

p. 660) indicates, that $T_{b_{pts}}$ would have to lie still pretty much higher, and therefore T_{kHe} pretty much lower (probably $<$ about 4°)¹⁾. Of this result we availed ourselves in the treatment of the estimation of the critical temperature of He in Comm. N°. 96b.

(To be continued).

Physics. — “Contributions to the knowledge of the ψ -surface of VAN DER WAALS. XIV. Graphical deduction of the results of KUENEN's experiments on mixtures of ethane and nitrous oxide.” Supplement 14 to the Communications from the Physical Laboratory of Leiden. By Prof. H. KAMERLINGH ONNES and Miss T. C. JOLLES.

(Communicated in the meeting of Januari 26, 1907).

§ 1. *Introduction.* In what follows we have endeavoured to derive quantitatively by first approximation the behaviour of the mixtures of N_2O and C_2H_6 (mixtures of the II type²⁾), which has become known through KUENEN's experiments³⁾, by the aid of VAN DER WAALS' free-energy surface. The ψ -surfaces construed for this purpose (see plate I) are the counterparts of those construed in Comm. N°. 59 (These Proc. Sept. 1900) and Comm. N°. 64⁴⁾ for the derivation of the results of KUENEN's and HARTMAN's experiments on mixtures of CO_2 and CH_3Cl (mixtures of the I type). In the graphical treatment⁵⁾ of our problem we have chiefly followed the method given in Comm. N°. 59, where the critical temperature and pressure of some mixtures were borrowed from KUENEN's determinations, and then the results of another group of experiments — those referring to the conditions of coexistence of two phases at a certain temperature — were deduced by the aid of VAN DER WAALS' theory.

KUENEN's results for N_2O and C_2H_6 are principally laid down in

¹⁾ If b_{22}/b_{11} is taken larger than $1/3$ (Cf. Footnote 3 p. 660) this supposition too makes the upmost limit for T_{kHe} on the said supposition smaller. This is seen when we compare with table I that we obtain $T_{b_{nl}}/T_{k_1} = 0.679$ for $b_{22}/b_{11} = 1/4$ with $T_{k_2}/T_{k_1} = 0.15$.

²⁾ HARTMAN, Leiden Comm. Suppl. no. 3, p. 11.

³⁾ KUENEN, Leiden Comm. no. 16, Phil. Mag. 40, p. 173, 1895, cf. also KAMERLINGH ONNES and ZAKRZEWSKI, Leiden Comm. Suppl. no. 8. (These Proc. Sept. 1904).

It is remarkable that the possibility of this case was foreseen by VAN DER WAALS, Contin. II, p. 49 [added in the English translation].

⁴⁾ Arch. Néerl. Serie II, Tome V, p. 636.

⁵⁾ Only graphical solutions for definite cases are here possible. (Cf. Suppl. 8, These Proc. Sept. 1904. § 1).

four figures ¹⁾; one of them gives the critical quantities from which we shall start in our deduction, and the border curves for mixtures of different concentration; the three others, which represent the *xv*-projection of the connode with the connodal or tangent chords at the temperatures 20° C, 25° C, 26° C, show the contraction of the transverse plait with rise of temperature, and finally its splitting up into two plaits.

We have thought that we could obtain a better comparison of observation and calculation, when representing the observations by the *xv*-figures for 5° C., 20° C. and 26° C., and the *pT*-figure, instead of by the *xv*-figures at the before mentioned temperatures and the *pT*-figure.

§ 2. *Basis of the calculation. Law of the corresponding states and reduced equation of state.* We start (cf. Suppl. N°. 8, These Proc. Sept. 1904 § 1) from the supposition that the law of the corresponding states — at least within the region of the observations — holds as well for C₂H₆ and N₂O as for their mixtures. As reduced equation of state we chose equation V. s. 1 of Comm. N°. 74²⁾ p. 12. For a region of reduced temperature and pressure which incloses the region which corresponds to that of the observations under investigation, this equation is as closely as possible adjusted to CO₂, which in thermical properties has much in common with N₂O, and there is no reason to suppose that this will not be the case with C₂H₆.

In the application we are, however, confronted by this difficulty, that V. s. 1 deviates most strongly from the observations on CO₂, exactly in the neighbourhood of the critical state. (Cf. Comm. N°. 74 and later KEESOM, Comm. N°. 88). If from V. s. 1³⁾ the point is derived, for which

$$\frac{\partial p}{\partial v} = 0 \text{ and } \frac{\partial^2 p}{\partial v^2} = 0 ,$$

we find $t = 1.010595$, $2v = 1.0407 \cdot 10^{-3}$, $p = 1.06566$. KEESOM's observations, Comm. N°. 88, give for the critical volume, when it is sought by the application of the law of the rectilinear diameter, for CO₂,

$$v_k = 0.00418 \text{ and for } \lambda = \frac{p_k v_k}{T_k} = 1.0027 \cdot 10^{-3} . . . (1)$$

¹⁾ Where it was necessary, KUENEN's figures have been rectified in accordance with the results of observation given by him.

²⁾ Arch Néerl. Vol. Jubil. Bosscha. Serie II, tome 6, 1901.

³⁾ In the calculations T is put 273° 04 for the freezing point of water, because V. s. 1 was calculated with this value.

We find then:

$$t_k = 1.010595 \text{ instead of } t_k = 1$$

$$v_k = 1.0379 \quad , , \quad , , \quad v_k = 1$$

$$p_k = 1.06566 \quad , , \quad , , \quad p_k = 1.$$

The isotherms from which V. s. 1 has been derived by the computation of the virial coefficients \mathfrak{B} , \mathfrak{C} etc. (See comm. N°. 71, These Proc. June 1901), indicate therefore, by means of interpolation according to this mode of calculation, a critical state, which, drawn in the pv -diagram, has shifted with respect to that which was found by immediate observation; the critical temperature according to V. s. 1 is namely $t_k T_k$ when T_k is the observed critical temperature.

So are also the values found for $p_{max.}$, $v_{liq.}$ and $v_{vap.}$ at t by the application of MAXWELL'S criterion, different from those which we should find when dividing $p_{max.}$ by p_k , $v_{liq.}$ and $v_{vap.}$ by v_k . The deviations are of the same order as the deviations of the substances inter se, when they are compared by the law of the corresponding states. At $t = 0.9$ they are about zero, but they increase as we approach the critical state, so that the deviations agree with a gradual transformation of the net of isotherms. The following table gives a survey of the deviations in the corresponding values.

Column *A* refers to V.s. 1 and implicitly to p_k , T_k of CO_2 ,

„ *B* „ „ the observations „ CO_2 ,

„ *C* „ „ „ „ „ N_2O .

<i>A</i>		<i>B</i>		<i>C</i>	
<i>t</i>	<i>p</i>	<i>t</i>	<i>p</i>	<i>t</i>	<i>p</i>
1.0106	1.066	1.	1.	1.	1.
0.975	0.826	0.975	0.845	0.975	0.854
0.950	0.695	0.950	0.709	0.950	0.720
		0.925	0.589	0.925	0.599
0.900	0.490	0.900	0.494	0.900	0.486

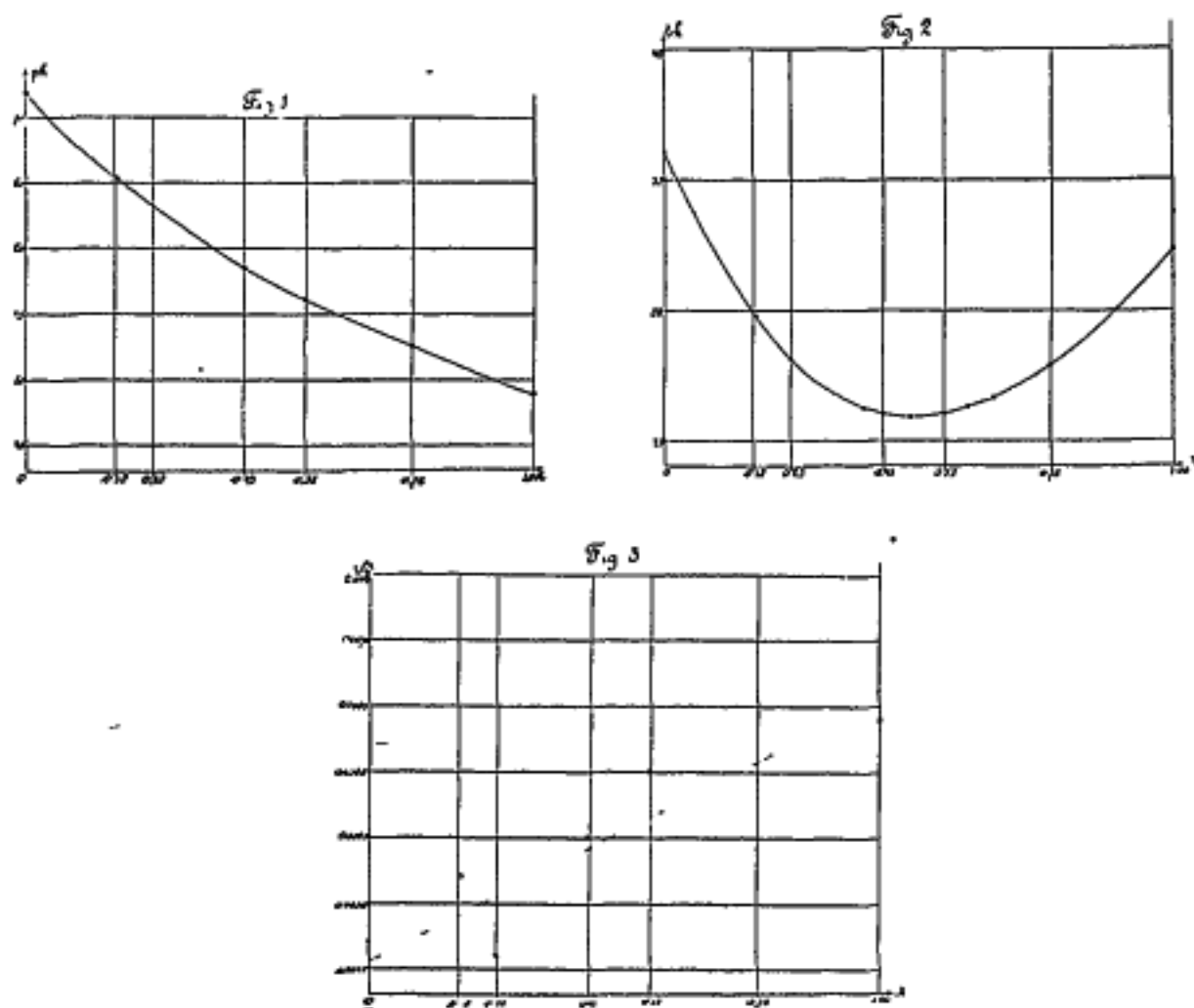
In the neighbourhood of the critical temperature the phenomena are governed by the difference of the temperature of observation and the critical temperature, $T - T_k$; for this reason we have chosen for the detailed model of 26° such a temperature T' for the com-

parison of the observations at that temperature T with the result of computation that

$$T_k' - T = t_k T_k - T'.$$

At the general survey for 26° we have applied to $t = \frac{T}{T_k}$ a correction $= \Delta t$, so that $\Delta t = 0.0106 \theta$, when $\theta = 10(t - 0.9)$ for $0 < \theta < 1$, whereas $\Delta t = 0$ for all other values of θ . The correction Δt to t was accompanied by a correction Δv to v and Δp to p , so that $\Delta p = 0.0657 \theta$ and $\Delta v = 0.0379 \theta$, which together represent a regular increase of the corrections from $t = 0.9$ to the critical state. For the detailed model of the ψ -surface for 26° , on which only the part from $x = 0.35$ to $x = 0.65$ was represented, we used everywhere the same correction viz. $\Delta t = 0.0106$, $\Delta p = 0.0657$, $\Delta v = 0.0379$.

§ 3. *Critical quantities for the mixtures.* KUENEN has determined the plaitpoints T_{plx} , p_{plx} , v_{plx} , for some mixtures with the molecular concentration x . T_{rx} , p_{rx} , v_{rx} , the critical points of contact, and T_{kx} , p_{kx} , v_{kx} the critical states of the mixtures taken as homogeneous differ so little¹⁾ from these values, that this difference may be disregarded for our purpose, and so they are also known for the mixtures investigated by KUENEN.



¹⁾ This has been fully treated by VAN DER WAALS, Cont. II, § 11.

The critical quantities for the other mixtures were found by graphical interpolation. Fig. 1 gives p_{kx} , fig. 2 T_{kx} as function of x ; in fig. 3 v_{kx} has been calculated from p_{kx} and T_{kx} , by the aid of λ (see formula (1)); the v_{kx} observed by KUENEN have been indicated there.

By carrying out the construction for the connode by the aid of the p , $\frac{\partial \psi}{\partial x}$ and $\psi - v \frac{\partial \psi}{\partial x} - v \frac{\partial \psi}{\partial v}$ curves (see Comm. N°. 59a¹⁾), which the models for those different temperatures yield, we may derive $v_{kx} - v_{pl,x}$, $p_{kx} - p_{pl,x}$ in first approximation (see Comm. N°. 59a). Applying these corrections we should then have to repeat the calculation from the beginning, to obtain more accurate values for v_{kx} , p_{kx} . We have confined ourselves to a first approximation in all our constructions, as also a further correction of the equation of state V.s. 1., which can cancel the deviations mentioned in § 2, has not been applied and we were the more justified in this, as these latter deviations are larger than those we have now in view.

§ 4. Construction of the ψ -surfaces.

From the equation of state V. s. 1 we find immediately the reduced $\psi_x T$ curves, from which are then deduced the ordinary ψ -curves according to Suppl. N°. 8, § 4; or the ordinary virial coefficients, which have then used for the calculation of ψ according to Comm. N°. 59

For the construction (cf. Comm. 59) use was made of:

$$\begin{array}{ll} \text{at } 5^\circ & \psi' = \psi + 0,10 x + 25 v \\ \text{,, } 20^\circ & \psi'_{20} = \psi + 0,10 x + 36,5 v \\ \text{,, } 26^\circ & \psi'_{26} = \psi + 0,24 x + 57,3 v, \end{array}$$

while a suitable constant was subtracted from every ψ . Here v is expressed in the theoretical normal volume, just as in the diagrams. From the $\psi_x T$ curves (cf. fig. 1, pl. II) the ψ_x curves (see fig. 2, pl. II) and the $p T$ curves were graphically derived. The models for ψ were construed on a scale 5 times larger than the diagrams on pl. II, pl. III and pl. IV.

§ 5. Determination of the coexisting phases.

Applied was both the construction by rolling a glass plate on the

¹⁾ In giving the figure 3 in Comm. N°. 59a for this construction it was stated that this figure was very imperfect. It appears now that the loop ought to contain two cusps. We found out the error by the aid of the general properties of the substitution-curves treated by VAN DER WAALS (Comp. Proceedings of this meeting). This error shows the more how necessary it is that graphical solutions are controlled by such general properties as VAN DER WAALS is now publishing. [Added in the English translation].

model, which yields the connode and the tangent chords, and the simplified construction in the plane given in Suppl. N°. 8, § 7, to which a small correction was applied. After viz., a provisional connode, that of the mixtures taken as homogeneous, has been found by tracing curves of double contact to the $\psi_x T$ -curves, and by determining conjugate points b on the gas branch at some points a on the liquid branch of that connode, so that every time $\frac{\partial \psi}{\partial x}$ is the same for the two conjugate points, the lines which join every two of these points a and b , are produced outside the provisional connode, till they cut the isobars which pass through a , in points c , which together represent the required gasbranch of the connode; c and a are then considered as conjugate points. In the ψ -surface at 5° C. the two constructions yielded fairly well corresponding results, both with regard to the chords and to the connode itself, as appears from pl. II fig. 4, where — — — — denotes the connode and the connodal tangent-chords found by rolling a glass-plate on the model, — — — — those found by means of the just mentioned construction. That the simplified construction, which was more particularly plotted for equilibria far below the critical temperature (see Suppl. N°. 8, § 7) still leads to our end, is probably due to the fact, that we have here to deal with a mixture of the II type.

With the ψ -surface for 20° the slight depth of the plait rendered it necessary, to considerably diminish the longitudinal scale for the v -coordinate of the model. This compression (cf. pl. I, fig. 2) rendered the plait sufficiently clear to determine the connode and the place of the connodal tangent chords by rolling a glass plate. By means of the simplified construction the connode was still to be obtained, but the determination of the tangent-chords became uncertain.

With the ψ -surface of 26° the depth of the plait (here split into two) becomes so exceedingly slight, that it does not appear but with a computation with 7 decimals, and even then it manifests itself almost quite in the two last decimals. Hence it is not possible to model a ψ' -surface (we mean a surface derived from the ψ -surface, on which the coexisting phases are still to be found by rolling a plane), on which this plait is visible, nor is it of any avail to confine ourselves to a small part of the surface, because the curvature of the $\psi_x T$ -curves is very strong exactly there where something important might be shown. The determination of the connode and the connodal tangent chords by construction according to § 8 of Comm. N°. 59a, which can always be carried out provided enough decimals are worked with, remained still uncertain up to 7 decimals, so that we have

not pursued it any further. Thus the represented part of the ψ -surface for 26° from $x=0.35$ to $x=0.65$ and from $v=0.0038$ to $v=0.0070$, has been given by us chiefly to demonstrate how exceedingly small the influences must be on which a plait depends, and how much care is required to determine a plait experimentally which is not at all to be seen on the surface. The curves drawn on the surface, which relate to the plait, were found by indirect ways, partly by construction, partly by calculation. To facilitate a comparison of the models inter se the region of x and v , on which the model for 20° and that for 26° extends, has been indicated on the model for 5° , on the model for 20° that for 26° .

§ 6. *Further remarks on the different models and drawings obtained by construction.*

a. The ψ' -surface for 5° . The model, pl. I, fig. 1, and the drawings pl. II, figs. 1, 2 and 3 show curves of equal concentration, $\psi'_x T$, equal volume and equal pressure, the connode and the connodal tangent chords. As $-\frac{\partial \psi'}{\partial v} = p - 25$, some pressures are represented by negative slopes on the stable part of the ψ' -surface, in consequence of which the character of this ψ' -surface does not in this respect immediately express that of the ψ -surface, where all the slopes are positive. A connodal tangent-chord, near the concentration with maximum pressure, almost touches the ψ'_x -line. With the concentration of maximum pressure this would be just the case. Just as the connodal tangent chords the isobars are traced in the projection on the xv -plane (Pl. II, fig. 3) in full lines, the connode is denoted by ———.

For the isobars¹⁾ we may note several peculiarities, to which VAN DER WAALS has drawn attention in his theory of ternary systems²⁾. The isobar which touches the connode on the liquid and vapour side, belongs to the pressure $p = 36.6$, which is found for the mixture which when behaving as a simple substance should have a maximum coexistence pressure. The pressure curve π determines the transition between the continuous isobars (taking the region outside the drawing into consideration) and those split up into two branches. The parts of the continuous isobars which point to P , have each a point of inflection on either side of the top. The shape of the curves $\frac{\partial^2 \psi}{\partial v \partial x} = 0$ and $\frac{\partial^2 \psi}{\partial v^2} = 0$

¹⁾ Cf. the sketch by HARTMAN, Leiden Comm., Suppl. n^o. 3, pl. II, fig. 5.

²⁾ These Proc. March 1902, p. 540.

is as has been indicated by VAN DER WAALS ¹⁾. The points of intersection of these two curves are the centre Q of the isobars and the double point of the pressure curve π , P .

b. The ψ -surface for 20° . Fig. 1, pl. III denotes the ψ_{xT} -curves and the connode. Fig 2, pl. III the ψ_{vT} -curves and the connode. Fig. 3 gives the projection on the xv -plane of the connode, of the tangent chords and of some isobars. The connode is denoted by ———. Pl. I fig. 2 gives a representation of the model.

c. The ψ -surface for 26° . Fig. 1 pl. IV gives the ψ_{xT} -curves, fig. 2 pl. IV gives the critical states, K_1 and K_2 , the isobars and the connodes for the mixtures which are taken as homogeneous, and whose gas branch as well as whose liquid branch is almost a straight line. Though in the calculations (see § 2) the plaitpoint x_{Tp} and the critical point of the homogeneous mixture x_{Tk} , have been considered as coinciding, a distance has now been given between these points which has been fixed by estimation ²⁾. The dotted parabola has been taken from VERSCHAFFELT's calculation, Suppl. N°. 7, p. 7, though properly speaking it holds only for the case that the maximum pressure falls in P_1 or P_2 ; the produced connode denotes the probable course of this part by approximation. Pl. I, fig. 3 gives a representation of the model. All this refers to a small region of x and v ; fig. 3 pl. IV, however, indicates by ——— the connode according to the construction for the mixtures taken as homogeneous all over the width of the ψ -surface. The square drawn denotes the extension of the just treated part of the ψ -surface.

d. The contraction and the subsequent splitting up of the plait appears from fig. 4 Pl. III, where the xv -projections of the connode and some connodal tangent chords of the three models have been drawn on the same scale after the xv -figures for 5° , 20° and 26° mentioned under *a b c*.

¹⁾ Prof. VAN DER WAALS was so kind as to draw our attention to a property which might also have been represented in the figure, when also the curve for $\frac{\partial^2 \psi}{\partial v^2 \partial x} = 0$ had been drawn, viz. that the minimum volume in the vapour branch,

and the maximum volume in the liquid branch lie on the curve $\frac{\partial^2 \psi}{\partial v^2 \partial x} = 0$ which

has a course similar to that of the curve $\frac{\partial^2 \psi}{\partial v \partial x} = 0$, more particularly it has the same asymptotes, and it deviates from it only in this, that with greater density the curve passes over larger volumes.

²⁾ Here the representation of the plait must come into conflict with the theory or with the simplification introduced at the basis of the calculation. With a view to the illustration of the theory by figures the latter has been chosen.

§ 7 *Comparison of the construction with the observation.* On the whole this is very satisfactory, taking the degree of approximation into consideration.

a. In pl. II fig. 4 the diagram for the plait at 5° indicating KUENEN's observations, has been drawn in full lines. The figure contains at the same time that obtained by construction. The single observations have been denoted by \square (see § 6*a*). Besides the construction with the model indicated by — — — — and by ∇ , also the simplified constructions in the plane indicated by — — — — and by \odot , the outermost of which refers to the less simplified construction, represent the character and also the numerical values satisfactorily.

b. In pl. III, fig. 3 the figure representing KUENEN's observations for the plait of 20° , has been indicated by — — — —. The figure contains at the same time the — — — —, obtained by construction on the model (see § 6*b*). The correspondence at $x = 0.3$ is the worst, which is no doubt in connection with this, that here we have already got very near the critical temperature, and that strictly speaking, different values should be assigned to T' (see § 2) for all x , and corresponding Δv and Δp should have been taken into consideration.

c. In pl. IV fig. 3 the figure representing KUENEN's observations, have been indicated by full lines, the figure contains also the figure derived in § 6*c* denoted by — — — — curves.

d. Plate IV fig. 4 and 5 may serve for a comparison of KUENEN's pT -figure (fig. 4) with that derived by construction (fig. 5). In accordance with the remark on T' in § 2, we have proceeded for 26° as follows:

For 5° and 20° the values of p and T have simply been taken from the construction with the model, mentioned under *a* and *b*. Then we marked α) the p 's and T 's, obtained by multiplying KUENEN's p_k and T_k by v_k and t_k (see § 2), β) for the different values of x the values of T' and of θ for the temperature of 26° have been calculated, and then Δt and Δp determined by the aid of this θ according to § 2; the values of p and T corrected in this way have been denoted by $+$ $+$ $+$ and joined by — — — — curves with the points mentioned under α). The full and the dotted curves give the corrected values. Between the parts where we started from the critical temperature, and the pT -lines derived from the models of 5° and 20° a space has been left open.

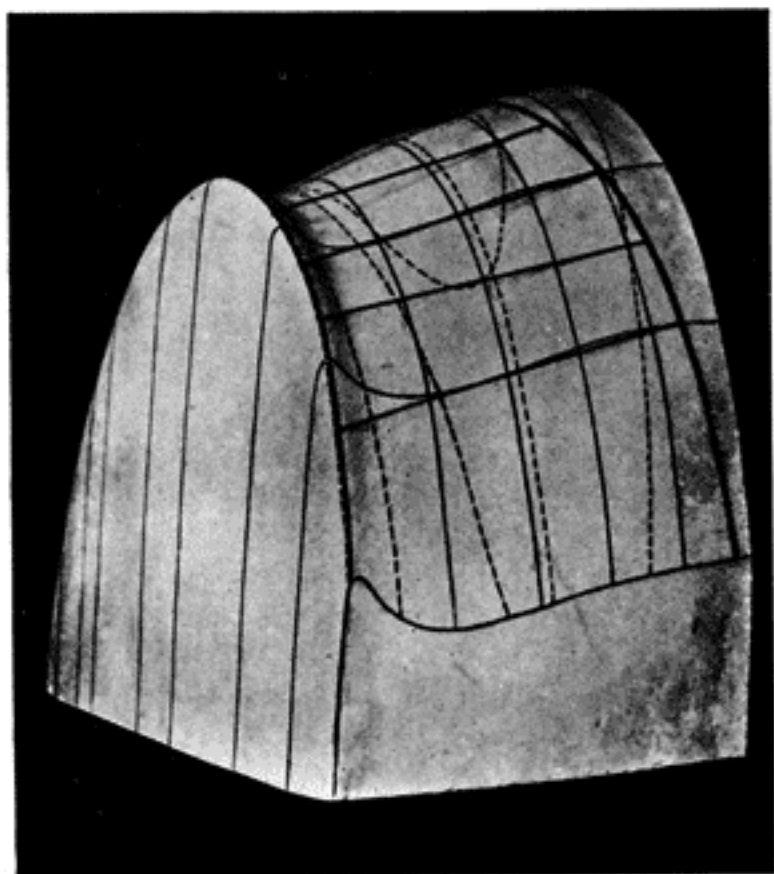


Fig. 1.



Fig. 2.

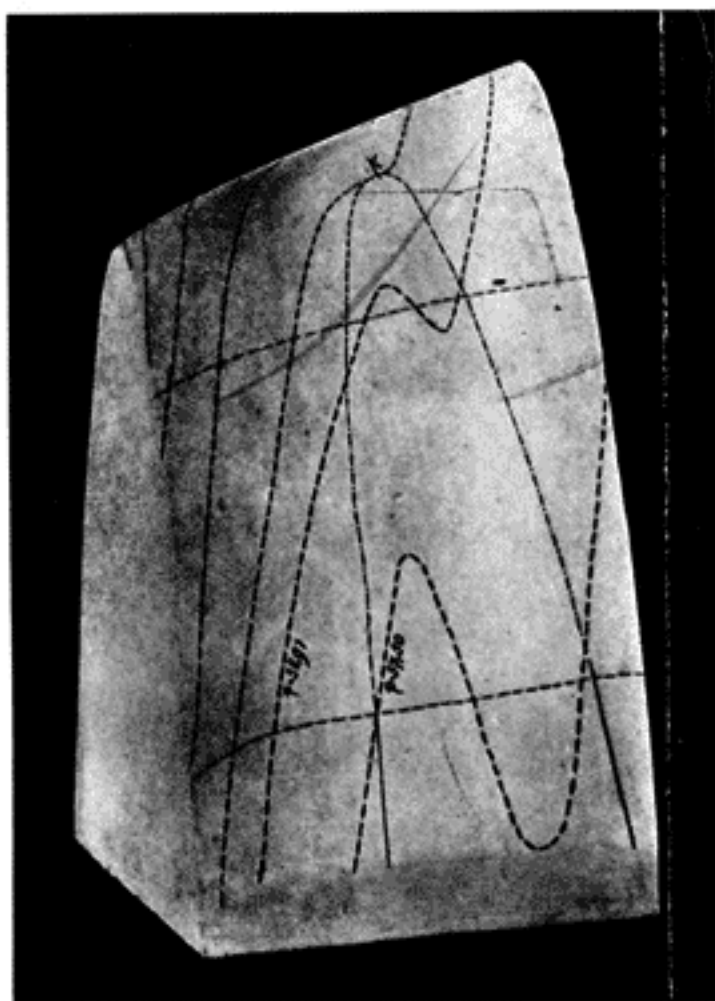


Fig. 3.

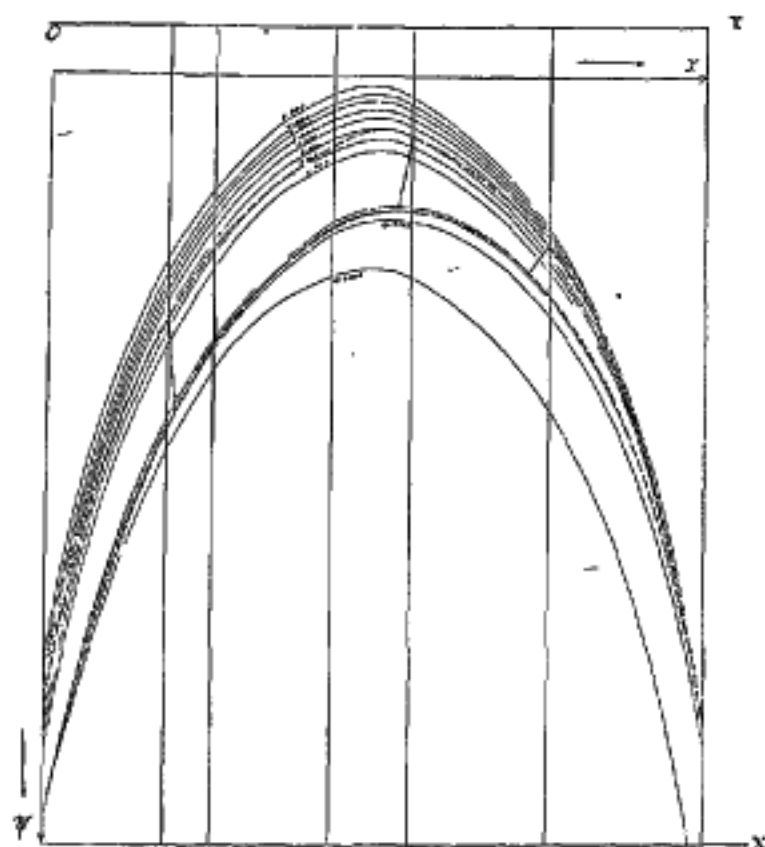


Fig. 2.

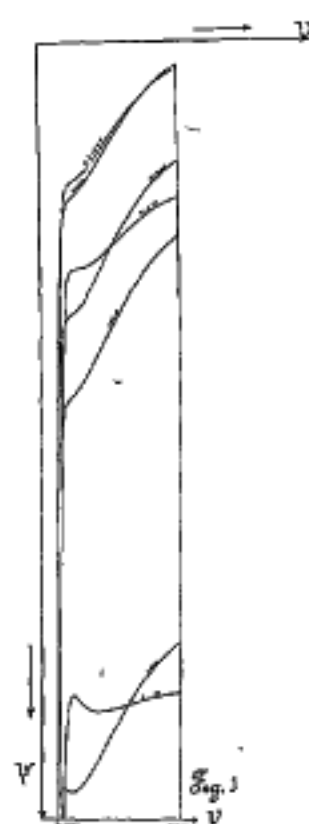


Fig. 1.

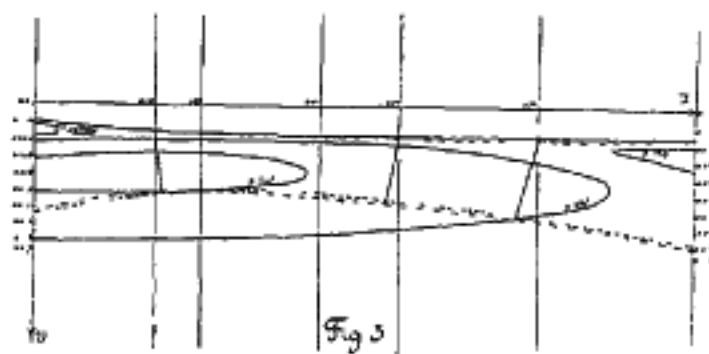


Fig. 3.

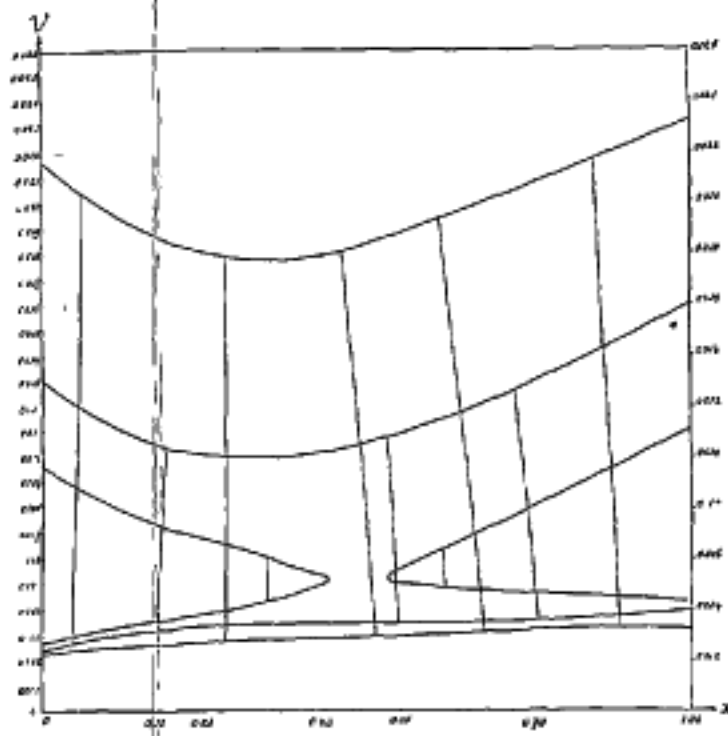


Fig. 4.

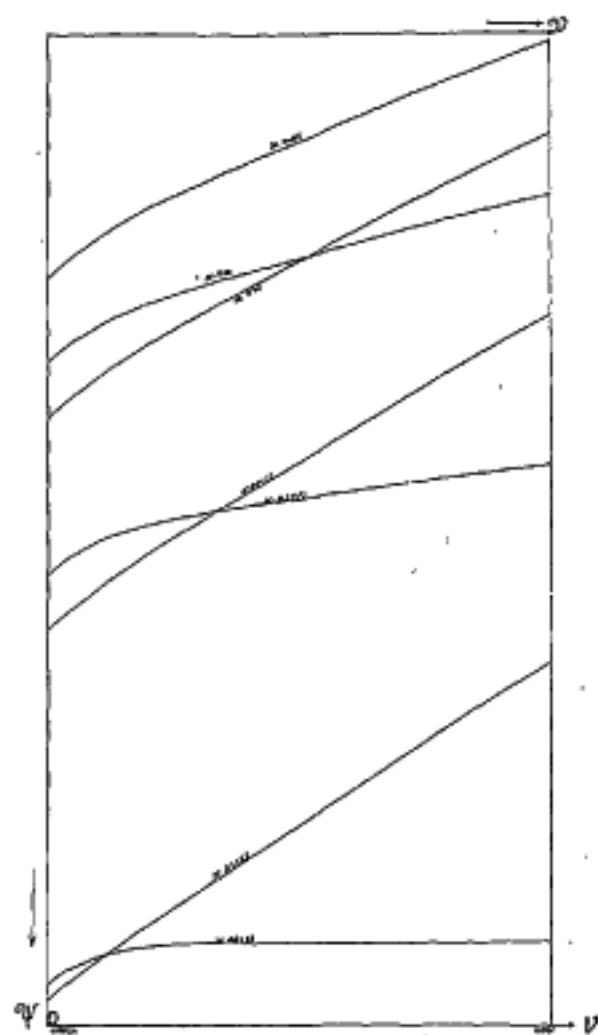


Fig. 1.

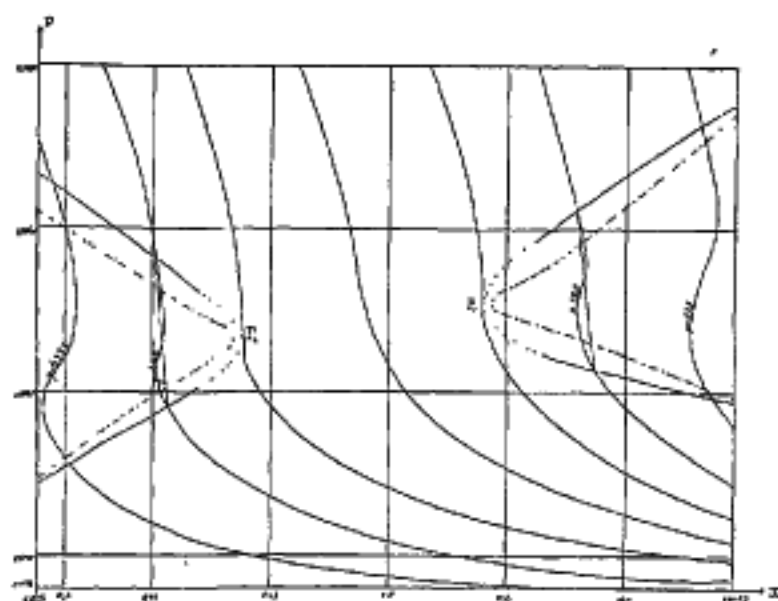


Fig. 2.

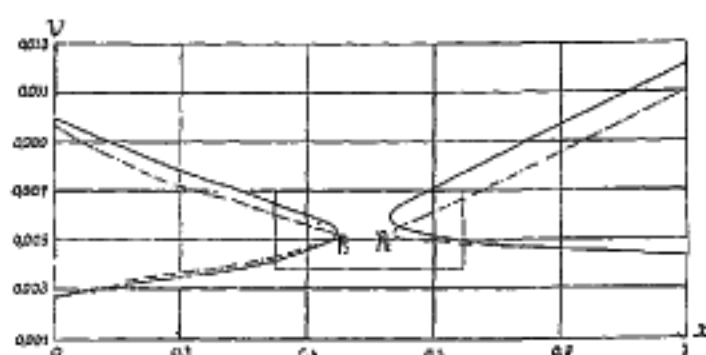


Fig. 3.

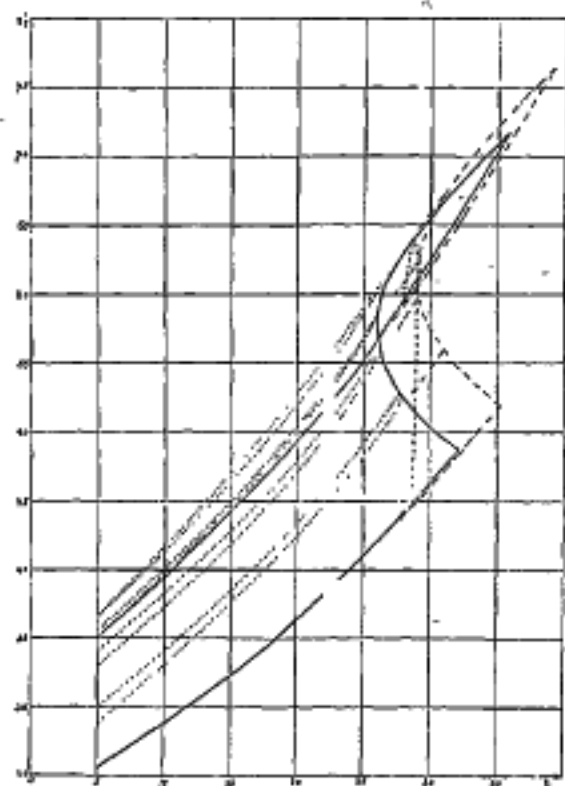


Fig. 5.

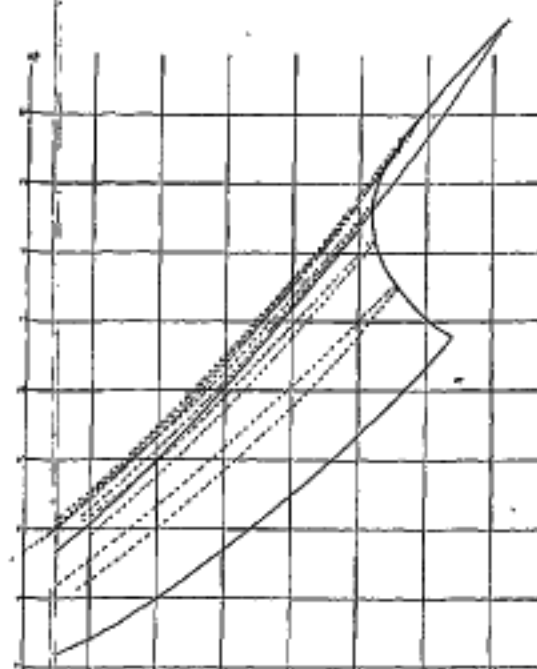


Fig. 4.