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·Physics. — *"Contributions to the knowledge of the* ψ-*surface of* van der Waals. XVI. *On the gas phase sinking in the liquid phase for binary mixtures in the case that the molecules of one component exert only a feeble attraction."* By Prof. H. Kamerlingh Onnes and Dr. W. H. Keesom. Supplement N°. 16 to the Communications from the Physical Laboratory at Leiden.

§ 1. *Introduction.* In Comm. N°. 96[b], These Proc. Dec. 1906, p. 501 a gas phase sinking in a liquid phase[1]), the barotropic phenomenon, was treated for binary mixtures for a gas liquid plait, which crosses the ψ-surface as a transverse plait at lower temperature. Then the treatment for temperatures, at which the appearance of a longitudinal plait brings about a disturbance, was deferred to a later communication. Moreover, more special cases, as the appearance of minimum or maximum critical temperature or minimum or maximum pressure of coexistence, were left out of consideration, and the discussion was restricted to the case that retrograde condensation of the first kind occurs.

When for binary mixtures the conditions for the sinking of a gas phase in a liquid phase were treated in Comm. N°. 96[r], These Proc. Dec. '06, p. 508 and Febr. '07 p. 660, it appeared in the first place that at least if the hypotheses mentioned there are valid, and pairs of substances are found with proper a_{22M}/a_{11M}, b_{22M}/b_{11M} and M_2/M_1 the theory of van der Waals' ψ-surface leads us to expect that barotropic plaitpoints[2]) will occur. [3]) Further that for mixtures with

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[1]) Considerations which are not in accord either with the limited compressibility of a gas at high pressures, first stated by Natterer in 1844, or with our present views on the mixing of two substances, induced Jamin, C.R. 96 (1883) p. 1448, Journ de phys. (2) 2 (1883) p. 389 to raise the question whether it should be possible that with compression of a mixture of CO_2 with air or with hydrogen, a liquid phase would collect above the gas phase. Cailletet (Jamin l c.) did not succeed in realizing this.

[2]) On the peculiar phenomena which are met with in case of a barotropic plaitpoint, we hope shortly to make a communication.

[3]) That the barotropic plaitpoint found in Comm. N°. 96c, Dec. '06 § 5 belongs to the gas liquid plait (cf. Comm. N° 96c, Febr, '07, p. 660 footnote 1) was derived from the shape of the spinodal curve for this case, in connection with the course of the plaitpoint curve. The same thing may appear as follows: By applying the criterion (3) in Suppl. N°. 15, March '07, p. 796, we find that mixtures of a pair of substances of ratios indicated in the mentioned § belong to case (c), (cf. p. 276) while we may derive from van Laar's fig. 22, Arch. Teyler (2) 10 (1907) p. 138, These Proc. Sept. '06, p. 226, fig. 1, that the plaitpoint curve crosses from the side $x = 0$ to the side $v = b$ (van Laar's type I).

certain ratio v_{k2}/v_{k1} for not too large T_{k2}/T_{k1} (from 0 up to a certain value, see Table I loc. cit. p. 662) only one barotropic plaitpoint occurs, which in connection with Comm. N°. 96^{b} p. 503 and 504 pointed to the fact that for the knowledge of the course of the barotropic phenomena at lower temperature considerations in which only the transverse plait is taken into account, are not sufficient for these mixtures [1] (see Comm. N°. 96^{c} p. 663).

In Comm. N°. 96^{c} p. 660 footnote 2 an estimation [2] was derived about the critical temperature of helium from the observation of the barotropic phenomenon for a mixture of helium and hydrogen described in Comm. N°. 96^{a} These Proc. Nov. '06, p. 459. In this estimation the supposition already mentioned in Comm. N°. 96^{a}, p. 460, that the molecules of helium exert only an exceedingly slight mutual attraction, was found confirmed.

This suggested the investigation already announced in Comm. N°. 96^{b}, p. 502 on binary mixtures one of whose components is a gas the molecules of which exert no or only feeble attraction (Suppl. N°. 15, These Proc. March '07, p 786). Here a plait was described for the first time which at descending temperature appears on the

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[1] For mixtures of pairs of substances as meant in table I p. 662, for which $0.2'9 > T_{k_2}/T_{k_1} > 0.196$, three barotropic plaitpoints will occur one of which, however, does not belong to the absolutely stable region. At least for the larger ones of the mentioned ratios T_{k_2}/T_{k_1}, the two others belong to a plait which enters the ψ-surface from K_1, and crosses the ψ surface as a transverse plait at lower temperature For this the considerations of Comm. $N^{'}$. 96^{b} will hold at least in so far as solid phases do not cause a disturbance. For the smaller ones of these ratios one of these two barotropic plaitpoints will also fall in the not absolutely stable fluid region, and so also for these we shall have to take the occurrence of three phase equilibria into account.

[2] For the calculations in note 2, p. 660 of Comm. N°. 96^{c} we availed ourselves for a and b of hydrogen of the values calculated for this by KOHNSTAMM (LANDOLT-BÖRNSTEIN-MEYERHOFFER's Physik. Chem. Tables 1905), which values had $T_k = 38.6$, $p_k = 20$ according to OLSZEWSKI, Wied. Ann. Bd. 56, p. 133, 1895 as starting point. If we derive the a and b for H_2 from $T_k = 29$ à 32, $p_k = 15$ according to DEWAR (B. A. Report 1902), the estimation for T_{kHe} yields about $1°$, OLSZEWSKI's newer data, Ann. d. Phys. 17 (1905) p. 986: $T_k = 32.3$, $p_k = 14.2$, give it a value of more than $1°$ (the calculation according to note 2 l.c. yields $a_{22M}/a_{11M} = 1/50$, $T_{kHe} = 1\ 3$).

This would bring about these modifications in the classification of the helium mixtures mentioned in Suppl. N°. 15, Sept. '07, § 8, that mixtures of He with H_2O, O_2, A, Ne, NO, NH_3 would belong to case (b), those with H_2, H_2S, CO_2 to case (c). For the modification which another assumption about a_{12M} (cf. p. 280) would cause in the circumstances under which the plait starting from $v = b$ occurs see Suppl. $N^{'}$. 15 l.c. p. 234. A smaller a_{12M} might even again bring about a shifting in the classification in the direction from (c) towards (a).

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ψ-surface from the side of the small volumes, reaches the side $x = 0$ at $T = T_{k_1}$, and then passes into a plait crossing in a slanting direction from $v = b$ to $x = 0$. This description was accompanied by remarks about limited miscibility in the gas state.

In Suppl. N°. 15 § 7 These Proc. March '07, p. 795 three cases were distinguished for mixtures in which one component is a gas with a feeble attraction. They are indicated as cases (a), (b) and (c) in § 9, These Proc. Sept. '07, p. 235. Case (a) corresponds with the above mentioned one; in case (b) a plait coming from $v = b$ and one coming from $x = 0$ join to a single plait in a double plaitpoint[1]; in case (c) a plait starts from $x = 0$, comes in contact with $v = b$

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[1] On the suppositions mentioned in Comm. N°. 96c p. 509 and p. 510 the data for the two double points in the net of spinodal curves, of which this double plaitpoint is one (a node) may be found in the following way (cf. Comm. Suppl. N°. 15, p. 233, note 1):

The equation for the v,x-projection of the spinodal curve on the molecular ψ-surface:

$$RTv_M^3 = 2(1 - x_M)(v_M\sqrt{a_{11M}} - b_{11M}\sqrt{a_M})^2 + 2x_M(v_M\sqrt{a_{22M}} - b_{22M}\sqrt{a_M})^2 \quad (1)$$

(cf. Suppl. N°. 15, March '07, p. 788) gives as conditions for the appearance of a double point after some obvious reductions:

$$(v_M\sqrt{a_{11M}} - b_{11M}\sqrt{a_M})^2 = 2b_{11M}\sqrt{a_{11M}}.(1-x_M)(v_M\sqrt{a_{11M}} - b_{11M}\sqrt{a_M}) +$$
$$+ 2b_{22M}\sqrt{a_{11M}}.x_M(v_M\sqrt{a_{22M}} - b_{22M}\sqrt{a_M}) \quad . \quad . \quad . \quad (2)$$

and

$$(v_M\sqrt{a_{22M}} - b_{22M}\sqrt{a_M})^2 = 2b_{11M}\sqrt{a_{22M}}.(1-x_M)(v_M\sqrt{a_{11M}} - b_{11M}\sqrt{a_M}) +$$
$$+ 2b_{22M}\sqrt{a_{22M}}.x_M(v_M\sqrt{a_{22M}} - b_{22M}\sqrt{a_M}) \quad . \quad . \quad . \quad (3)$$

From (2) and (3) follows:

$$\frac{(v_M\sqrt{a_{11M}} - b_{11M}\sqrt{a_M})^2}{\sqrt{a_{11M}}} = \frac{(v_M\sqrt{a_{22M}} - b_{22M}\sqrt{a_M})^2}{\sqrt{a_{22M}}} \quad . \quad . \quad (4)$$

Extracting the root from this equation, we may (2) and (3) reduce to:

$$\frac{v_M\sqrt{a_{11M}} - b_{11M}\sqrt{a_M}}{\sqrt{a_{11M}}} = 2b_{11M}(1 - x_M) \pm 2b_{22M}x_M\sqrt{a_{22M}/a_{11M}} \quad . \quad (5)$$

and

$$\frac{v_M\sqrt{a_{22M}} - b_{22M}\sqrt{a_M}}{\sqrt{a_{22M}}} = 2b_{22M}x_M \pm 2b_{11M}(1-x_M)\sqrt{a_{11M}/a_{22M}}. \quad (6)$$

By eliminating v_M from (5) and (6) we obtain for x_M the equation (1) of Suppl. N°. 15, March '07, p. 796 (cf. errata Proc. Sept. '07, p. 239).

The further derivation of v_M and T (see Suppl. N°. 15, March '07, p. 798) may be left to the reader (compare with these developments VAN LAAR, These Proc. May '07, p. 38 sqq. and Arch. TEYLER (2) 11 (1907) 1re partie § 5).

at lower temperature, and passes then into a plait crossing in a slanting direction [1]).

For this distinction a_{22M}/a_{11M} was always supposed so small in connection with the value of b_{22M}/b_{11M}, that the plaitpoint curve crosses from K_1 to the line $v = b$ and that three phase equilibria not yet occur at the temperatures under consideration [2]).

Now that the estimations concerning the a and b of helium justify the supposition that the plaitpoint curve [3]) crosses from $x = 0$ to the

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[1]) Kundt, Berl. Sitzb. Oct. 1880, S. 812—824 was of opinion that it would always be possible to convert a liquid to the gas state by pressing in a gas. This view was maintained in van Eldik's thesis (Leiden 1898, p. 7, cf. Comm. Phys. Lab. Leiden, Suppl. N'. 3, p. 45), where it says that the operation mentioned, if it is realized, would be the determination of the plaitpoint pressure corresponding to the temperature of observation of the pair of substances which is subjected to the experiment. There it was tacitly assumed that with sufficiently high pressure the plaitpoint state could be reached for every temperature between the critical temperatures of the components as e.g. for mixtures of methyl chloride and carbonic acid, even though it would have to be found above 750 atmospheres for hydrogen and ether, as van Eldik derived taking into account the diminution which with increasing pressure is found in the decrease of the surface tension caused by one and the same increase of pressure (Kundt loc. cit. p. 818, van Eldik Thesis, p. 5, cf Suppl. N⁰. 3, p. 52). If we pay attention to the possibility now foreseen by the theory, that this diminution continues outside the region of observation, it seems probable in the light of the observations mentioned, that it would not be possible — here we treat as infinite, pressures which exert forces on the molecules greater than those joining the parts of them — to reduce the surface tension to 0 for the pair of substances mentioned (and the same remark applies to hydrogen and ethylalcohol) at the temperature of observation (Kundt 21', van Eldik 9°.5), so that already at that temperature a plait crossing obliquely from $x=0$ to $v=b$ would exist on the ψ-surface.

In fact we should also derive from van Laar's figure cited p. 274 footnote 3 that ether-hydrogen (and also alcohol-hydrogen) belong to van Laar's type I, while according to the criteria laid down by us, they should belong to case (c) of this type. Van der Waals' equations Contin. II p 43, however, would point out a critical temperature of complete miscibility of about — 200°C. in the supposition of $a_{12M} = \sqrt{a_{11M} a_{22M}}$, so that according to these suppositions an obliquely crossing plait would only make its appearance below this temperature. If the existence of an obliquely crossing plait at the temperature of the above mentioned experiments should be confirmed, this might, among other things, point to the fact that a_{12M} would be considerably smaller than $\sqrt{a_{11M} a_{22M}}$ for the pair of substances mentioned (cf. p. 280).

[2]) According to this restriction case (c) cannot occur e.g. for b_{22M}/b_{11M} larger than a certain value (cf. Suppl. N⁰. 15 These Proc. March '07, p. 797).

[3]) Kuenen, These Proc. Febr. '03, p. 473 was the first to find experimentally a plaitpoint curve starting from $x = 0$, and directed to the side $v = b$ for mixtures of ethane and methylalcohol.

line $v = b$ for mixtures of helium and hydrogen [1]), it is desirable to subject the barotropic phenomena for the cases mentioned to a closer examination. In this discussion for mixtures one component of which is a gas with feeble attraction, we shall again restrict ourselves and suppose that in the considered cases at the considered temperatures the second branch of the plaitpoint curve (VAN LAAR, These Proc. May '05 p. 37), starting from K_2, does not make its influence felt, so that three phase equilibria do not yet make their appearance.

§ 2. *The course of the barotropic phenomena for binary mixtures, one component of which is a gas whose molecules exert only a feeble attraction.*

In this discussion we shall have to distinguish the cases a, b, and c mentioned in § 1.

a. In this case a plait starting from $v = b$ and closed towards the side of the large v's, appears for $T_{km} > T > T_{k_1}$, which plait we have called gas-gasplait in Suppl. N°. 15, March '07, p. 793. If

$b_{22} < b_{11}$, then θ_{pl} will be $> \dfrac{\pi}{2}$ for $T > T_{bpls}$ (see Comm. N°. 96[b]

p. 504); at $T = T_{bpls}$ a barotropic plaitpoint occurs (cf. Suppl. N°. 15 March '07 Pl. I, fig. 1); at $T < T_{bpls}$ we find a barotropic nodal line on the gas-gasplait (cf. Suppl. N°. 15, Pl. I, fig. 2). At $T = T_{k_1}$ the gas-gasplait passes into an obliquely crossing gas liquid plait. A barotropic nodal line will exist on it (see fig. 1) till it disappears under the three phase triangle, and so passes into the not absolutely stable region. As mentioned in § 1 we shall not give the description of what happens when three phase equilibria have appeared. In the same way we shall for the present disregard more complicated cases, as the appearance of two barotropic nodal lines on the gas-gasplait, three on the obliquely crossing plait etc., till further investigation may teach that these cases are possible.

If $b_{22} > b_{11}$, the plait coming from $v = b$ may reach the side $x = 0$, and pass into an oblique plait without it being necessary that a barotropic tangent chord occurs.

b. For $b_{22} < b_{11}$ a barotropic plaitpoint will occur at $T_{bpls} > T_{dul}$ (cf. Suppl. N°. 15, March '07 p. 798). This barotropic plaitpoint, and also at $T_{bpls} > T > T_{dul}$ the barotropic tangent chord, may

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[1]) This follows, also from VAN LAAR's fig. 22, Arch. TEYLER (2) 10 (1907) p. 38 with the mentioned estimations on the critical temperature and pressure of helium (cf. p. 275 note 2) and on the suppositions made (cf. These Proc. Dec. '06 p. 509 and 510).

occur both on the plait starting from $v = b$ and on that starting from $x = 0$ (figs. 2 and 3). If in the homogeneous double plaitpoint the isobar should run parallel to the x-axis, T_{bpls} would coincide with T_{dpl}. For $T < T_{dpl}$ a barotropic chord exists on the obliquely crossing plait, just as in case (a)[1].

For $b_{22} > b_{11}$, as in this case for a, the existence of barotropic tangent chords is not required.

c. If $b_{22} < b_{11}$, a barotropic plaitpoint will make its appearance for $T_{bpls} < T_{k_1}$ and $> T_{km}$; at lower temperatures a barotropic tangent chord is found on the plait starting from $x = 0$ and closed on the side of the small v's, and at $T < T_{km}$ on the obliquely crossing plait (fig. 4). For $b_{22} > b_{11}$ as for a and b.

In fig. 5 the course of the spinodal curves (continuous) and of the connodal curves (lines consisting of dashes) on the ψ-surface for the unity of weight has been more fully represented for a case c. The figure has been construed with a view to mixtures of helium and hydrogen. In this we adopted the hypotheses mentioned in Comm. N^0. 96', Dec. '06, p. 509 and 510, and put for hydrogen $T_{k_1} = 32,3$, $p_{k_1} = 14.2$, for helium $T_{k_2} = 1,3$, $b_{MHe} = \frac{1}{2} b_{MH_2}$ (p. 275 note 2)[2]. The volume v is expressed in the theoretical normal volume of a molecular quantity as unity. The point K_m has been calculated according to VAN DER WAALS Cont. II, p. 43. The spinodal curves have been constructed as in Suppl. N^0. 15, March '07, p. 788. P_b is the barotropic plaitpoint, calculated in the way indicated in Comm. N^0. 96^c, Dec. '06, p. 510. Further the plaitpoint curve $K_1 K_m$ calculated according to the equation given by VAN LAAR,

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[1] In the light of our present knowledge of the behaviour of mixtures and divested of the considerations which are incompatible with it (cf. p. 274 footnote 1) the phenomenon deemed possible by JAMIN, C. R. 96 (1883) p. 1451, Journ. phys. (2) 2 (1883) p. 383, would be described as follows: On compression of a gas above a suitable quantity of liquid (see p. 281 note 2), this liquid is made to dissolve at first under plaitpoint circumstances, after which on further pressing in of the gas into the thus formed homogeneous phase a phase richer in the least volatile component (called by JAMIN liquid, by us in certain cases, cf. Suppl. No. 15, March '07, § 4, second gas phase) may separate above the phase which is richer in the most volatile component. If this phenomenon could be realized, we should have to deal with a case b for a temperature $T > T_{dpl}$, and in which the line RQ (see fig. 6) intersects the plait starting from $v = b$ in such a way that for the intersected connodal tangent chords $\vartheta > \dfrac{\pi}{2}$.

[2] However, on account of the uncertainty which still prevails about T_{kHe} and p_{kHe}, and in view of the probability that $a_{12M} < \sqrt{a_{11M} a_{22M}}$ (see p. 280) it is still to be considered as quite possible that He—H$_2$ belongs to case (b), as was supposed in Suppl. N^0. 15.

These Proc. April '05 p. 652 has been included in the diagram. The second branch of the plaitpoint curve is not to be distinguished from the straight line HK_2 on the scale on which the diagram has been drawn.

For the connodal curves the points of intersection with the line $x = 0$ representing the points of saturation for pure hydrogen have been calculated. For this purpose the constants of saturation have been used, which have been calculated by DALTON[1]) for a substance that follows the equation of state of VAN DER WAALS with constant a and b. For the rest the course of the connodal curves for which for $T \geq T_{km}$ also the plaitpoints are known, has been represented schematically. This applies particularly to the points of intersection of the connodal curve for $T = 20$ with the line $v = b$, so that also the course of the connodal curve, particularly of the gas branch, is uncertain in the neighbourhood of the line $v = b$. The line CD represents the experimentally determined barotropic tangent chord for $T = 20$ (see Comms. N°. 96^a and N°. 96^c Febr. '07 p. 660 footnote 2).

The situation of the line CD with respect to the connodal curves might point to T_{km} being higher than was calculated by us, which may be due either to the critical temperature of helium being lower than was assumed by us here, or to a_{12M} being $< \sqrt{a_{11M} a_{22M}}$ for mixtures of He—H$_2$ [2]).

The course of the barotropic plaitpoints and barotropic tangent chords in case (c), and also in case (b), if they occur on the plait starting from $x = 0$, corresponds for the higher temperatures with that for the case that the branch of the plaitpoint curve starting from K_1 crosses the ψ-surface from $x = 0$ to $x = 1$, for which case the course was described in Comm. N°. 96^b. For the lower temperatures we meet with this difference that in the cases considered in this comm. the barotropic tangent chord continues to exist on the plait, till it disappears under the three phase triangle, whereas in the cases considered in Comm. N°. 96^b the barotropic tangent chord may also vanish from the plait through a barotropic plaitpoint (lower barotropic plaitpoint temperature, see Comm. N°. 96^b p. 504). The latter must even be the case if for $T \geq T_{k_2}$ no three phase equilibria appear as yet (cf. p. 275 note 1).

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[1]) J. P. DALTON, Phil. Mag. April 1907, p. 520.

[2]) The same remark concerning a_{12M} for mixtures of H$_2$ with other substances might be derived as follows: for CO$_2$ — H$_2$ (the same holds for CO$_2$—O$_2$) from a comparison of the experimentally determined portion of the plaitpoint curve with that calculated in the same way as above for He—H$_2$; for H$_2$ — ether and H$_2$ — alcohol see § 1 p. 277 note 1).

VAN DER WAALS, These Proc. Jan. '07 p. 528 calls attention to the influence of b_{22} b_{11} on the occurrence of barotropic phenomena by stating this rule: "When the most volatile substance has the greatest limiting density, the gas phase can be specifically heavier than the liquid phase." In connection with what was discussed above we may now supplement this rule as follows: If of a binary mixture the more volatile component has the greater limiting density, the gas phase will be made to sink in the liquid phase by compression with suitable concentration and temperature, provided the more volatile component has so feeble an attraction that pressing in of this latter component cannot make the liquid phase of the less volatile component dissolve in the gas phase at definite [1]) temperatures even at the highest (comp. p. 277 note 1) pressures. [2]) It is implied in the terms of this rule that it has been supposed that no two liquid phases occur.

It is not excluded that also in other cases sinking of the gas phase in the liquid phase might occur. [3])

If we apply this rule to pairs of substances of which data are available for a_{22M}, a_{11M} and b_{2rM}, b_{11M}, it appears that only for He—II, it may be expected on reasonable grounds [4]) that barotropic phenomena occur at not too high pressures[5]). Further investigations will have to reveal whether for mixtures of pairs of substances as nitrogen

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[1]) Also at higher temperatures than these barotropic phenomena may then occur.

[2]) In the case of compression of a gas above a liquid, starting from the pure substance in the way as was done in KUNDT's experiments we describe on the ψ-surface a curve the v, x-projection of which is a straight line joining a point of the line $x = 0$ with the point $v = 0$, $x = 1$. For the liquid phase to disappear at a definite, suitable temperature just under plaitpoint circumstances, we must start from a definite quantity of liquid so that the volume is represented by SQ (see fig. 6). If the quantity of liquid from which we start, is smaller, the liquid phase will evaporate (be dissolved in the gas phase), if it is larger the gas is dissolved in the liquid phase (cf. VAN DFR WAALS, Cont. II, p 136). Only if the diffusion is not rapid enough to ensure equilibrium all through the tube, solution of the liquid under plaitpoint phenomena may be observed also with other quantities of liquid as corresponding with v_Q, as has been set forth by KUENEN's experiments on the influence of phenomena of retardation.

[3]) See e.g. § 1, p 275, note 1.

[4]) Though for mixtures of e.g. helium and acetonitril the available data with application of the special hypotheses assumed in this § (concerning the equation of state etc) would point to the fact that at high pressures barotropic phenomena might still just occur, it is impossible to express a definite expectation with regard to this on account of the influence of the uncertainties, both in the data and in the validity of the mentioned suppositions.

[5]) This was mentioned in Comm. No. 96b Dec. '06 p. 504.

and a light oil with high critical temperature [1]), nitrogen-lithium, argon-kalium, mercury-iron etc. sinking of the gas phase in the liquid phase could be realized.

§ 3. *On the conditions for the occurrence of barotropic phenomena.*

It appeared in § 2 that with a suitable ratio of the limiting densities the occurrence of the barotropic phenomena depends to a great extent on the ratio of the attractions of the molecules of the two components, hence on the ratio of the critical temperatures. The same thing may also be derived in the following way, more independent of the particular hypotheses which have led to the consideration of obliquely crossing plaits.

To bring about the phenomenon of the gas phase sinking in the liquid phase, the gas phase will have to be much more compressible than the liquid phase, and even on compression the gas phase must not dissolve in the liquid phase. For this the temperature will have to be pretty far below the critical temperature of the least volatile component (T_{k_1}), but still far above that of the second component (T_{k_2}). This points to a large difference between the critical temperatures of the components.

If for the pair of substances considered retrograde condensation of the first kind occurs, the coexisting phases indicated by the points L and G on the ψ-surface for the molecular quantity (see fig. 7) [2]), can only have the same density if $M_2 > M_1$.

Only when on the plait on the molecular ψ-surface connodal tangent chords appear for which the angle with the axis $x = 0$:

$\theta > \dfrac{\pi}{2}$, the coexisting phases can have equal density for $M_2 < M_1$.

As the difference between x_g and x_l is larger, and so the connodal tangent chords deflect more rapidly from the side $x = 0$, a smaller difference between M_2 and M_1 will suffice to establish equal densities in G and L.

This will be the more the case the more the plait extends towards the side $v = b$.

The latter is particularly furthered by a small ratio a_{22M}/a_{11M} (cf. Comm. Suppl. N°. 15 Pl. I fig. 1 and Pl. II), so by a small ratio of the critical temperatures, b_{22M} smaller than b_{11M} also tending in this direction.

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[1]) Mr. F. M. GILLEY of Boston drew our attention to mixtures of air and oil.

[2]) The dotted lines indicate that the considerations of this § hold both for the case that at lower temperature the plait crosses the p-surface as a transverse plait, and for the case that it extends towards $v = b$.

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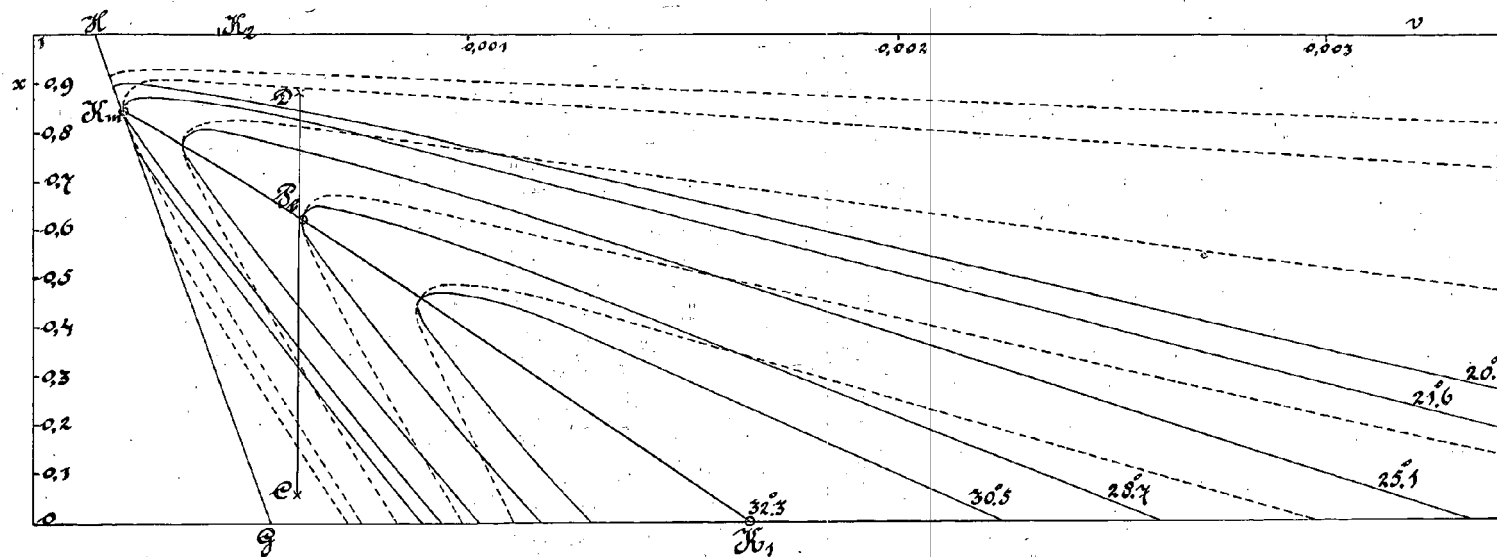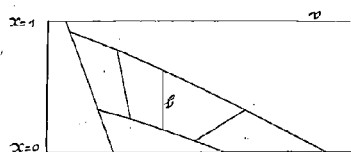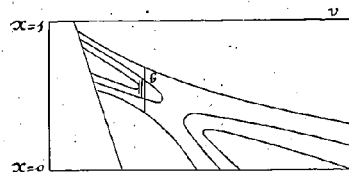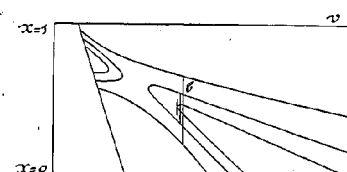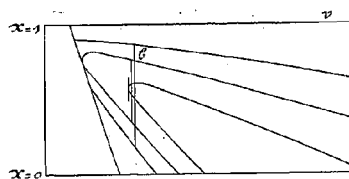

Fig. 5.

Fig 1.

Fig. 2.
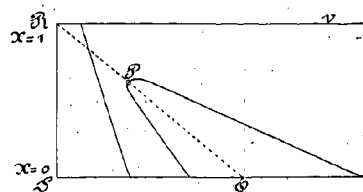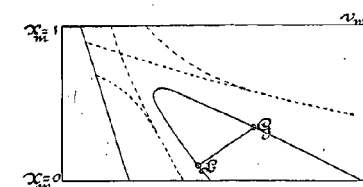

Fig. 3.

Fig. 4.

Fig. 6.

Fig. 7.

Hence we get as conditions for the possibility of the occurrence of barotropic phenomena:

The second component must have: T_{k_2} small compared with T_{k_1}, and by preference also: $M_2 > M_1$ and $b_{22M} < b_{11M}$.

This becomes still clearer by the application of equations (2) and (4) of Comm. N°. 79, April '02, p. 659:

$$x_l = x_g \, e^{\dfrac{\varphi'_q - \varphi'_l}{MRT}}$$

$$\frac{\varphi'_q - \varphi'_l}{MRT} = \left\{ \alpha \frac{T}{p_m} \frac{dp_m}{dT} - \beta \right\} \frac{p_m (v_g - v_l)}{MRT}$$

which determine the ratio of the concentrations of gas and liquid phases of a binary mixture in which the quantity of one component is small, if the law of the corresponding states may be applied. The connodal tangent chord will rapidly deflect from the side $x = 0$, if the exponent of e assumes a considerable negative value. The greatest influence on this exerts $\alpha = \dfrac{1}{T_{k_1}} \left(\dfrac{dT_{xk}}{dx} \right)_{x=0}$, on account of the value of the coefficient $\dfrac{T}{p_m} \dfrac{dp_m}{dT}$ (> 7); so T_{k_2} will have to be small with respect to T_{k_1}. The influence of $\beta = \alpha - \gamma$, if $\gamma = \dfrac{1}{v_{k_1}} \dfrac{dv_{xk}}{dx}$ (cf. Comm. N°. 81, Oct. '02 p. 325) is only of secondary importance. To tend at least in the right direction, γ would have to be negative, so $b_{22M} < b_{11M}$[1]).

Physiology. — *"An investigation of Mr. J. W. A. GEWIN, on the relation of pepsin to chymosin."* By Prof. C. A. PEKELHARING.

That gastric juice possesses the power, on the one hand to digest proteins under acid reaction, on the other hand, to curdle milk under neutral or scarcely acid reaction, is generally attributed to the presence of two different enzymes in the gastric juice, viz. pepsin and chymosin. This opinion is chiefly based upon an observation of HAMMARSTEN, who was the first to throw light on the changes that take place in milk when it is coagulated by means of rennet. HAMMARSTEN found that an extract from the mucous membrane of the stomach, which, when prepared fresh, could digest proteins as well

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[1]) The more elaborate mathematical treatment of the conditions for the occurrence of barotropic phenomena, as sequel to Comm. N°. 96c, will be postponed till further experiments call for a further discussion.