*Citation:*

H. Kamerlingh Onnes & W.H. Keesom, Contributions to the knowledge of the psi-surface of Van der Waals. XV. The case that one component is a gas without cohesion with molecules which have extension. Limited miscibility of two gases, in:
KNAW, Proceedings, 10 I, 1907, Amsterdam, 1907, pp. 231-237

**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 which have extension. Limited miscibility of two gases.*" (Continuation). 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 May 24, 1907).

§ 8. *On the temperatures and the pressures on the gas-gasplait.* In order to form a provisional opinion as to the experimental conditions which must be satisfied that limited miscibility in the gas state may be observed, and to be able to derive what pairs of substances must be considered suitable for this purpose, it is desirable to examine for some cases what temperatures and pressures occur on the gas-gasplait[1]). In the case (§ 2, March '07) of a component without cohesion[2]) or almost without cohesion ($m < m_1$, see § 7), the gas-gasplait will occur for all temperatures between the critical temperature of the less volatile component and the critical temperature of complete miscibility[3]). Its pressures will then be larger than

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[1]) In our opinion Mr. VAN LAAR (These Proc. May '07, p. 35, note 2) is wrong in thinking that in the case of a three-phase-equilibrium, as e g. in the system water ether, our terminology with regard to the distinction between gas and liquid does not agree with that used by VAN DER WAALS. According to what has been said about this distinction in § 4, for a three phase equilibrium of a system of the type water-ether the denser phase which is rich in water, *must* be called liquid as belonging to the liquid branch of the connode, just as the less dense phase which is rich in ether, *must* be called gas phase; whether the denser phase which is rich in ether is to be called liquid or gas, is not determined by the principle of the continuity of the phase along the connode; if the reduced temperatures at which this phase appears, are taken into account, also the last mentioned phase will be called liquid for the system ether-water in accordance with what has been said in § 4.

[2]) The second branch of the plaitpoint curve in Fig. 1 § 2 (These Proc. March '07, p. 787), about which VAN LAAR speaks in These Proc. May '07, p. 36, has there ($a_{22} = 0$) contracted to a point $x = 1$, $v = b_{22}$. It is true that in the case of our § 7 (Plate II, These Proc. March '07) a second branch of the plaitpoint curve occurs, but it has been explicitly stated there (p. 795 at the bottom and p. 797) that we did not discuss the spinodal curves at the lower temperatures at which this branch of the plaitpoint curve makes its influence felt, referring inter alia with a view to these temperatures to VAN LAAR's papers.

[3]) As mentioned in § 1 this idea was introduced by VAN DER WAALS, who also gave the formulae for the calculation of this temperature (VAN LAAR calls it "third critical temperature").

the critical pressure of the least volatile component. If the suppositions mentioned in § 2 might be applied for this, and the values of $a_M$ and $b_M$ for He might be borrowed from Comm. N°. 96$^c$, Febr.-'07, p. 660 footnote 2, so that $a_{MHe} = {}^1/_{175}\, a_{MH_2} = 0.0000024$ and $b_{MHe} = {}^1/_2\, b_{MH_2} = 0.00044$, this case would be realized for mixtures of He and water [1]). Then we should find $T_{km} = 1.056\, T_{k_1}$, so that the gas-gasplait would occur over a range of temperature of 36° above 365° C., and at pressures above 195 à 200 atms.

In the case that the molecules of the least volatile component act on each other feebly, but still exert such an attraction that a double plaitpoint [2]) occurs in the net of the spinodal curves, the pressure in this plaitpoint and its temperature in connection with the critical temperature of complete miscibility give important indications as to the pressures and temperatures of the gas-gasplait.

In table II these data, calculated for the case that the suppositions

TABLE II.

| Pair of substances | $T_{km}/T_{k_1}$ | $T_{dpl}/T_{k_1}$ | $T_{dpl}/T_{kx}$ | $p_{dpl}\, p_{k_1}$ |
|---|---|---|---|---|
| Hydrogen-helium | 0.933 | 0.915 | 4.44 | 41.6 |
| Oxygen-helium | 0.962 | 0.957 | 8.64 | 61.3 |
| Argon-helium | 0.970 | 0.962 | 7.90 | 64.5 |
| Neon-helium | 1.007 | 0.961 | 3.72 | 18.8 |
| NO-helium | 1.031 | 0.991 | 3.76 | 13.1 |
| $NH_3$-helium | 1.009 | 0.969 | 6.20 | 25.2 |
| $H_2S$-helium | 0.972 | 0.970 | 13.79 | 171 |
| $CO_2$-helium | 0.9540 | 0.9536 | 15.89 | 1045 |

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[1]) The $a_M$ and $b_M$ for water have been borrowed from LANDOLT-BÖRNSTEIN-MEYERHOFFER's Physik. Chem. Tabellen.

[2]) The appearance of a double plaitpoint near $K_m$ was already observed by VAN LAAR (These Proc. May 1905 p. 42). The conditions for its appearance, however, were not correctly defined by him (cf. § 9 II). In view of this latter fact we thought that we drew sufficient attention to this result of VAN LAAR by referring the reader to VAN LAAR's papers. (see p. 797 footnote 1). The detaching of a longitudinal plait at high temperatures, which leaves the $\psi$-surface with its open side turned to $v = b$, follows immediately (see These Proc. April '07 p. 848 footnote) from the general considerations and calculations of VAN DER WAALS Cont. II § 19 sqq. and VAN DER WAALS' diagram in Zittingsverslag Kon. Akad. Nov. 1894 p. 133, when the case *a*) cf. § 9. I, a case which VAN LAAR has not included in his considerations, does not occur.

mentioned in § 2 might be applied, have been given for some helium mixtures. $T_{km}$ has here been calculated according to VAN DER WAALS Cont. II, p. 43 (cf. § 6), $T_{dpl}$ according to the formula mentioned in § 7, $p_{dpl}$ from the equation of state with the just mentioned $T_{dpl}$ and the $v_{dpl}$ also represented in formula in § 7 [1]).

The reduced temperature of the double plaitpoint $T_{dpl}/T_{kx}$, mentioned in this table, gives an idea in how far the phases in its neighbourhood behave as compressed gas-phases.

The values of $a$ and $b$ of the different components have been borrowed from KOHNSTAMM, LANDOLT-BÖRNSTEIN-MEYERHOFFER's Physik. Chem. Tabellen; for those of helium see above; for neon we have made use of the ratio of its refractive power [2]) to that of helium according to the determinations of RAMSAY and TRAVERS [3]), and of the estimation concerning the critical temperature by TRAVERS, SENTER and JAQUEROD [4]).

It appears from table II that when the gas-gasplait can make its appearance, the range of temperature within which this is the case between $T_{km}$ and $T_{dpl}$), on the mentioned suppositions is small for most of these pairs of substances, for some even exceedingly narrow.

For the pressures on the gasplait higher values than $p_{dpl}$ will have

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[1]) Though originally we did not consider the developments which led us to the explicit expressions for the double plaitpoint mentioned These Proc. March '07 pp. 796 and 798 of sufficient importance, now that VAN LAAR (see These Proc. May '07 p. 41) thinks the derivation of such like expressions impossible there is a reason for communicating them on a following occasion.

[2]) HAPPEL, Habilitationsschrift Tübingen 1906, p. 30, found that the refractive power for argon, crypton and xenon would yield values for $b$ which greatly deviate from the $b$'s derived from the critical data. When according to the principle of the corresponding states (cf. HAPPEL loc. cit. p. 31, note 1) we compare the ratios of the refractive powers for these gases with those of their critical volumes (derived from $p_k$ and $T_k$) the deviations are far less considerable. So with regard to this property, these one-atomic gases form a group, just as is the case with the bi-atomic and with a great many more-atomic substances (GUYE, Journ. de phys. (2) 9 (1890) p. 312).

[3]) RAMSAY and TRAVERS, Phil. Trans. A197 (1900) p. 81. Yet we must remark that when comparing this ratio for helium and argon according to RAMSAY and TRAVERS with the ratio of $b_{He}$ according to our estimation and $b_A$ derived from $p_k$ and $T_k$, we should find an important deviation (cf. note 1). Also in view of this the data concerning mixtures of helium and neon are very uncertain.

[4]) TRAVERS, SENTER and JAQUEROD, Phil. Trans. A 200 (1902) p. 177. Their views, however, on a connection between atomic weight and critical temperature lead to an unlikely result for the critical temperature of helium.

The determinations of isotherms of neon by RAMSAY and TRAVERS, loc. cit. have been of as little use to us as those of helium for the determination of $a$ and $b$ (different particulars in the course of the isotherms of the one-atomic gases given by these scientists in plate 2 loc. cit. do not seem very probable to us).

to be expected as a rule. Thus it appears from table II that these pressures become very high, if the circumstances are not very favourable.

It would have a very favourable influence on the circumstances of temperature and pressure at which limited miscibility in the gas state might be observed, if it should prove that for mixtures of helium with another gas $a_{12M}$ is smaller than is expressed by $\sqrt{a_{11M}\,a_{22M}}$[1]).

§ 9. *Mr.* van Laar's *remarks*, (These Proc. May '07 p. 34—46) which imply that we have set forth some of our results as new, whereas they had been already derived and published by him before, compel us to the following explanations in order to show the incorrectness of these assertions.

I. As to part of these observations, they are best refuted by shortly repeating the train of thought followed by us.

When we applied the equations laid down by van der Waals with regard to the spinodal curve[2]) in Cont. II, § 19 sqq., transferred to the $\psi$-surface for the unity of weight, to the case that one of the components is a gas without cohesion[3]) with molecules which have extension, we arrived on the suppositions[4]) mentioned in § 2 at a *plait which starts from the side of the small volumes, comes*

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[1]) These Proc. March '07 p. 796 note 1, and van der Waals These Proc. April '07 p. 831.

[2]) The equation for the spinodal curve of the molecular $\psi$-surface (cf. Van Laar These Proc. May '07 p. 37 at the top) was given by Van der Waals in Cont. II. p. 45, equation (1) in a form which after substitution of $\frac{da}{dx}$, $\frac{db}{dx}$ and $\frac{d^2a}{dx^2}$ passes immediately into that used by van Laar. (See van Laar, These Proc. May '05 p. 33 at the bottom). The equation given by us p. 788 referred to and was derived from the equation for the $\psi$-surface for the unity of weight (These Proc. Dec. '06 p. 510). For the rest we differ from the opinion repeatedly expressed by Van Laar (inter alia These Proc. May '05 p. 34), that it would be more difficult and more elaborate to derive the equation of the spinodal curve and also that of the plaitpoint curve from the $\psi$-function than to do the same from the $\zeta$-function.

[3]) This investigation was announced in Comm. No. 96*b*, Dec. '06 p. 502.

[4]) When we were not allowed to put $\frac{\partial^2 b}{\partial x^2} = 0$ for and in the immediate neighbourhood of $v = b$, as we did (cf. Van der Waals Cont. II p. 42), the spinodal curve will always be closed towards the side $v = b$ as Van der Waals observes l.c. and These Proc. April '07 p. 848. It is then to be expected, at least for small $\frac{\partial^2 b}{\partial x^2}$, that the plait in question makes its appearance for the first time at a maximum plaitpoint temperature, and for the rest extends to the large $v$'s in the same way as the plait described here.

*into contact with the line* $x = 0$ *at a certain temperature, and crosses in a slanting direction from* $v = b$ *to the side* $x = 0$ *at lower temperature* (§ 2 These Proc. March '07 p. 787). Comparison of this result with VAN LAAR's papers induced us then to cite (p. 786 footnote 1) that the latter already treated the projection of the plaitpoint curve on the $v, x$-plane for the case of a gas without cohesion, but without further investigating the shape of the spinodal curve and of the plait for this case. Now that VAN LAAR (These Proc. May '07 p. 35) says: "The case that a plait *starts from* $C_0$[1] *to* $C_2$[2], or also at the same time from $C_2$ to $C_0$ (when there is a minimum temperature in the plaitpoint line) is not new (see KAMERLINGH ONNES and KEESOM, p. 788 below), but has been before described and calculated by me in all particulars", we have once more looked through his papers.

It would have been good if Mr. VAN LAAR had indicated the place where we had to look for this description of the plait treated in § 2 and indicated by VAN LAAR in the italicized words (the italics are ours); we have not been able to find this description in his preceding papers even on this renewed careful perusal[3].

That the shape of the plait described by us occurs for temperatures above the critical temperature of the least volatile component led us to the considerations on limited miscibility in the gas state mentioned in § 3 sqq.

Always availing ourselves of the above mentioned equations of VAN DER WAALS, we examined then if also with $a_{22} > 0$ such a plait may occur for values as they are to be expected for mixtures with helium. We saw in § 7 (These Proc. March '07 p. 795) that for the case of the plaitpoint curve running from $K_1$ to $K_m$ (called type I by VAN LAAR) 3 cases are to be distinguished: *a*) that with falling temperature the plaitpoint gets from $K_m$ on the $\psi$-surface, and proceeds regularly towards $K_1$; *b*) that with falling temperature a plaitpoint coming from $K_m$ and one coming from $K_1$ unite to a double plaitpoint; *c*) that the plaitpoint gets from $K_1$ on the $\psi$-surface and proceeds regularly towards $K_m$ (without double plaitpoint with minimum

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[1] Our $K_m$.

[2] Our $K_1$.

[3] On the contrary he says in his paper These Proc. Sept. 1906 p. 231 (cf. VAN LAAR, These Proc. May 1905, p. 42 at the bottom): ": In former papers it has been demonstrated that in the neighbourhood of $C_0$ a minimum plaitpoint temperature makes its appearance both with type I in the line $C_0C_2$ and with type II in the line $C_0A$, and that therefore with decrease of temperature a *separate plait* begins to detach itself starting from $C_0$ at a definite temperature $T_0$ (the plaitpoint temperature in $C_0$), which plait will merge into the main plait (or its branch plait) later on in an homogeneous double point.

plaitpoint temperature). The conditions for the occurrence of these cases were defined by us by means of the equations (2) and (3) there. From this appeared that with very feeble attraction the case *a*) occurs, with greater attraction the case *b*), whereas with still greater attraction case *c*) occurs (supposing the system to belong to type I).

We have found neither the case *a*) as we already observed above, nor the case *c*) in VAN LAAR. We did find the case *b*), chiefly with regard to the treatment of what takes place at lower temperatures, when three-phase-equilibria occur. For this treatment we referred to VAN LAAR (cf. These Proc. March '07 p. 797).

From the fact that VAN LAAR has declared this shape *b*) to hold universally for type I (cf. p. 235 footnote 3; see also VAN LAAR p. 36) it appears in our opinion, that VAN LAAR has not only left the cases *a*) and *c*) unmentioned, but has decidedly overlooked them. [1])

II. One more remark remains to be discussed. In § 7 we put as the *two* criteria of the case *b*), the course of the plaitpoint curve being from $K_1$ to $K_m$ (see above), in which case a minimum plaitpoint temperature occurs (supposing $b_{22M} < b_{11M}$):

$$\sqrt[4]{a_{22M}/a_{11M}} > \frac{1}{3}\left\{-1+\sqrt{1+3\,b_{22M}/b_{11M}}\right\}$$

and

$$\sqrt[4]{a_{22M}/a_{11M}} < -(1-b_{22M}/b_{11M})+\sqrt{1-b_{22M}/b_{11M}+(b_{22M}/b_{11M})^2}.$$

Mr. VAN LAAR points out (These Proc. May '07, p. 45, appendix), that the first-mentioned condition corresponds with a condition for the occurrence of a minimum plaitpoint temperature, derived by him These Proc. Dec. '05, p. 581 (and VERSCHAFFELT These Proc. March. '06 p. 751). In our opinion, however, Mr. VAN LAAR is mistaken when he thinks that the *one* condition stated by him is sufficient in all cases to decide as to the occurrence of a minimum plaitpoint tem-

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[1]) We might consider the course of the spinodal curves in case *b*), if this is also extended to values of $x > 1$ and $< 0$, and of $v < b$, as a more general case, from which the cases *a*) and *c*) might be obtained, at least qualitatively and when we restrict ourselves to the region of the $\psi$-surface ($1 > x > 0$ and $v < b$) that is of importance for the treatment of mixtures. This might be done by cutting out a region bounded by $x = 0$ and $x = 1$, and a suitable line $v = b$ in the same way as VAN DER WAALS These Proc. Feb. '07, p 621 sqq. treats the course of the isobars (cf. § 7 p. 796 of this Communication). We have not found a single indication that VAN LAAR's description of case *b*) is to be interpreted in this way; from the phrase, quoted p. 235 footnote 3 e.g. we should much sooner conclude to the contrary.

At any rate the distinctions which are of physical importance, have not been made.

perature. Nor can his considerations of Dec. 1905 give an indication to conclude to the occurrence of a minimum plaitpoint temperature in the branch $K_1 K_m$ of the plaitpoint curve. For there VAN LAAR starts from the value of $dT_{xpl}\ dx$ at the critical temperature of the most volatile component called $T_{k_2}$ by us. The condition that at $T_{k_2}$, the *lower* of the critical temperatures of the components, $dT_{xpl} / dx < 0$, implies that *if the plaitpoint curve crosses from* $K_2$ *to* $K_1$, a minimum temperature must occur in it [1]) VAN LAAR (These Proc. May '07 p. 43), considers now the value of $dT_{xpl} / dx$ for the least volatile component (for $K_1$). It is clear in our opinion, that at the *highest* critical temperature the condition $dT_{xpl} / dx < 0$, which coincides with the first of the inequalities mentioned (cf. p. 797 last sentence of the alinea at the top), does not give any indication to conclude to the occurrence of a minimum plaitpoint temperature. That if for $K_1$ $dT_{xpl} / dx < 0$, really *one* of the conditions for the occurrence of a minimum plaitpoint temperature in the branch $K_1 K_m$ of the plaitpoint curve has been fulfilled, VAN LAAR has, in our opinion, only shown by his considerations on the situation of the double plaitpoint, not given until April (translated in These Proc. of May) at the same time with his remarks, which considerations agree with those which had led us a month before to the statement of the two conditions mentioned.

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[1]) Only if the plaitpoint curve crosses from $K_1$ to $K_2$, this condition is sufficient to conclude to the occurrence of the minimum plaitpoint temperature (cf. VAN LAAR p. 46); for if the branch of the plaitpoint curve starting from $K_2$ bends round to VAN LAAR's point $A$ ($x = 1$, $v = b_{22}$ in our notation), we cannot speak of a minimum plaitpoint temperature in the sense which is generally attached to this word.

A similar consideration gave rise to our remark in note 2 p. 795, which remark we are obliged to maintain in spite of Mr. VAN LAAR's contradiction, p 46. (Wrongly Mr. VAN LAAR thinks there, note 1, that in our note instead of "maximum-temp." "minimum-temp." should be read, which might also immediately appear by comparison with the cited text of VERSCHAFFELT).