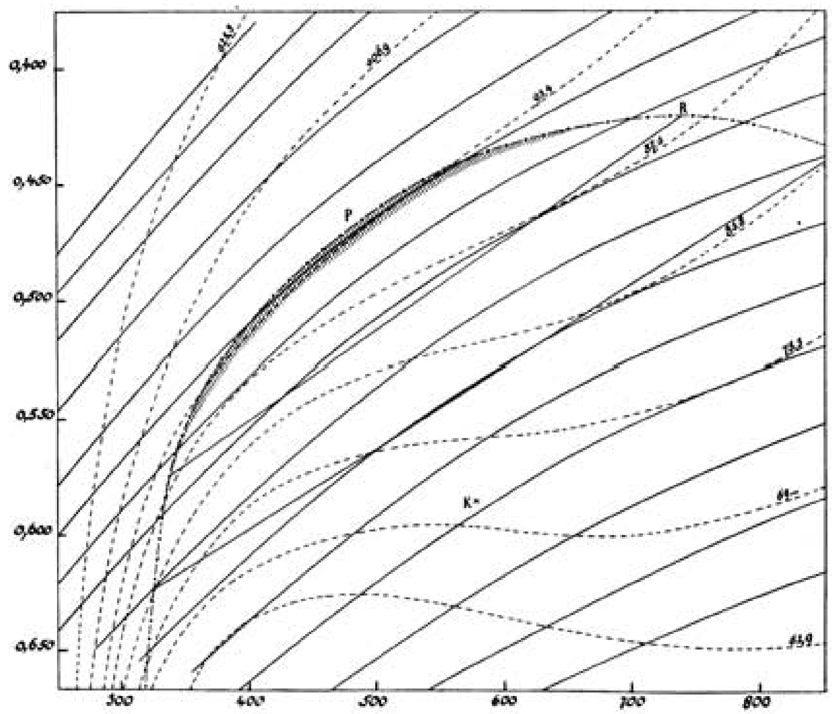
Fig. 3.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