Physics. — Communication N⁰. 59ᵃ from the Physical Laboratory by Prof. H. Kamerlingh Onnes: *"Contributions to the knowledge of* van der Waals' *ψ-surface. I. Graphical treatment of the transverse-plait"*.

1. According to van der Waals' theory it is possible by means of a sufficient number of well selected observations with mixtures of two known normal substances, to determine the constants (a_{12} and b_{12} of van der Waals), which allow us to construct the general equation of state for the mixtures of these substances and especially to predict the phenomena of condensation by ψ-surfaces derived from that equation of state.

Kuenen, who among other things aimed at determining van der Waals' constants for mixtures of methyl chloride and carbon dioxide, has mentioned already in his thesis for the doctorate that calculations had been made in order to construct the ψ-surfaces from the observations for mixtures of these substances.

I have carried out and very nearly completed these calculations for the temperature at which Kuenen has made his most important observations, i. e. those on the retrograde condensation.

For each of the values of the molecular proportion of CO_2 in his mixtures $x = 0$, $x = \frac{1}{4}$, $x = \frac{1}{2}$, $x = \frac{3}{4}$, $x = 1$ Kuenen gives the values of the constants R_x, b_x, β_x, $K_x = Ta_x$ in the equation of state

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

($p =$ the pressure in atmospheres, $v =$ the volume referred to the normal-volume, $T =$ absolute temperature).

By means of this I calculated the free energy for mixtures of the composition x,

$$ \psi_x = - \int p\, dv + R\, T \left\{ x\, log\, x + (1-x)\, log\, (1-x) \right\}, $$

(to which [1]) a temperature function linear in x can be added [2])) for equal

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[1]) In the drawings we have used for $\int p\, dv$: $\int_{\infty}^{v} p\, dv + 9.4383$.

[2]) van der Waals, Théor. Moléc. p. 11.

molecular quantities and then represented them graphically (see Pl. II, fig. 2); the abscissae represent 100,000[th] parts of the theoretical normal volume, and the ordinates give — ψ_x in atmospheres $\times$ the theoretical normal volume, so that these lines are projections on the $x\psi$-plane of sections of the ψ-surface by planes $x = 0$, $x = \frac{1}{4}$, $x = \frac{1}{2}$, $x = \frac{3}{4}$, $x = 1$. The x-coordinate is chosen perpendicular to the ψv-plane as in the case of VAN DER WAALS. For the mixtures $x = \frac{3}{8}$ and $x = \frac{5}{8}$ values of a_x, b_x, β_x, R_x were chosen as nearly as possible in agreement with those given by KUENEN and ψ-lines were calculated with these also.

We then derived from these lines the projections on the $x\,\psi$-plane of the sections of the ψ-surface by planes $v = $ const., which are represented in Pl. II, fig. 1 and other auxiliary lines were drawn, which lines together with their projections on the $x\,v$-plane, shown in fig. 3 and 4, will be considered in the following §§.

In this way we succeeded in obtaining by means of the constants a_x and b_x derived from the observations a representation of the entire first plait in the case of KUENEN's experiments.

Originally however I expected to attain more in a graphical manner. For the condensation phenomena can be easily followed in all their details when the binodal curve and the direction of the tangent-chords are known (comp. following communication § 5), whereas the determination both of the binodal curve and the tangent-chords themselves from the equation of state by analytical processes is certainly exceedingly complicated even when it is feasible.

I had hoped that this problem of VAN DER WAALS' theory could be graphically solved using as a basis the graphical representation mentioned and that it would have enabled me to determine numerically all the phenomena of condensation from the knowledge of a small number of constants (VAN DER WAALS' a_{12} and b_{12}, if necessary augmented by some empirical constants of correction) in the way mentioned in the beginning of this paper for any mixture at any temperature. But this proved to involve great difficulties.

2. The difficulties which hinder us from obtaining an exact numerical solution, proceed from the fact that VAN DER WAALS' theoretical equation of state both as originally given and as modified empirically by KUENEN according to CLAUSIUS, do not give with sufficient accuracy the real behaviour of the pure substances and the mixtures.

We tried whether from isothermals, experimentally determined by KUENEN at higher temperatures combined with RAMSAY's simple

relation for the variation of the pressure with the temperature $p = AT + B$, the isothermals in the unstable part could be extrapolated. But this did not lead to a satisfactory result.

Therefore it is absolutely necessary to use an equation of state in sufficient agreement with the observations, however empirical its form may be, in order to foretell from other observations on mixtures of two substances the phenomena of condensation of mixtures of those same substances under definite circumstances.

In the equation of state used by KUENEN we have allowed for the fact that a_{11} and a_{22} are temperature functions as has been also assumed by VAN DER WAALS for other developments. The identity used by KUENEN $Ta_x = K_x$ where $K_x = K_{11} x^2 + 2K_{12} x (1-x) + K_{22} (1-x)^2$ causes the replacement of a_{12}, which probably is also a temperature function, by the less variable K_{12}, but this K_{12} cannot, any more than a_{12} be determined with sufficient accuracy from the observations.

As for the empirical correction by means of CLAUSIUS' β, we cannot accept that this would lead us to the calculation of the pressure of the mixtures with a definite composition, volume and temperature, at any rate not to the calculation of the pressure in conditions such as that of the co-existing phases, with an accuracy within the limits of the errors of observation. For it is only within a limited range that this empirical correction holds in the case of a simple substance. Much more is to be expected in this direction from the rational method for the determination of empirical corrections of VAN DER WAALS' a and b, followed by REINGANUM in his thesis for the doctorate [1].

In order to obtain, regardless of any equation of state, empirically true representations of observed isothermals, I have tried to represent these accurately by means of a series within the limits of the errors of observation. The investigation relating to this, has been progressing, so that I hope to be soon able to give a communication on this subject. The following however has been worked out independently of the results obtained thereby.

Even if one has at one's disposal a sufficiently accurate series or other empirical representation for one simple normal substance, from which might be calculated that for a second similar substance [2] (i. e. belonging to the same class of substances) according to VAN DER WAALS' law of corresponding states by means of two constant relations (for instance that of the critical pressures and that of the critical

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[1] M. REINGANUM, Theorie u. Aufstell. einer Zustandsgleichung. Diss. Gottingen 1899.

[2] KAMERLINGH ONNES, Verh. Kon. A. v. W. Amsterdam 1881, p. 11.

temperatures) even then the question remains how far the homogeneous mixtures of two similar normal substances satisfy the law of corresponding states. At present it is doubtful whether this is the case in the same degree as for simple substances of the same group, as a mixture is generally not mechanically similar to a simple substance [1]. According to VAN DER WAALS' law however the homogeneous mixtures satisfy his law of corresponding states. Therefore we may call this theory, the theory of the *ideal mixture*. According to that theory we can calculate the isothermal for each mixture from that of a simple standard substance by means of 2 constant relations, e.g. those of the critical temperatures T_{xk} and critical pressures p_{xk} of mixtures of the composition x, provided they are homogeneous; or expressed differently: the ψ-curve can be obtained from that of the simple substance by linear magnification in two directions [2]. As a given ψ-surface corresponds to a given T, the ψ_x-lines appearing on it (given by

$$\psi_x = -\int p\,dv + RT \left\{ x \, log \, x + (1-x) \, log \, (1-x) \right\}$$

$$\Psi_x = \frac{\psi_x}{C p_x \, v_k} = \frac{\psi_x}{R T_{kx}} = -\int \frac{p \, dv}{C p_k \, v_k} + \frac{T}{T_{kx}} \left\{ x \, log \, x + (1-x) \, log \, (1-x) \right\}$$

$$\Psi_x = \frac{\psi_x}{R T_{kx}} = -\frac{1}{C} \int \pi \, d\omega + \tau_x \left\{ x \, log \, x + (1-x) \, log \, (1-x) \right\},$$

where π and ω are the reduced pressure and the reduced volume, Ψ_x the reduced ψ_x and C a constant identical for all substances of the same group [3])), can be derived from the ψ-curves for a simple similar substance, but they relate to the reduced temperatures

$$\tau_x = \frac{T}{T_{xk}} \; [4]).$$

In how far mixtures of normal substances deviate from this ideal case has not yet been investigated, to solve this problem it will

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[1]) Comp. ibid. p. 24.

[2]) Comp. ibid. p. 23.

[3]) Comp ibid. § 4.

[4]) The conditions for thermodynamical similarity have been given by me in Comm. n°. 23. Zittingsverslag 25 Jan. '96. Only when these conditions are satisfied, the temperature function which is linear in x will vary in a corresponding manner for the different temperatures.

be necessary to make observations, not less extensive than those by AMAGAT for simple substances.

If we accept that the mixtures obey the law of corresponding states, we must yet consider how far we may express the critical temperatures, pressures (and volumes) for such mixtures by means of two constants a_{12} and b_{12} by the equations

$$T_{xk} = C_1 \frac{a_{11} x^2 + 2 a_{12} x (1 - x) + a_{22} (1 - x)^2}{b_{11} x^2 + 2 b_{12} x (1 - x) + b_{22} (1 - x)^2}$$

$$p_{xk} = C_2 \frac{a_{11} x^2 + 2 a_{12} x (1 - x) + a_{22} (1 - x)^2}{\{b_{11} x^2 + 2 b_{12} x (1 - x) + b_{22} (1 - x^2)\}^2}$$

$$v_{xk} = C_3 \{b_{11} x^2 + 2 b_{12} x (1 - x) + b_{22} (1 - x)^2\}$$

in which C_1, C_2 and C_3 are the same constants for all substances, or whether more complex functions of x are required therefor.

For the treatment of these two last problems in the case of KUENEN's experiments I refer to a joint communication by Dr. M. REINGANUM and myself [1]).

With reference to KUENEN's experiments, it may be mentioned that a new reduction of the combined observations (by means of graphical representations and by series) is being worked out, from which we can deduce more satisfactorily than is now possible what degree of accuracy is attained in these experiments.

3. Now I return to the treatment of the problem to be solved.

I have made use for this purpose of two methods, and have sometimes completed the results of the one with those of the other method.

In the first place, from the drawings mentioned in § 1, other graphical representations are deduced by means of constructions, which lead to the solution of the problem in hand, (comp. for instance § 8); this will be called *the graphical method in a plane*. In the second place, a plaster cast of VAN DER WAALS' surface was made [2]) in order to make constructions on it, for instance to determine the connodal curve by rolling a glass-plate covered with lamp black over the plait. This will be called *the graphical method by the model*. With the first method, when the equation of state $p = f$ (v, x, T) has once been given, the accuracy can be raised indefinitely without any material difficulties. The only thing

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[1]) Same Proceedings, following paper.

[2]) A diagrammatical model of the ψ surface has been made by VAN DER WAALS and is represented in Théor. Mol. p. 28.

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necessary is to make new drawings on a larger scale relating to those parts of the surface that are to be investigated more in detail (comp. 59^b).

With the second method the material difficulties increase, whether we desire to make casts of greater dimensions, or to add separate detailed casts on a larger scale as auxiliary figures to the original casts, as soon as we wish to attain a higher degree of accuracy (comp. 59^b). This becomes obvious when we see how little defined are the plaits by which the phenomena of condensation are determined, especially in the neighbourhood of the plait-point which strikes one immediately when one compares Pl. I.

For my first treatment of KUENEN's experiments I used only the graphical method in a plane. But as the numerical treatment of the problem became more difficult, the value of the qualitative treatment increased.

As soon as I could avail myself of the assistance of a modeller, Mr. ZAALBERG VAN ZELST, I had a plaster-cast of the ψ-surface made from the graphical representation in plane. For this purpose moulds were used constructed from curves calculated and drawn by me for $\psi_x = f(v)$ and $\psi_v = f(x)$ (comp. § 1).

When the cast — 30 cm. long, 20 cm. wide and 40 cm. high — was ready, though able to give a distinct representation of the plait, it appeared too small for several constructions and so a new cast was made of twice these dimensions, based on the same drawings. This larger pattern, even when hollowed, is rather heavy (80 K.G.) but it proved to be highly satisfactory for several constructions. By rolling the glass plate over it, a fairly regular binodal line with the tangent-chords was obtained, and so the relative positions of the critical point of contact and of the plaitpoint could be demonstrated. For the construction of the curves $\dfrac{d\psi}{dv} = p =$ const., the curves of pressure, and $\dfrac{d\psi}{dx} =$ const., the curves of substitution potential, (obtained in the graphical representation in plane by drawing lines of contact), a hinged pair of bars with level and scale was used (see fig. 1), which is placed on the cast by means of two pins separated by one cm. The curves drawn on the cast can be easily projected by means of a system of curves $v =$ const. and $x =$ const. The tangent-chords to the cast were represented by stiff wires.
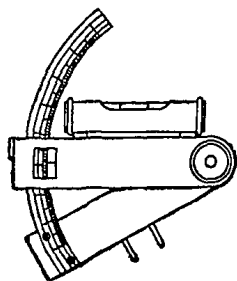
Fig. 1.

The cast thus obtained was in the main the

same as that represented photographically on Plate I. Among other
things fig. 5 Plate I in HARTMAN's thesis for the doctorate was
derived from it [1]. Photographs of this surface were given by me
to some colleagues at the Naturforscherversammlung at Dusseldorf
(1898), also I presented a few persons interested in it with casts
of the smaller pattern and of that part of the larger pattern which
is near the plaitpoint.

4. If at the time, the construction of a model to accurately represent
the reality involved many difficulties resulting from the complications
mentioned in § 2, it appeared to me, as the number of the applic-
ations of VAN DER WAALS' theory increased, to become more and more
desirable to know in detail the properties of the plait obtained, especi-
ally in the neighbourhood of the plaitpoint, and to render the gra-
phical construction of the connodal line, the tangent-chords and
the condensation phenomena now more useful rather for explaining
this theory than for calculating the numerical results of the observations
from VAN DER WAALS' theory. For it is obvious that a true know-
ledge of the behaviour of ideal mixtures is an indispensable guide
in experimental researches of real mixtures. And the difference will
not be so very important if we allow the ψ-curves in this illustration
to deviate as they approach the side of the small volumes, provided
that this is done in a corresponding manner. I resolved therefore to
modify the cast in order to make it suit the desired purpose.

For this care must be taken, that at any rate the ψ-curves assumed
for the simple substances strictly satisfy the law of corresponding
states. But on the other hand, the desire to illustrate VAN DER
WAALS' theory for a case, which agrees as well as possible
with actual measurements — in this case KUENEN's — remained
justified. Therefore it seemed to me desirable to apply the empirical
correction, obtained by including CLAUSIUS' β_x into the equation of
state, which also analytically only slightly changes most of the deve-
lopments of VAN DER WAALS. Here the β_x must satisfy the condition

that $\dfrac{\beta_x}{b_x} = n$ for all mixtures has the same value as for the two mixed

substances.

For a given ψ-surface, it is of no moment that we put $Ta_x = K_x$,
yet this supposition has been included in VAN DER WAALS' equa-
tion of state in order to link the latter to the observed isothermals

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[1] CH. M. A. HARTMAN, Metingen omtrent de dwarsplooi op het ψ-vlak van VAN
DER WAALS bij mengsels van chloormethyl en koolzuur. Diss. Leiden 1899,

for other temperatures and to better deduce the critical temperatures and the critical pressures of the homogeneous mixtures T_{xk}, p_{xk}.

(The two above mentioned empirical corrections used by CLAU-SIUS were chiefly employed to obtain a better agreement with the density and the tension of the saturated vapour. And so it is obviously useful to apply them where we have especially in view the phenomena of condensation.)

For K_x and b_x we kept to the (ideal) form of the second degree in x of VAN DER WAALS.

For these reasons we chose as the equation of state

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

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

$$\beta = n\,b$$

v expressed in terms of the theoretical normal volume.

The reasons for choosing the new values for a_{11}, a_{22}, a_{12}, b_{11}, b_{12}, b_{22} and for $n = \dfrac{\beta}{b}$, are explained in a combined communication with

Dr. REINGANUM, who to my great satisfaction I found ready to undertake together with me the accurate graphical investigation of that part of the surface near the plait-point which on fig. 3, Pl. II is shown by the small rectangle. The original cast was modified in connection with that combined investigation until it agreed with the new data. I owe thanks for the valuable assistance of Dr. REINGANUM in this and in the following constructions.

5. Plate I shows a photographical reproduction of the cast obtained in this way, taken from the side corresponding to the methyl-chloride. The ψ-curve of pure methylchloride stands out clearly by the shadow and has moreover been dotted. The depth in the plait is revealed by the shadow cast by the tangent-chords. The representation of the casts did not appear to be so much improved by stereoscopic photographs, that it outweighed the greater complication of the process.

Fig. 1, 2 and 3 of Pl. II are the above mentioned projections on the ψx ψv, and xv planes of curves drawn on the ψ-surface.[1]) In fig. 1

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[1]) In order not to render the drawings indistinct we have not drawn a rectangular system of equidistant lines a thing which can easily be done by every one who wants to make numerical readings on the drawings.

(projection on the $x\psi$-plane) the projections of the substitution potential curves, or more simply the *substitution curves*, $\left(\dfrac{d\psi}{dx} = \text{const.}\right)$ have been dotted. In fig. 3 (projection on the xv-plane) the *pressure curves* $\left(-\dfrac{d\psi}{dv} = p = \text{const.}\right)$, are drawn, and the substitution curves are dotted. In fig. 4 the substitution curves are dotted and the curves for which

$$\psi + \frac{d\psi}{dx}(1-x) - \frac{d\psi}{dv}\ v\ = \mu_2 = \text{const., the } potential\ curves \text{ of the second}$$

component, are lined. According to van[der Waals' theory (Théor. Moléc.) these three curves are sufficient for the determination of the co-existing phases.

How the substitution- and the pressure-curves have been obtained is mentioned in § 3. The graphical determination on the cast was tested with that on the plane.

6. First must be mentioned briefly how the potential curves are determined, both by construction on the plane and on the cast. In the first case I started from the figures 1 and 2, Pl. II, which give the sections of the ψ-surface by planes containing the line $v=0$, $x=1,000$ (the ψ-axis on the side of the methylchloride). If in fig. 2 we rotate [1]) the xv-plane with the lines $x = \text{const.} = A, x = B$ etc., (the projections of the ψx-curves) drawn on it, round the v-axis on the ψv plane, the plane of the figure; the sections a, b etc. of the planes just mentioned, containing the line $x=1,000$, $v=0$, by the xv-plane, rotate into the plane of the figure and appear as radii (starting) from the point $x = 1.000, v = 0$, whose points of intersection aA, aB with the rotated lines $x = A, x=B$ etc. give the value of v for the point of intersection aA, aB, etc. of the plane a with the curves ψ_A, ψ_B etc. The line drawn in Pl. II fig. 2 through the point of intersection perpendicularly to the v-axis determines through the intersection aA with the ψ_A-curve the value of the perpendicular height above the v-axis, for the point aA' in the rotated figure; while the value of v for this point in the rotated figure is found by rotating the radius drawn from $x = 1,000\ v = 0$ to Aa on the v-axis. The points aA', aB' etc. combined give the rotated oblique section a'. From one point μ_2 on the ψ-axis (line $x=1,000, v = 0$ for the ψ-surface, $v = 0$ for the plane fig. 2) tangents are drawn to these rotated oblique sections a', b', whose points of contact

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[1]) The drawing with these constructions can be omitted as it is somewhat complicated.

$\mu_{a'}$, $\mu_{b'}$, $\mu_{c'}$ are points of contact of a plane drawn through the point μ_2, with the ψ-surface, which points of contact $\mu_{a'}$ $\mu_{b'}$ etc. are rotated on the plane of drawing round the line $\bar{x} = 1,000$, $v = 0$. The co-ordinate $\psi_{\mu a'}$ of $\mu_{a'}$ in the drawing is also the co-ordinate $\psi_{\mu a}$, of the point of contact in the section with the plane a, returned into its previous position, while the abscissa $v_{\mu a}$, measured along the radius a gives the place of the projection on the xv-plane of the point of contact μ_a The points μ_b, μ_b . . . are therefore combined by a smooth line into a potential curve for the value μ_2. The different curves, obtained by repeating the last constructions with several values of μ, give the system of potential curves in the xv-plane, fig. 4, Pl. II when the v-axis of fig. 2 is again considered as v-axis and the ψ-axis of fig. 2 as x-axis.

The construction by means of the model is immediately derived from this. We used a pair of sliding compasses with points, long enough to continue the construction also within the plait. One of the points has the ordinary form, and is placed on the top of a rod
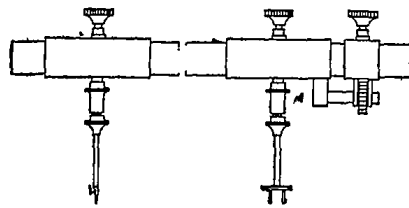

Fig. 2.

which is movable in the line $x = 1,000$ $v = 0$ and terminating at the height μ. The other movable point is fork-shaped (see fig. 2) of which the two prongs one cm. apart are situated in a straight line with the fixed point. When, during the sliding of the fork, we try where the two teeth rest on the cast, we find the place where a line of contact to the surface, goes through the point μ. In order to obtain the projection of the potential curve found on the cast, we use again the system formed by the curves $v = $ const. $x = $ const. on the ψ-surface.

7. The figures drawn seem to me well adapted for giving us a very clear representation of the thermodynamical properties of the mixtures according to VAN DER WAALS' theory.

Many peculiarities are to be observed in the course of the different lines. I shall draw attention to only a few. The limiting-forms of the pressure-curves are for very large volumes straight lines across the surface, parallel to the x-axis; with small volumes the curve tends again to become rectilinear, but in that case its general direction is at some small angle with regard to the x-axis. This follows immediately from the theory. The point of inflection of the pressure-curves through the plaitpoint is situated, reckoned from the liquid-side, farther than the plaitpoint (this property was formerly

communicated orally to me by VAN DER WAALS). Through both the ends of a tangent-chord pass the same curves of pressure, of substitution and of potential (a thing which we can see for ourselves by laying the tracing of one figure on the other). Through these points pass also the potential lines for the first component. These are the chief conditions advanced by VAN DER WAALS.

The curve of pressure touches the tangent-chord in the critical point of contact. This has been pointed out by HARTMAN (Comm. N°. 56).

The points of intersection of the theoretical and the experimental isothermals are situated almost in a straight line going through the critical point of contact. The point of inflection of the pressure curves in the unstable part is situated also in a line deviating but slightly from a straight line towards the side of the small volumes; the critical point of the homogeneous mixture lies also towards the side of the small volumes, with regard to the point of intersection with the experimental isothermal. (Comp. HARTMAN, footnote Comm. N°. 56).

The substitution curves run parallel to the v-axis for large volumes. For smaller volumes they begin to incline towards the plait, this inclination increases as they reach farther down into the plait, it attains a maximum and decreases again in the direction of the smaller values of x. The lowest point of the bend is outside the plait.

The substitution-curve of the plaitpoint envelops the connodal line, according to properties found by KORTEWEG, and shows a point of inflection that comes within the plait from the side of the smaller volumes. The substitution lines intersect the pressure curves within the connodal line. The divergence of their general direction in the plait agrees best with that of the tangent-chords.

The general direction of the potential lines for larger volumes lies obliquely over the ψ-surface from the side of the smaller volumes and smaller composition-ratios towards the side of the larger volumes and larger ratios. Towards the plait they show a bend, which is more acute than that of the substitution-line and on entering further into the plait these increase rapidly in acuteness, so that they, like the pressure curves project beyond the limits of the surface. The lowest point of the bend lies within the plait. The greatest convexity towards the plaitpoint of the substitution lines and of the potential lines coming from the side of the large volumes within the plait is situated together with the greatest concavity of the pressure-curves on that side more or less on the axis of the parobola by which

the projection of the connodal-line is approximately represented (in other respects it is better represented by a hyperbola).

8. *The determination of the co-existing phases by graphical solution in the plane surface.* Attention has been drawn to the difficulties, attending the precise graphical solutions by means of the plaster-cast. These are very great when we want to determine the connodal-line by means of rolling a lampblacked glass plate over the cast, which method is in other respects the most direct expression of VAN DER WAALS' solution of the problem. Hardly perceptible deviations of the surface have a great influence on the shape of this curve. Therefore it is desirable to be able to determine the connodal-line and also the tangent-chords by a construction for which we only need to make drawings on a plane [1]). The graphical representations discussed in the former sections offer a means for this. For if we return to the condition advanced by VAN DER WAALS for the co-existence of two phases, namely

$$\left(\frac{d\psi}{dx}\right)' = \left(\frac{d\psi}{dx}\right)'', \quad \left(\frac{d\psi}{dv}\right)' = \left(\frac{d\psi}{dv}\right)'', \quad \mu_2' = \mu_2'',$$

where ' refers to one phase and " to the other, then we get to know the co-existing phases as those, in which μ_2 considered as a function of $\frac{d\psi}{dx}$ and $\frac{d\psi}{dv}$ for the same value of $\frac{d\psi}{dv}$ and $\frac{d\psi}{dx}$ twice has the same value.

If now we trace the course of a curve $\mu_2=$const. in the curvilinear system of the pressure- and the substitution-lines in the xv projection, and if we transform this system of curves into one which is rectilinear and rectangular and on which along the axis of ordinates a suitable function of $\frac{d\psi}{dx}$ is measured, and along the axis of abscissae a suitable function of $\frac{d\psi}{dv}$, the μ-line by this process will become a loop-shaped figure, of which the double-point is at the values of $\frac{d\psi}{dv}$ and $\frac{d\psi}{dx}$, which correspond to the composition and the volume of the co-existing phases.

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[1]) RIECKE, Ueber die Zustandsgleichung von CLAUSIUS. Wied. Ann. **54**, p. 739, treats the co-existing phases of a simple substance graphically) Comp. also H. K. O. Verh. Kon. Akad. v. Wet. XXII, p. 13, 1881), and mentions p. 744 that by means of the thermo-dynamical potential this could be done in a similar way for mixtures.

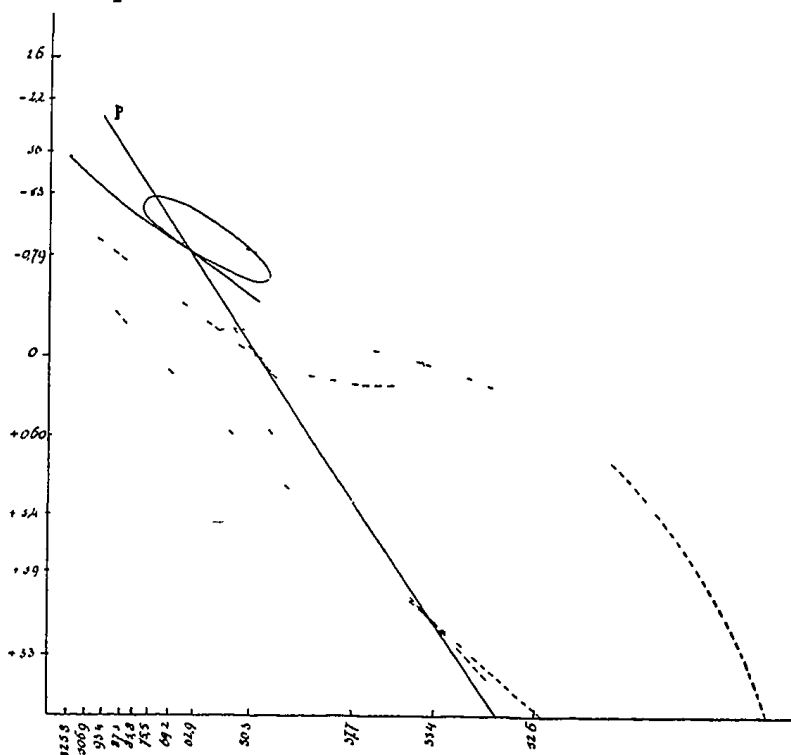For the representation of μ_2 as ordinate we have chosen in fig. 3

Fig. 3.

such a function of $\dfrac{d\psi}{dx}$, $s = f\left(\dfrac{d\psi}{dx}\right)$ that the substitution-lines, belonging to regularly increasing values of this s for large volumes, run at equal distances in the $x\iota$-plane. For simplicity's sake we have in order to determine s in this way not taken an infinitely large volume, for which we should have

$$s = \frac{e^{\frac{1}{RT}\frac{d\psi}{dx}}}{1 + e^{\frac{1}{RT}\frac{d\psi}{dx}}}$$

but the volume at the end of the drawing (0,034) fig. 3, Pl. I; where the value can be read directly. It does not deviate much from that for an infinitely large volume. As function of $\dfrac{d\psi}{dv}$ we might choose $w = \left(\dfrac{d\psi}{dv}\right)^{-1} = \dfrac{1}{p}$ so that for large volumes the pressure curves belonging to regularly increasing values of this w run at equal distances. But in order to be able to read the value immediately on the drawing fig. 3, Pl. II, we have chosen that function of p, which for $x = 0$ becomes equal to v.

The shape of the closed loops in the annexed fig. 3, obtained in this way, still shows small irregularities, which are owing to inaccuracies in the construction. However I thought the figure of sufficient importance to give it here even in its imperfect state. Part of the loop-shaped figure for small proportions of the most volatile substance is in this case cut off by the curve $s = 0$. The line which connects the double points and therefore determines the pressure for co-existing phases as a function of the *substitution potential* $\dfrac{d\psi}{dx}$, is in this figure a straight line. As the substitution and the pressure-curves belonging to regular increasing values of w and s in the xv-plane for large volumes, form a nearly regular rectangular system, the connodal line in the xv-plane will also be a straight line for large values of the volumes. In connection· with this result I may remark that according to an oral communication to me VAN DER WAALS has derived from his theory, that the connodal line for the plait into which the one investigated here passes at 9°,5 the temperature at which HARTMAN made his experiments, would be almost a straight line on the side of the large volumes, which is substantially verified by those experiments.

This appears from fig. 4 drawn by Dr. HARTMAN, in which the projections of the connodal line with the tangent-chords are represented for 9°.5. In order to make a comparison the plait on the model (almost that of KUENEN) has been added on the same scale as the drawing.

Fig. 4.
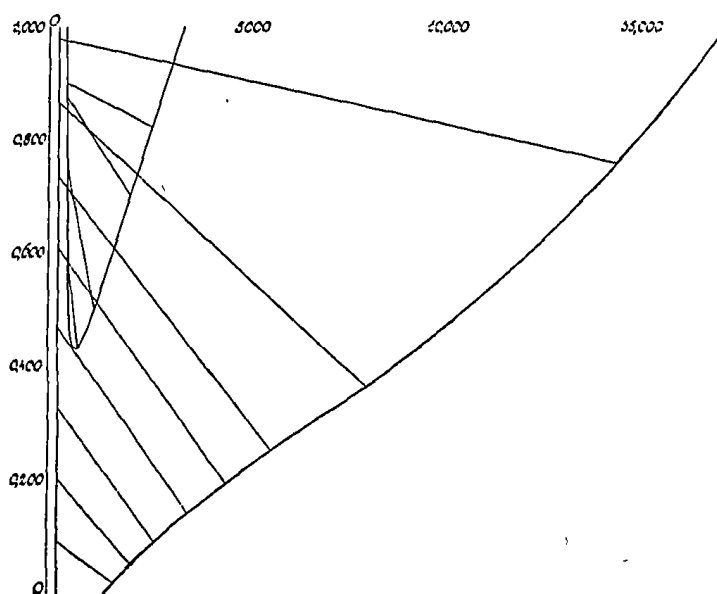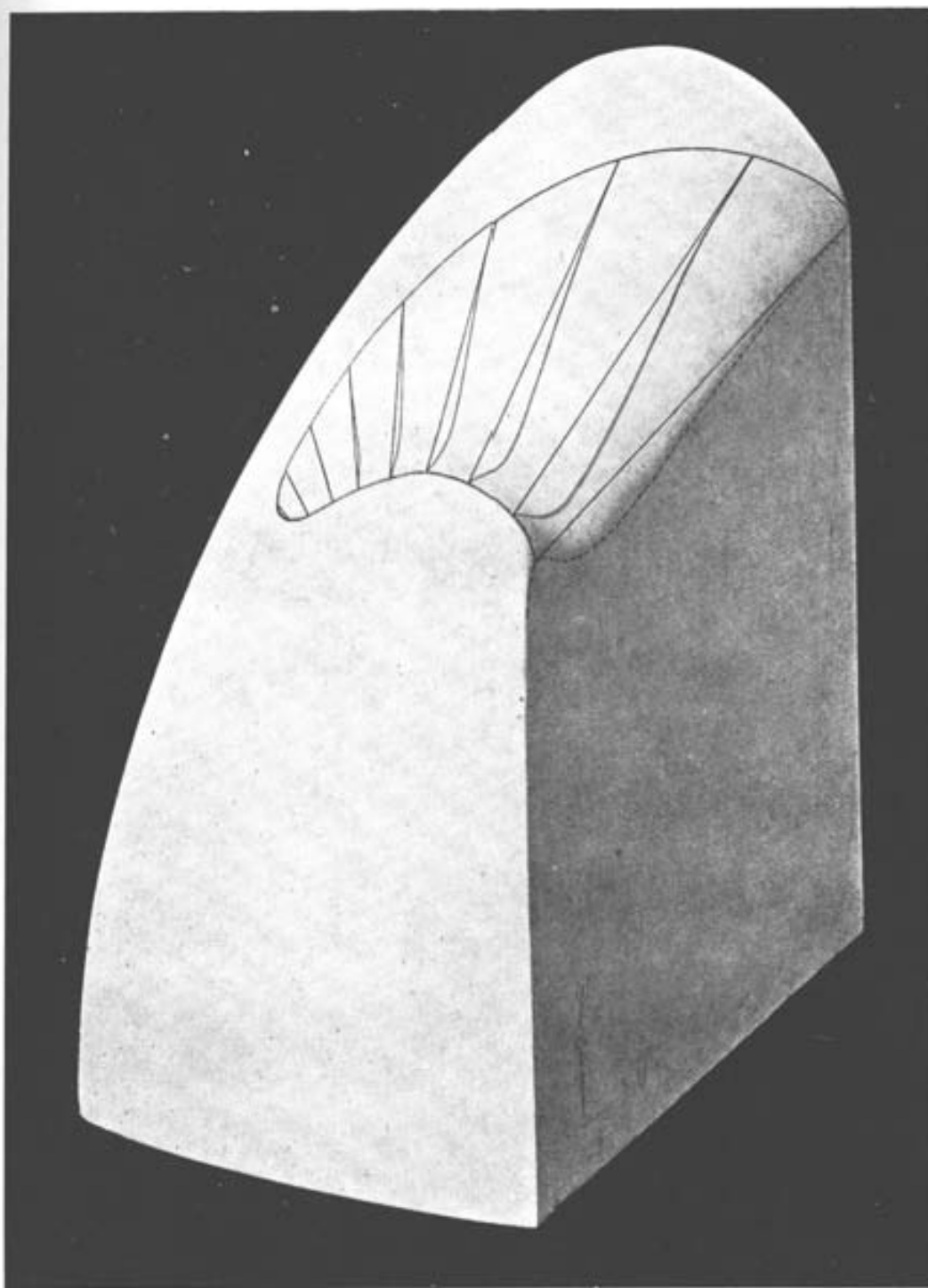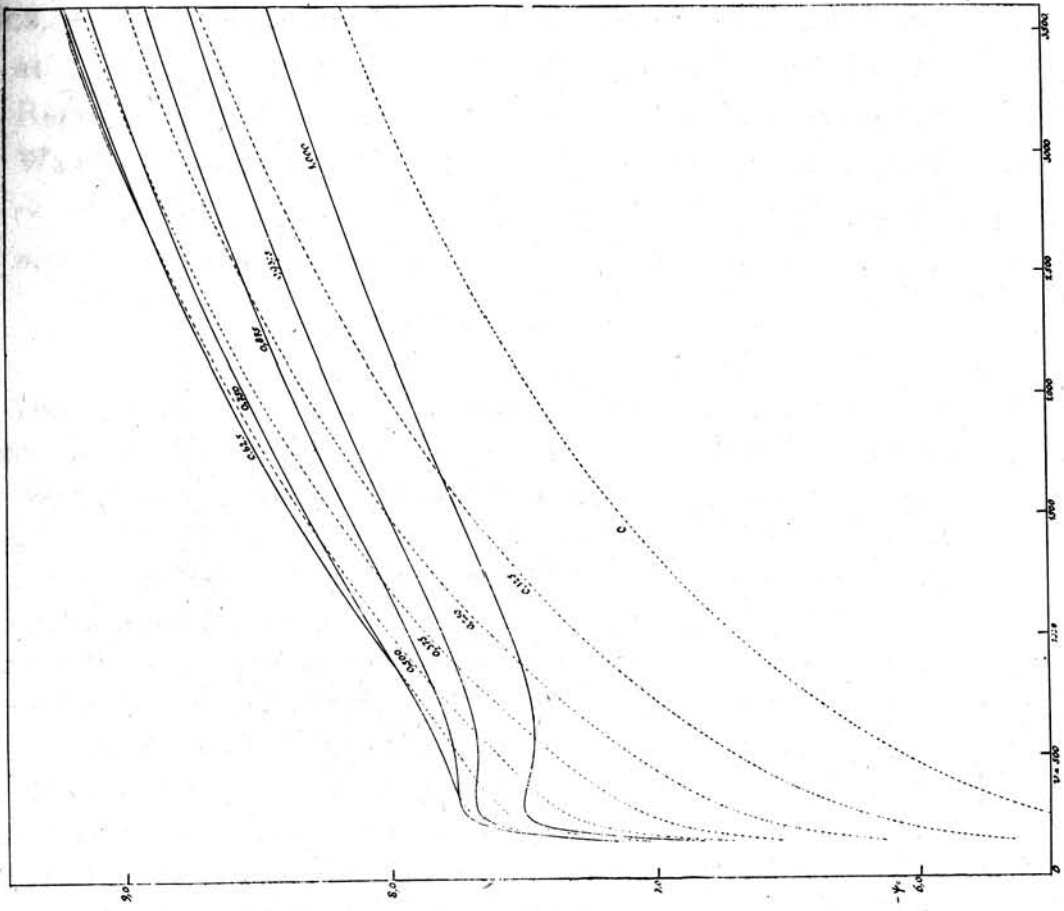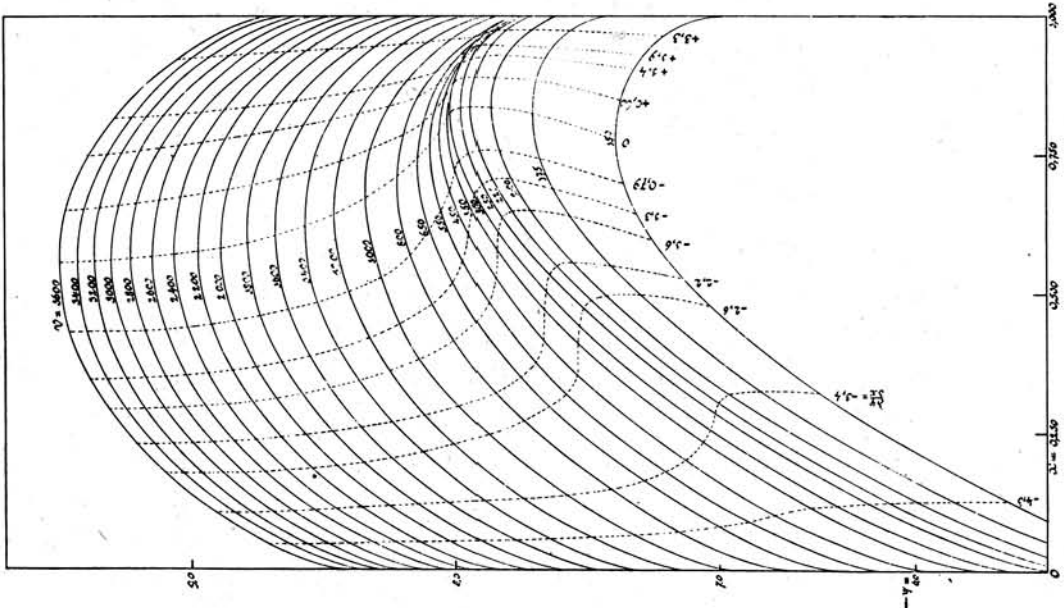
Prof. H. KAMERLINGH ONNES. „Contributions to the knowledge of VAN DER WAALS' ψ-surface. I. Graphical treatment of the transverse plait."

PLATE I.

PLATE II.

Fig. 2.

Fig. 1.

Fig. 3.

Fig. 4.