Huygens Institute - Royal Netherlands Academy of Arts and Sciences (KNAW)

Physics. — *"Contributions to the knowledge of the* ψ-*surface of* VAN DER WAALS. XV. *The case that one component is a gas without cohesion with molecules that have extension. Limited miscibility of two gases."* By Prof. H. KAMERLINGH ONNES and Dr. W. H. KEESOM. Supplement N°. 15 to the communications from the Physical Laboratory at Leiden.

(Communicated in the meeting of Februari 23, 1907).

§ 1. *Introduction.* In the Proceedings of Dec. '06, p. 502. (Comm. N°. 96b) it was mentioned that the investigation of the ψ-surface of binary mixtures in which the molecules of one component have extension but do not exert any attraction, would be taken in hand as a simpler case for a comparison with what the observations yield concerning mixtures of He, whose molecules are almost without cohesion. Before long we hope to give a fuller discussion of such a ψ-surface [1]). In the meantime some results have already been obtained in this investigation, which we shall give here.

Thus it has appeared, that at suitable temperatures, at least if the suppositions concerning the applicability of VAN DER WAALS' equation of state with a and b not depending on v and T for constant x, mentioned in § 2 hold for these mixtures,[2]) *two different phases may be in equilibrium which must be both considered as gasphases.* Then the two substances which are the components of these mixtures, are not *miscible in all proportions even in the gas state.* And if certain conditions are fulfilled this may continue to be the case when the one component is not perfectly without cohesion, but possesses still some degree of cohesion, which, however, must be very slight.

From the considerations of VAN DER WAALS, Contin. II p. 41 et sqq. and p. 104, follows that the mixing of two substances in the fluid state is brought about in consequence of the molecular motion depending on the temperature T, and promoted by the mutual attraction of the molecules of the two components determined by the quantity a_{12}, whereas the attractions of the molecules of each component inter se determined by a_{11} and a_{22}, oppose the mixing.

---

[1]) VAN LAAR, These Proc. May '05, p. 38, cf. p. 39 footnote 1, treated the projection of the plaitpoint curve on the v, x-plane for such a mixture, without, however, further investigating the shape of the spinodal curve and of the plait.

[2]) The possibility of the occurrence of a longitudinal plait at temperatures above the critical ones of both components was supposed by VAN DER WAALS in his treatment of the influence of the longitudinal plait on critical phenomena. (Zittings-versl. Kon. Akad. v. Wetensch. Amst. Nov. 1894, p. 133). [Added in the English translation].

If the mutual attraction of the molecules of the two components a_{12} is small compared with the attraction of the molecules of one of the components inter se, a_{11}, the appearance of complete miscibility will be determined solely by the molecular motion, and then the temperature will have to be raised to an amount which, if some proportions of the b's can occur then, may greatly exceed the critical temperature of the least volatile component, T_{k_1} [1]), and with it the critical temperatures of all·mixtures of these components. Thus from the equation (a) of VAN DER WAALS, Contin. II p. 43, follows $T_{km} = 1.6875 \, T_{k_1}$ for the critical temperature of complete miscibility (VAN DER WAALS l. c.) T_{km}, if $a_{22} = a_{12} = 0$ and $b_{11} = b_{22}$ may be put. At a lower temperature the two substances considered are only partially miscible, whereas for such a temperature above T_{k_1} there may be coexistence of two phases which, as will be further explained in § 3 and 4, are to be considered as gas phases.

Now it seems to follow from the nature of most of the substances known to us, most likely from the structure of their atoms, that b_{22} is also small, when a_{22} becomes very small; hence for a gas without cohesion b_{22} may not be put equal to b_{11} of a gas with cohesion, and as according to the equation cited of VAN DER WAALS a small value of b_{22} furthers the mixing greatly, the critical temperature of complete miscibility cannot rise as high as was derived iust now. But though most likely the case mentioned just now as example does not occur in nature, yet it is certainly conducive to a better insight of what is to be expected for gases of exceedingly slight cohesion.

§ 2. *The shape of the spinodal curves and the form of the plait on the ψ-surface for binary mixtures of which one component is a gas with molecules with extension and without cohesion.* In fig. 1 Pl. I the spinodal curves are represented for such a case. The figure refers to the ψ-surface for the unity of weight of the mixtures, as we hope to give a further discussion of such a ψ-surface (comp. § 1), also with a view to the treatment of the barotropic phenomena which may occur for these mixtures [2]) in case of a suitable proportion of the molecular volumes of the components, for which treatment the use of the ψ-surface for the unity of weight readily suggests itself. As was also mentioned in Comm. N°. 96 b, the conditions for

---

[1]) VAN DER WAALS, in the paper cited p. 786 footnote [1], brought this in connection with the great amount of heat absorbed at the mixing of such substances. [Added in the English translation].

[2]) Cf. Comm. N°. 96 a (Nov. '06), 96 b (Dec '06) and 96 c (Dec. '06, Febr. '07).

coexistence may be studied by the aid of the ψ-surface for the unity of weight in the same way as by the aid of that for the molecular quantity; moreover it is easy to pass from the former to the latter, which offers advantages for the treatment of many problems (cf. § 6) if this is desired.

The equation of the spinodal curve on the ψ-surface for the unity of weight of mixtures, for which VAN DER WAALS' equation of state for binary mixtures with a and b not depending on v and T for constant x may be applied, and for which $a_{12} = \sqrt{a_{11}a_{22}}$, $b_{12}M = \frac{1}{2}(b_{11}M + b_{22}M)$ (cf. Comm. No. 96c, Dec. '06, p. 510) may be put, [1]) runs:

$$R_1 R_2 T v^3 = 2 R_2 (1-x)\{v\sqrt{a_{11}} - b_{11}\sqrt{a}\}^2 + 2 R_1 x\{v\sqrt{a_{22}} - b_{22}\sqrt{a}\}^2 .$$

Here R_1 and R_2 are the gas constants for the unity of weight of the components concerned. For $a_{22} = 0$ this equation passes into:

$$\cdot \quad 4\,\tau\omega^3 = (1-x)\,[\{3\,\omega - (1-x)\}^2 + \frac{R_1}{R_2} \cdot \frac{b^2_{22}}{b^2_{11}}\,x\,(1-x)]$$

if we put $\dfrac{T}{T_{k_1}} = \tau$, $\dfrac{v}{v_{k_1}} = \omega$. The roots of this equation in ω have been determined by a graphical way for definite values of x and τ. The figure has been construed for mixtures for which $R_2/R_1 = \frac{1}{2}$, $b_{22}/b_{11} = \frac{1}{4}$ (cf. Comm. N°. 96c, Febr. '07, p. 600, footnote 2).

With reference to Fig. 1 we point out that for $T < T_{km}$ ($= 1.299\ T_{k_1}$) and $> T_{k_1}$ a spinodal curve closed on the side of the increasing v's, and together with it a similar plait, extends on the ψ-surface from the side of the small v's. At $T = T_{k_1}$ this plait reaches the side or the least volatile component. At lower T the spinodal curve has two distinct branches, and the plait runs in a slanting direction from the line $v = b$ to the side of the least volatile component.

Thus the investigation of mixtures with a gas without cohesion calls attention to a plait that starts from the side of the small volumes, and at lower temperature runs in an oblique direction to the side of the figure, which plait can be distinguished from the transverse and from the longitudinal plait.

The spinodal curve for $\tau = 1.040$ has a barotropic plaitpoint P_b. (see Fig. 1). For $1.299 < \tau < 1.040$ the angle with the v-axis of the tangent to the plait in the plaitpoint [2]) $\theta_{pl} > \dfrac{\pi}{2}$, for $1.040 < \tau < 1$ is $\theta_{pl} < \dfrac{\pi}{2}$. The barotropic phenomena for such a plait will be further

---

[1]) The quantities a_{11}, a_{22}, a_{12}, b_{11}, b_{22}, b_{12}, etc. relate to the unity of weight, $a_{11}{}^M$, $a_{22}M$ etc. to the molecular quantity.

[2]) Cf. Comm. N°. 96b.

discussed in a following communication (cf. N⁰. 96c Febr. '07, p. 660, footnote 1).

In Fig. 2 the course of the plait has been schematically represented for a temperature between the barotropic plaitpoint temperature and the critical temperature of the first component. The — · — · — curves denote the pressure curves, the — — — — curve the spinodal curve, the continuous curve the connode. The straight line AB is the tangent chord joining the coexisting phases A and B, CD is the barotropic tangent chord (Comm. 96b).

§ 3. *Limited miscibility of two gases.* For mixtures where as in fig. 2 a plait giving rise to phases *separated by a meniscus* which coexist in pairs, represented in the figure e.g. by A and B, while mixtures in intermediate concentrations are not stable, extends on the ψ-surface from the side of the small v's at temperatures above the critical temperature of the least volatile component, we shall call not only the phase B a gas phase, for which it is a matter of course, but also the other A; so the latter may be called a *second gas phase*, and we may speak of *equilibria between two gaseous mixtures* at those temperatures. That there is every reason to do so in the case treated in § 2 appears already from this, that the reduced temperature of the phase A, calculated with the critical temperature of the unsplit mixture with the concentration of A, is so high that already through its whole character the phase must immediately make the impression of a gas phase (so a second one).

The shape of the p-lines in fig. 2 shows further, how the two coexisting gas phases may be obtained by isopiestic and isothermic mixing, in which nothing would indicate a transition to the liquid state, from the gas phases M and N of the simple substances [1]).

We shall explain in the following § that it is really in accordance with the distinction between gas state and liquid state for binary mixtures in general, when we call A a second gas phase.

§ 4. *Distinction between gas and liquid state for binary mixtures.* It is. true that since the continuity of the gas and the liquid state of aggregation has been ascertained, it may be said with a certain degree of justice that it is no longer possible to draw the line between the two states, but when in the definition of what is to be understood by liquid and what by gas we wish properly to express the difference ·and the continuity in the character of the heterogeneous region and the homogeneous region and to preclude con-

---

[1]) Cf. footnote 1 p. 792.

clusions [1]) which are irreconcilable with the most obvious conception of phenomena, then the limits allowed for making this definition, are very narrow.

Thus for a simple substance no other distinction will be possible than by means of the isotherm of the critical temperature, and the border curve (connodal curve on GIBBS' surface), which is divided into two branches by the critical state (plaitpoint of the connodal curve), of which the branch with the larger volumes is to be defined as gas branch, that with the smaller volumes as liquid branch [2]). Liquid phases are only those which by isothermic expansion may pass into such as lie on the liquid branch of the connodal curve, and also the metastable [3]) phases lying between the connodal and the spinodal curves, which may be brought on the liquid branch of the connodal curve by isothermic compression [4]).

For binary mixtures the consideration of the ψ-surface of VAN DER WAALS leads in many cases to definitions which are just as binding.

---

[1]) So THIESEN's definition, Z.S. für compr. und fl. Gase 1 (1897) p. 86, according to which e.g. strongly compressed hydrogen at ordinary temperatures would have to be called a liquid.

[2]) This is in harmony with the principle of *continuity of phase along the border curve* according to which a change of the character of the phases on a border curve can only occur in a critical point. For substances which at temperatures near the critical one, in states represented by points on, or in the vicinity of that branch of the connodal curve on GIBBS's surface which connects the liquid states at low temperatures with the plaitpoint, should be associated, to multiple molecules of which the volume is *greater* than the volumes of the composing molecules together, this principle would admit the possibility that on the liquid branch of the border curve liquid phases should occur with greater volume than the coexisting gasphase. Such simple substances would then show the barotropic phenomenon, till now only found for binary mixtures There is nothing known that points in the direction, of making the existence of such simple substances probable but there can be no more given a reason why it should be impossible. [Added in the translation].

[3]) The metastable states have not been included in BOLTZMANN's definition Gastheorie II, p. 45.

[4]) We do not accept the principle of the distinction of LEHMAN, Ann. d. Phys. 22 (1907) p. 474 : "Erst die unterhalb der betrachteten Isotherme liegenden Kurven, welche in ihrem S-förmigen Teil unter die Abszissenachse hinunterreichen, entsprechen wahrer (tropfbarer) Flüssigkeit, d. h. einem Zustand, der negativen Druck zu ertragen im stande is", as depending on the meaning that the existence of capillary surface tension in liquids which can form drops, would presuppose that these liquids can bear external tensile forces, i. e. negative pressures without splitting up (cf ibid p. 472 in the middle, and p. 475 at the top). [Added in the translation].

When discussing this we shall leave out of account the case of solid states of aggregation and three phase equilibria.

In the first place gas states are all the states on the ψ-surfaces on which there are no plaits. As criterion to divide states which belong to the stable or metastable[1] region of ψ-surfaces which show plaits, into gas states and liquid states, analogy with the simple substance indicates their relation with the connodal curves of those plaits while for the metastable states the help of spinodal curves is to be called in.

For this first of all the distinction between the two branches of the connodal curve of a plait is required. For in the first place we shall have to give the same name to each of the two branches of a connodal curve separated by one or two plaitpoints throughout its length[2].

Now, on account of the existence of the barotropic phenomenon we cannot simply call gas branch of the connodal curve that at which one of the isopiestically connected states has the smallest density[3]. It is therefore the question to indicate if possible on each branch a state whose nature is already known through the definition holding for simple substances or for those which behave as such when splitting up into two phases. In this different cases are to be distinguished.

For the case that the considered plait[4] extends from one of the side planes $x = 0$ or $x = 1$ over the ψ-surface, follows from the definition of gas phase and liquid phase of a single substance that the branch of the connodal curve from the gas state of the pure substance to the plaitpoint is to be called gas branch, and also that the branch from the liquid phase of the simple substance to the plaitpoint is to be called liquid branch. The gas branch and the liquid branch of the spinodal curve may be distinguished in the same way as those of the connodal curve.

Let us restrict ourselves for the present to the distinction of gas and liquid in this case. In the first place we make use for this purpose of the isomignic (Comm. N°. 96b) compression and expansion.

---

[1] It follows from the nature of the case that unstable states have not to be considered here.

[2] Cf. p. 790 footnote [2].

[3] Even it if we wish to leave gravity out of account, and pay only attention to the molecular volume of the phase, the barotropic phenomena have yet called attention to the possibility that we may find the gas volume first larger and then smaller than the liquid volume when passing along the same connodal curve.

[4] The case of the two plaits at minimum critical temperature is comprised in this.

Every phase which cannot be brought on the connodal curve through this operation, or if it can, comes on the gas branch, will have to be called a gas phase, every phase which is made to lie on the liquid branch through isomignic expansion is a liquid phase. Besides the phases lying between the connodal and the spinodal curve which isomignically may be brought on the liquid branch of the connodal are metastable liquid phases.

Besides the isothermic and isomignic compression without splitting there is another operation already mentioned in § 3, which may help us to form an opinion about the similarity of different phases, viz. the isopiestic and isothermic mixing. [1]) With regard to this phases which have been obtained by isopiestic admixing without splitting from phases of which it has been ascertained that they are to be called liquid phases, must be called liquid phases until in another way, (e. g. because no splitting takes place with isomignic compression and expansion) they have been proved to have passed into gas phases. [2]).

Proceeding to the case that the plait from higher temperature appears as a closed plait on the ψ-surface, as long as the plaitpoint which first comes into contact with the side with decrease of temperature, has not yet come into contact, and with decrease of temperature the plait has not yet reached a mixture which on splitting behaves as a simple substance, and for which the distinction in liquid state and gas state is therefore fixed, we shall have to consider that branch of the connodal curve on the side of this plaitpoint, which passes into that of the gas phase at lower temperature, as belonging to the ordinary gas phase, whereas the branch which passes into the liquid branch at lower temperature may be looked upon as a *second gas phase*, and we are the more justified in doing so as the temperature should lie further above the critical tempera-

---

[1]) With the continuous isothermic and isopiestic mixing of two similar phases a and b the case may present itself (divided plait in the case of minimum crit. temp.), that an intermediate phase c of the other kind is obtained. So in general we cannot conclude to the similarity of c from the isothermic and isopiestic mixing of similar a and b.

[2]) This criterion is particularly of application to the retrograde condensation 2nd kind. For then phases on the connodal curve between the plaitpoint and the critical point of contact are liquid phases, phases on the p-curve through the plaitpoint and phases with the same x as the critical point of contact just the transitions to gas phases. The phases within the triangle bounded by these two lines and the connodal curve are also to be considered as liquid phases.

Here we abstract from the small uncertainties which would be caused in these definitions when capillarity ought to be taken into account. [Added in the translation].

tures of the unsplit mixtures belonging to the phases lying on them.

Whereas in the case, that at a temperature comparatively little lower also the other side of the ψ-surface is reached by the originally closed plait, the difference of the second gas phase with a liquid phase is still not very conspicuous, this may become very clear for the case of § 2, to which we have now got at last, that viz. with decreasing temperature a plait comes from the side $v = b_x$ on the ψ-surface, and the plait appears for the first time as longitudinal plait. Now we may again call $PBDF$ the branch of the first gas phase, $PACE$ the branch of the second gas phase. It will certainly be obvious to speak of gas phases when *all* the parts of the plait are found above the critical temperatures of the unsplit mixtures, and we shall decidedly *have* to speak of two gas phases, when the second branch of the connodal curve is intersected all over its length by isomignic lines on which beyond this plait no splitting up occurs, or if it is at most touched by one of them in the point $v = b$. For then it is beyond doubt that the final point of that branch must be called a gas phase.

Possibly also phases between the isomignic line of the critical point of contact, the line $v = b_x$ and the second gas branch belong to the second gas phase.

§ 5. *The surface of saturation for equilibria on the gas-gasplait.* In fig. 3, 4 and 5 the sections $T = $ const. of the p, T, x-surface of saturation for equilibria on the gas-gasplait have been schematically drawn for a mixture in which one component is a gas without, or almost without cohesion, in fig. 3 and 4 for temperatures higher than the critical temperature of the first component, in fig. 5 for this last temperature.

In these figures too the division of a gas phase into two gas phases, and the transition of a part of the gas region into the liquid region at $T = T_{k_1}$ is clearly set forth. The — — — — curve is the locus of the plaitpoints.

In a following communication, in which the properties of the ψ-surface for such mixtures will be further discussed, T, x-sections etc. will be drawn of this surface of saturation. At the same time it will then have to appear in how far *retrograde* unmixing of a phase into two other phases is to be expected.

That one of these phases may be called a second gas phase, appears in § 4.

§ 6. *On the conditions which must be fulfilled that limited mis-*

cibility of two gases may be expected. Now that it has appeared that on the suppositions mentioned in § 2 for mixtures in which one component is a gas without cohesion with molecules with extension, limited miscibility might be expected in the gas state, the question rises whether this phenomenon is also to be expected for mixtures with a gas of feeble cohesion. As on the said suppositions no maximum critical temp. is to be expected, this will be the case when $T_{km} > T_{k_1}$ is found. [1]) We have treated this question by the aid of the ψ-surface for the molecular quantity (cf. § 2). We arrive then at the equations developed by VAN DER WAALS Contin. II p. 43. The condition that $T_{km} > T_{k_1}$ is:

$$\{b_{22M}/b_{11M} - \sqrt{a_{22M}/a_{1\cdot M}}\}^2 > \frac{4}{27} b^3{}_M/b^3{}_{11M} \cdot \frac{1}{x_M(1-x_M)}$$

in which b_M and $x_M(1-x_M)$ follow from the equations given by VAN DER WAALS loc. cit. We find from this [2]) $T_{km} > T_{k_1}$,

for	$b_{22M}/b_{11M} = 2$	,	if	$a_{22M}/a_{11M} < 0.58$
	1			0.053
	$^1/_2$			0.0037
	$^1/_4$			0.00023
	$^1/_8$			0.000015

It appears on investigation that only for few pairs of substances the ratios of the a's and b's [3]) will be able to satisfy this condition. The still unknown relations. between a and b for a same substance, to which we alluded in § 1, and from which ensues that in general substances with small a also possess a small b, and that as a rule large b goes together with large a, seem to prevent this. H e, which with. a b which is still not very small compared with H_2 possesses a very small a, so feeble cohesion, and H_2O, which taking the value of a into consideration, has a comparatively small b, so a molecule of small volume, constitute exceptions to this general rule which are favourable for the phenomenon treated here.

If for H e — H_2: $b_{22M}/b_{11M} = {}^1/_2$, and $a_{22M}/a_{11M} = {}^1/_{175}$ (Comm. N°. 96c, Febr. '07. p. 660 footnote 2), $T_{km} < T_{k_1}$ must be expected on the above suppositions. Also for helium-argon and helium-oxygen e. g. the same thing must be expected. Most likely the ratios are

---

[1]) Whether limited miscibility in the gas state may also occur if $T_{km} < T_{k_1}$ in certain cases and at suitable temperatures, will be discussed in § 7.

[2]) For $b_{22M}/b_{1M} = {}^1/_8$ e g. we find also $T_{km} > T_{k_1}$ for $0.125 > a_{22M}/a_{11M} > 0.061$. These cases will be further discussed.

[3]) See c. g KOHNSTAMM, LANDOLT-BÖRNSTEIN-MEYERHOEFER's Physik. Chem. Tabellen.

H. KAMERLINGH ONNES and W. H. KEESOM. Contributions to the knowledge of the ψ-surface of VAN DER WAALS. XV. The case that one component is a gas without cohesion with molecules that have extension. Limited miscibility of two gases.
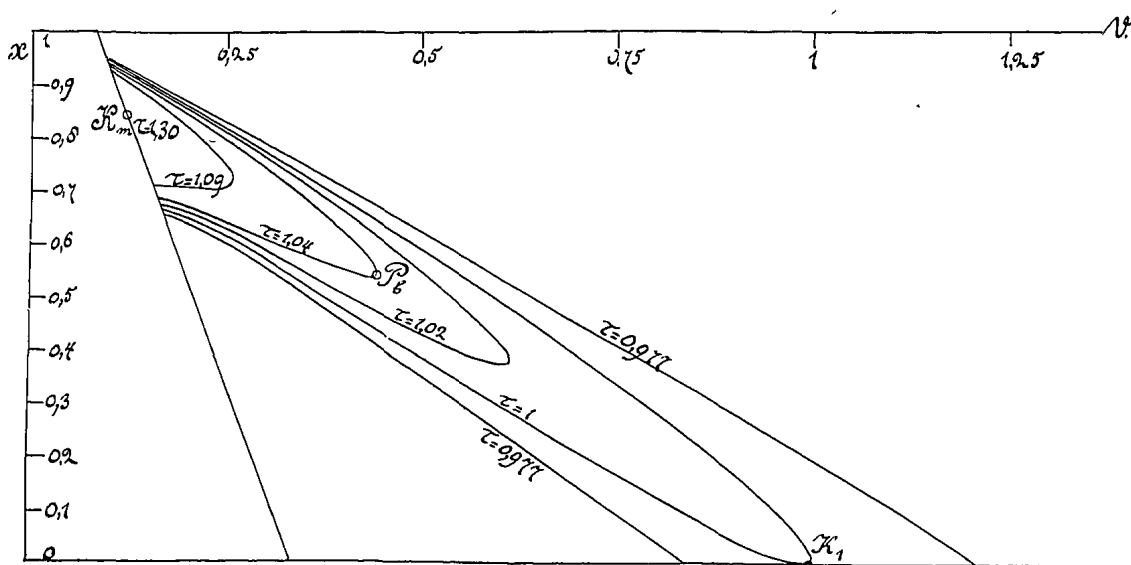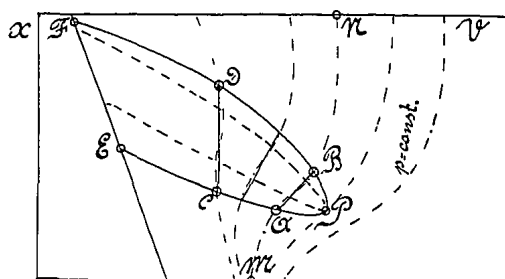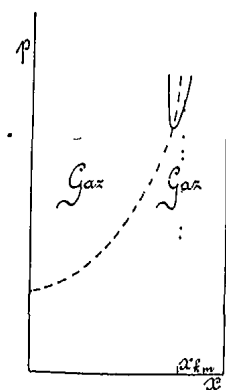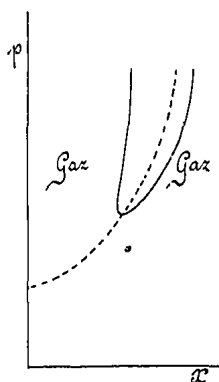
Plate I.

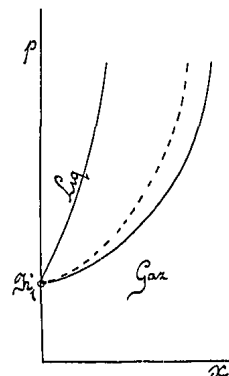Fig. 1

Fig. 2.

Fig. 3.

Fig 4.

Fig 5

more favourable for mixtures of helium and neon [1]) than for those oi helium and hydrogen.

For mixtures of helium and water the ratios for the above assumed a_{IIe} and b_{IIe} are such that for them limited miscibility in the gas state is to be expected, if the suppositions mentioned in § 2 are to be applied.

The coefficients of viscosity and of conduction of heat (cf. Comm. N^{0}. 96c, Febr. '07 p. 660 footnote 2) admit a value of b_{He} which is still somewhat though only little higher; this might render it possible to realise the said phenomenon perhaps also for the other pairs of substances mentioned, especially when we bear in mind that its appearance is not excluded for $T_{km} < T_{k_1}$ (cf. p. 794 footnote 1).

The experimental investigation of these mixtures has been taken in hand in the Leiden Laboratory.

(Communicated in the meeting of March 30).

§ 7. *The shape of the spinodal curves and of the plaits for the case that the molecules of one component exert some, though still feeble attraction.* With very small value of the mutual attraction a_{12} of the molecules of the two components, in connection with the feeble attraction a_{22} of the molecules of one component inter se, the spinodal curve will with decreasing temperature extend more and more on the ψ-surface as in Pl. I fig. 1 from the side of the small v's, come into contact with the line $x = 0$ at $T = T_{k_1}$, and then cross from the line $v = b$ to the side $x = 0$ in two isolated branches [2]). We leave here out of account what takes place at lower temperatures when the spinodal curve approaches and reaches the side $x = 1$ too.

To examine what shape the spinodal curve can have with greater attraction of the most volatile component, we shall avail ourselves of the suppositions introduced in § 2 and also applied in § 6 con-

---

[1]) Cf. RAMSAY and TRAVERS, Phil. Trans. A. 197 (1901) p. 47 for data concerning refractive power and critical temperature of neon.

[2]) Here $\dfrac{dT_{xpl}}{dx} > 0$ for $x = 0$. We see here that VERSCHAFFELT's conclusion (These Proc. March 1906 p. 751) concerning the maximum temperature in the plaitpoint curve for mixtures, for which the component is indicated by a point from the region OHK (see fig. 2) must be supplemented by the possibility that he branch of the plaitpoint curve starting from the first component, goes to infinite pressures.

54

cerning the equation of state and the quantities a_{12} [1]) and b_{12}. In the net of spinodal curves for a given pair of substances 2 singular points may then occur, belonging to the spinodal curves for different temperatures. The values of x for -these are determined by the equation:

$$\frac{x_M}{1-x_M} = \frac{3b_{11M}\sqrt{a_{22M}} \mp 2b_{11M}\sqrt[n]{a_{11M}a_{22M}} - b_{22M}\sqrt{a_{11M}}}{-b_{11M}\sqrt{a_{22M}} \mp 2b_{22M}\sqrt[n]{a_{11M}a_{22M}} + 3b_{22M}\sqrt{a_{11M}}} \quad (1)$$

For very small a_{22} we find from this two singular points with $x > 1$, so not belonging to that part of the ψ-surface which can denote phases of mixtures. Of these two singular points that for which the lowest signs hold, passes through infinity for increasing a_{22}, and then approaches the line $x = 0$ on the other side of the ψ-surface. This line is reached for.

$$\sqrt{a_{22M}/a_{11M}} = \frac{1}{3}\{-1 + \sqrt{1 + 3\,b_{22M}/b_{11M}}\} = m_1 \quad . \quad (2)$$

With increasing a_{22}/a_{11} the singular point, which appears to be a double point for this region, approaches the line $v = b$, which line is reached for:

$$\sqrt[n]{a_{22M}/a_{11M}} = -(1-b_{22M}\,b_{11M}) + \sqrt{1-b_{22M}/b_{11M}+(b_{22M}/b_{11M})^2} = m_2 \quad (3)$$

In this we assume $b_{22M} < b_{11M}$ [2]).

So if the mutual attraction of the molecules of the most volatile component and those of the other in connection with the attractions inter se attains a certain value — on the assumptions made for the calculations for $m = \sqrt[n]{a_{22M}/a_{11M}} = m_1$ — the spinodal curve for $T = T_{k_1}$ will no longer touch the side in K_1 (cf. fig. 1 Pl. I), but it

---

[1]) In this first investigation of what may be expected for mixtures of helium, with a view of forming some opinion as to the conditions under which the experiments for this purpose are to be made, we put (§ 2), $b_{12M} = \frac{1}{2}(b_{11M} + b_{22M})$ $a_{12M} = \sqrt{a_{11M}a_{22M}}$ (cf. Comm. Suppl. No. 8, These Proc. Sept. '04 p. 227) in the calculations, no data concerning a_{12} and b_{12} for those mixtures being available as yet. Also VAN DER WAALS (These Proc. Febr. '07, p. 630) assumes that as a rule $a_{12M} < (a_{11M} + a_{22M})$. It will be necessary for a complete survey concerning the different possibilities to make also other suppositions about a_{12M} (cf. VAN DER WAALS l.c., KOHNSTAMM ibid p. 642), at the same time taking care that a and b are not put independent of v and T. at least not both (cf. VAN DER WAALS, These Proc. Sept. '05 p. 289) and that they may only be put quadratic functions of x by approximation.

If also for mixtures with very small a_{22}, a_{12M} might be $< \sqrt{a_{11M}a_{2M}}$ (cf. KOHNSTAMM l c.) the phenomena of limited miscibility under discussion might still be sooner expected.

[2]) For $b_{22M} > b_{11M}$ the other singular point comes from side $x = 1$ on the ψ-surface for a smaller value of a_{22M}/a_{11M}. As probably this case does not present itself for the pairs of substances with small a_{22}/a_{11} known to us, we shall not discuss it.

will have a double point there, in which the two branches of the spinodal curve intersect each other and the line $x = 0$ at an angle. In this case the critical temperature of the least volatile component is not changed in first approximation by small quantities of admixtures.

With greater attraction of the most volatile component — on the suppositions mentioned for $m_1 < m < m_2$ — a spinodal curve on the ψ-surface will have a double point. This will lie the nearer to the side of the small v's, the more the attraction of the most volatile component increases. With a certain value of the attraction — $m = m_2$ — the spinodal curve reaches the line $v = b$ with a double point, with greater attraction the spinodal curve will proceed from $x = 0$ on the ψ-surface with decreasing T, and touch the line $v = b$ at $T = T_{km}$. On the suppositions mentioned for $b_{22M}/b_{11M} < {}^{16}/_{21}$ the contact with the line $v = b$ will here take place at temperatures $> T_{l_2}$, for $b_{22M}/b_{1,M} > {}^{16}/_{11}$ at $T < T_{k_2}$, so that in the latter case the spinodal curve comes first into contact with the line $x = 1$.

In the first case $(b_{22M}/b_{11M} < {}^{16}/_{21})$ a plait will come from $x = 0$ and at lower T, whereas for larger m a branch plait directed to the side $x = 1$ may develop: if $m < m_2$ it will be united through an homogeneous double plaitpoint (KORTEWEG, *Archiv. Neerl.* 24 (1891)), with a plait coming from $v = b$ to a plait that crosses from one side to the other, if $m > m_2$ it will pass into such a plait by contact with $v = b$.

In the second case the plait which becomes from $x = 0$ will again united with one coming from $v = b$ for smaller m; for larger m a branch plait will have developed before this union takes place or before the spinodal curve touches the line $v = b$.

The shape of the spinodal curve for these cases with always greater attraction of the most volatile component, where we shall have to consider three phase equilibria, need not be discussed for the present, as they do not belong to the case of a component with feeble attraction [1]).

For some values of b_{22M}/b_{11M} table I gives the values $a_{22M}/a_{11M} = m^4$, calculated from the equations (2) and (3). If we compare with this the values of a_{22M}/a_{11M} for which $T_{km} = T_{k1}$ (§ 6) we see that they really lie between those calculated here.

The shape of the spinodal curves for a case, in which $m_1 < m < m_2$, has been represented on plate II, for the ω-surface of the unity of weight (cf. § 2), with the relations and data assumed in § 2, except that $a_{22} a_{11} = 0.00049$ (or $a_{22M}/a_{11M} = 0.00196$).

---

[1]) Cf. moreover VAN LAAR, Arch. TEYLER (2) 10 (1906), These Proc. Sept. '06 p. 226.

TABLE I.

b_{22M}/b_{11M}	$m_1{}^4$	$m_2{}^4$
$\frac{1}{2}$	0.0014	0.0179
$\frac{1}{4}$	0.000134	0.000527
$\frac{1}{8}$	0.000011	0.000022

The plait extending on the w-surface from $v = b$ for a temperature $> T_{k_1}$, will have to be considered as a gas-gasplait according to § 4 (cf. § 6). Also a similar plait for $T < T_{k_1}$, if the connodal curve is not touched by an isomignic line, and is nowhere cut by an isomignic line which intersects the connodal curve of the plait coming from $x = 0$ [1]. According to § 4 we shall be justified in considering also the plait lying on the side of the small v's for $T_{k_1} > T > T_{dpl}$ (temperature for which the double plaitpoint considered occurs) as gas-gasplait, if the temperature is above the critical temperatures of the unsplit mixtures for all parts of that plait. That there can be some reason for doing so, appears when we calculate the reduced temperature for the double plaitpoint for some cases, e.g. for the ratios b_{22M}/b_{11M} and the m_2 belonging to it, mentioned in Table I.

Putting $b_{22M}/b_{11M} = n$ the double plaitpoint temperature is determined by :

$$ T_{dpl}/T_{k_1} = \frac{27}{4} m (1+m) \frac{(n-m^2)^2}{(n+m)^3} $$

and

$$ v_{dpl}/v_{k_1} = \frac{2}{3} \frac{m}{(1+m)^2} \cdot \frac{(n+m)^2}{m(2-m) - n(1-2m)} $$

So for the case represented on Plate II we find :

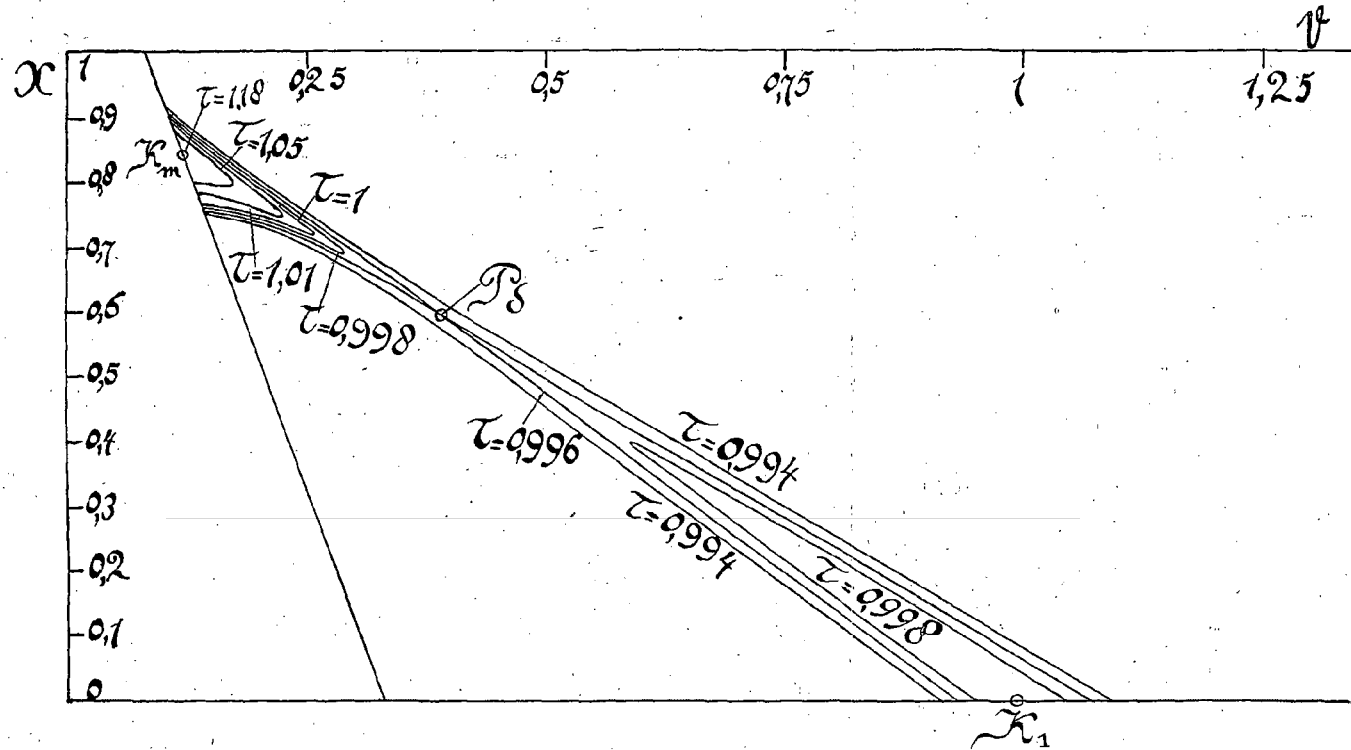$$ x_{dpl} = 0.587, \quad T_{dpl}/T_{k_1} = 0.966, \quad T_{dpl}/T_{k_1} = 2.17. $$

(*To be continued*).

---

[1] Here it appears that a gas-gasplait can occur also if $T_{km} < T_{k_1}$, and for temperatures $T < T_{k_1}$ with $T_{km} > T_{k_1}$, (cf. p. 794 note 1 and p. 794).

(April 25, 1907).

H. KAMERLINGH ONNES and W. H. KEESOM. Contributions to the knowledge of the λ-surface
of VAN DER WAALS. XV. The case that one component is a gas without cohesion with
molecules that have extension. Limited miscibility of two gases.

Plate II.