À more exact method may perhaps give numbers from which a better formula might be deduced, and which at the same time might give us some insight in the phenomenon.

I have tried to get more exact numbers by means of the KUNDT dust-figures but I did not succeed, though others might. Yet the oscillatory discharge of a Leyden jar through an inductive resistance easily gave regular dust-figures. The reason why the KUNDT-method proved refractory with the singing arc, is not easy to be understood: I can only suppose that the intensity of the sound is not large enough.

Physics. — Dr. J. E. VERSCHAFFELT. "*Contributions to the knowledge of* VAN DER WAALS' *ψ-surface. VII. The equation of state and the ψ-surface in the immediate neighbourhood of the critical state for binary mixtures with a small proportion of one of the components*". Communication n°. 81 from the Physical Laboratory at Leiden, by Prof. H. KAMERLINGH ONNES. [1])

(Communicated in the meeting of June 28, 1902).

Introduction.

In Communication n°. 65 from the Physical Laboratory at Leiden [2]) I have given the first results of a treatment of my measurements on mixtures of carbon dioxide and hydrogen [3]) by the method which KAMERLINGH ONNES [4]) alone and with REINGANUM [5]) used for the measurements of KUENEN on mixtures of carbon dioxide and methyl chloride [6]). They confirm KAMERLINGH ONNES' opinion that the isothermals of mixtures of normal substances may be derived, by means of the law of corresponding states, from the general empirical reduced equation of statefor which he has given in communications nrs. 71 [7]) and 74 [8]) a development in series indicated in communication 59a. In this empirical reduced equation of state

$$ \mathfrak{p} = \frac{\mathfrak{A}}{\lambda \mathfrak{v}} + \frac{\mathfrak{B}}{\lambda^2 \mathfrak{v}^2} + \cdots , $$

[1]) The translation of the first and second part of this article are treated as a whole, hence some minor changes in text will be found.

[2]) Arch. Néerl., (2), 5, 644, 1900; Comm. phys. lab. Leiden, n°. 65.

[3]) Thesis for the doctorate, Leiden, 1899.

[4]) Proc. Royal Acad., 29 Sept. 1900, p. 275; Comm. 59a.

[5]) Ibid. p. 289; Comm., n°. 59b.

[6]) Thesis for the doctorate, Leiden, 1892.

[7]) Proc. Royal Acad., June 1901; Comm., n°. 71.

[8]) Arch. Néerl., (2), 6, 874, 1901; Comm., n°. 74.

where $\mathfrak{A}$, $\mathfrak{B}$ etc. represent series of the powers of the reduced absolute temperature t, with co-efficients which like λ are the same for all substances, we then put:

$$t = \frac{T}{T_{xk}}, \qquad \mathfrak{p} = \frac{p}{p_{xk}}, \qquad \mathfrak{v} = \frac{v}{v_{xk}},$$

T_{xk}, p_{xk} and v_{xk} standing for the critical elements of the mixture with molecular composition x, if it remained homogeneous, while

$$\lambda = \frac{p_{xk}\, v_{xk}}{T_{xk}}.$$

It must therefore also be possible to find expressions for the critical quantities of a mixture — these are the elements p_{xpl}, v_{xpl}, T_{xpl} of the plaitpoint and p_{xr}, v_{xr}, T_{xr} of the critical point of contact — in which only the co-efficients of the general empirical reduced equation of state and further the quantities characteristic of the mixture viz. T_{xk}, p_{xk}, v_{xk}, occur, or the co-efficients of the developments in series of these quantities in powers of x. In the case of mixtures with small values of x, it may, exclusive of exceptional cases, suffice, to a first approximation, to introduce the co-efficients:

$$\alpha = \frac{1}{T_k} \frac{dT_{xk}}{dx} \text{ and } \beta = \frac{1}{p_k} \frac{dp_{xk}}{dx}.$$

A first step towards realizing this idea of KAMERLINGH ONNES has been made by KEESOM [1]) who took for his basis the general equations by which VAN DER WAALS in his Théorie moleculaire and following papers has expressed the relation of the critical quantities and the composition; he has found what these equations would become for infinitely small x-values and has introduced into them the co-efficients α and β mentioned above, besides others which might be derived from the co-efficients of the general empirical equation of state. I have now tried to work out this idea in a method which is more closely connected to the treatment of the ψ-surface, namely by developing the co-efficients of the equation of state and the equation of the ψ-surface in the powers of x. On account of the great complication involved by the introduction of the higher co-efficients into the calculation, I have confined myself to the lower powers of x. However, the method followed by me can also be used to find the co-efficients of higher powers.

As I have confined myself to states in the neighbourhood of the critical point I could use instead of KAMERLINGH ONNES' empirical reduced equation of state the more simple one which it becomes within narrow limits of temperature and volume on developing the different

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[1]) Proc. Royal. Acad., 28 Dec. 1901, p. 293; Comm., n°. 75.

terms in powers of the small quantities $\mathfrak{v}-1$ and $t-1$. According to VAN DER WAALS' method [1] I wrote this new equation:

$$\mathfrak{p} = 1 + \frac{\partial\mathfrak{p}}{\partial t}(t-1) + \ldots\ldots \qquad + \frac{\partial^2\mathfrak{p}}{\partial_{\mathfrak{v}}\partial t}(\mathfrak{v}-1)(t-1) + \ldots \quad (1)$$

where the co-efficients $\dfrac{\partial\mathfrak{p}}{\partial t}, \dfrac{\partial^2\mathfrak{p}}{\partial\mathfrak{v}\partial t}$ etc. can be immediately derived from those of the above mentioned empirical reduced equation of state.

1. *The p, v, T diagram for a simple substance in the neighbourhood of the critical point.*

In order to limit the number of the continually re-occurring factors as much as possible, I shall not write the equation of state of the pure substance in a reduced form, but thus:

$$p = k_0 + k_1(v-v_k) + k_2(v-v_k)^2 + k_3(v-v_k)^3 + \ldots = f(v). \quad (2)$$

where k_0, k_1, k_2 etc. are temperature functions which can be developed in powers of $T-T_k$; as for instance:

$$k_0 = k_{00} + k_{01}(T-T_k) + k_{02}(T-T_k)^2 + \ldots \quad (2')$$

and it is evident that $k_{00} = p_k$ while k_{10} and k_{20} are zero.

We might clearly find the equations of several curves in this diagram, such as: the border curve, the curve of the maximum or minimum pressures, the curve of the points of inflection etc. I shall derive the former only, chiefly in order to apply to a simple case the method of calculation to be used afterwards for finding the pressure, volume and composition of the co-existing phases with mixtures.

If v_2 and v_1 represent the molecular volumes of the vapour and of the liquid, co-existing at the temperature T under the pressure p_1, then these 3 unknown quantities will be determined by the equations:

$$p_1 = f(v_1), \qquad p_1 = f(v_2) \quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot \quad (3)$$

and by MAXWELL's criterium

$$p_1(v_2-v_1) = \int_{v_1}^{v_2} p\, dv. \quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot \quad (4)$$

The two unknown quantities v_2 and v_1 I shall, however, replace by the two infinitely small quantities $\frac{1}{2}(v_2+v_1) - v_k = \Phi$ and $\frac{1}{2}(v_2-v_1) = \varphi$; Φ is therefore the abscissa of the diameter of the border curve for chords parallel with the v-axis, and φ is the half chord.

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[1] Zeitschr. f. physik. Chem., **13**, 694, 1894.

Equation (4) after division by 2 φ yields:

$$p_1 = k_0 + k_1\ \varPhi + k_2(\varPhi^2 + \tfrac{1}{3}\varphi^2) + k_3\ \varPhi(\varPhi^2 + \varphi^2) + k_4(\varPhi^4 + 2\varPhi^2\varphi^2 + \tfrac{1}{5}\varphi^4) + \ldots (5)$$

where for completeness I have not regarded the order of the different terms. Also taking equation (3) once for v_1 and once for v_2 and adding together, yields

$$p_1 = k_0 + k_1\varPhi + k_2(\varPhi^2 + \varphi^2) + k_3\varPhi(\varPhi^2 + 3\varphi^2) + k_4(\varPhi^4 + 6\varPhi^2\varphi^2 + \varphi^4) + \ldots (6)$$

and subtracting and dividing bij 2 φ gives

$$0 = k_1 + 2k_2\varPhi + k_3(3\varPhi^2 + \varphi^2) + 4 k_4\varPhi(\varPhi^2 + \varphi^2) + \quad . \quad . \quad . \quad (7)$$

while the, at least to a first approximation simpler equation:

$$0 = \tfrac{2}{3}k_2 + 2k_3\varPhi + 4k_4\left(\varPhi^2 + \tfrac{1}{5}\varphi^2\right) + \quad . \quad . \quad . \quad . \quad (8)$$

follows from (5) and (6).

The equations (6), (7) and (8) now determine the quantities $\varPhi$, φ and $p_1 - p_k$, for we find·

$$\varphi^2 = -\frac{k_{11}}{k_{30}}(T - T_k) - \quad . \quad . \quad . \quad . \quad . \quad (9)$$

$$\varPhi = -\frac{1}{k_{30}}\left(\frac{1}{3}k_{21} - \frac{2}{5}\frac{k_{11}\,k_{40}}{k_{30}}\right)(T - T_k) - {}^1) \quad . \quad . \quad (10)$$

$$p_1 - p_k = k_{01}(T - T_k) + \quad . \quad . \quad . \quad . \quad . \quad (11)$$

Along the border curve $v = v_k + \varPhi \pm \varphi$, so that we may write the equation of the border curve:

$$0 = (v - v_k)^2 - 2(v - v_k)\ \varPhi + \varPhi^2 - \varphi^2, \quad . \quad . \quad . \quad (12)$$

and to the first approximation this represents a parabola ²).

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¹) Just as v. D. WAALS (Arch. Néerl. (1), 28, 171) from the reduced equation of state $p = \dfrac{8\,t}{3\,v - 1} - \dfrac{3\,e^{1-t}}{v^2}$ has derived $\tfrac{1}{2}(v_2 - v_1) = 2\sqrt{2}\,(1 - t)$, I have also derived $\tfrac{1}{2}(v_2 + v_1)$ from the same equation by means of the reduced formula (10) and have found for it:

$$\tfrac{1}{2}(v_2 + v_1) = 1 + 7{,}2\,(1 - t),$$

whence, if ρ_1 and ρ_2 stand for the liquid and vapour densities :

$$\tfrac{1}{2}(\rho_2 + \rho_1) = \rho_k\,[1 + 0{,}8\,(1 - t)]$$

From AMAGAT's data for carbon dioxide I find·

$$\Delta = \tfrac{1}{2}(\rho_2 + \rho_1) = 0{,}464 + 0{,}001181\,(T_k - T),$$

or reduced $1 + 0{,}775\,(1 - t)$, and for isopentane (S. YOUNG's data)

$$\Delta = \rho_k\,[1 + 0{,}881\,(1 - t)].$$

The above equation of state, therefore, represents the diameter numerically in a satisfactory manner.

²) The same problem with regard to φ has been treated by v. D. WAALS (loc. cit.) in a somewhat different way; only φ is determined accurately by his method and the border curve can be derived from his formulae only to a first approximation.

2. *The p, v, T diagram of a mixture with a small value of x near the critical point of the homogeneous mixture.*

From the consideration we have started from it follows immediately that we obtain the system of isothermals of the mixture by moving that of the pure substance to an infinitely small amount parallel to itself so that the critical point (p_k, v_k) is brought on to the critical point of the homogeneous mixture (p_{xk}, v_{xk}), and at the same time by expanding it infinitely little parallel to its co-ordinates in multiplying the ordinates by $\dfrac{p_{xk}}{p_k}$ and the abscissae by $\dfrac{v_{xk}}{v_k}$. Moreover an isothermal, belonging to the temperature T in the first system will belong to the temperature $\dfrac{T_{xk}}{T_k} T$ after we have moved and magnified the system.

We put again:

$$p = l_0 + l_1 (v - v_{xk}) + l_2 (v - v_{xk})^2 + l_3 (v - v_{xk})^3 + \quad . \quad . \quad (13)$$

where l_0, l_1, l_2 etc. are once more functions of the temperature, thus:

$$l_0 = l_{00} + l_{01} (T - T_{xk}) + l_{02} (T - T_{xk})^2 + \ . \ . \ . \ . \ . \ (13')$$

According to the derivation from the reduced equation of state by means of T_{xk}, p_{xk}, v_{xk} the co-efficients l_{00}, $l_{01} \ldots l_{10}$, l_{11} etc. are only functions of x. Putting:

$$T_{xk} = T_k (1 + \alpha x + \alpha' x^2 + \ldots .)$$
$$p_{xk} = p_k (1 + \beta x + \beta' x^2 + \ldots .) \ . \ . \ . \ . \ . \ (14)$$
$$v_{xk} = v_k (1 + \gamma x + \gamma' x^2 + \ldots .)$$

where

$$\gamma = \alpha - \beta, \quad \gamma' = \alpha' - \beta' - \alpha\beta + \beta^2 \text{ etc.,} \quad . \quad . \quad . \quad (14')$$

we find

$$l_{00} = p_k[1 + \beta x + \ldots], \ l_{01} = k_{01}[1 - (\alpha - \beta)x + \ldots], \ l_{02} = k_{02}[1 - (2\alpha - \beta)x + \ldots], \ldots$$
$$l_{10} = 0 \qquad\qquad , \ l_{11} = k_{11}[1 - 2(\alpha - \beta)x + \ldots], \ l_{12} = k_{12}[1 - (3\alpha - 2\beta)x + \ldots], \ldots$$
$$l_{20} = 0 \qquad\qquad , \ l_{21} = k_{21}[1 - 3(\alpha - \beta)x + \ldots], \ldots$$
$$l_{30} = k_{30}[1 - (3\alpha - 4\beta)x + \ldots], \ldots$$
$$l_{40} = k_{40}[1 - (4\alpha - 5\beta)x + \ldots], \ldots ; \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

where all co-efficients l are expressed in co-efficients k as well as in KAMERLINGH ONNES' α's and β's.

From the values of T_{xk}, p_{xk}, v_{ok}, with mixtures of carbon dioxide with small quantities of hydrogen for $x = 0$, $x = 0,05$ and $x = 0,1$, [1] I find:

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[1] Comm., n⁰. 65.

$$T_{xk} = T_k \left(1 - 1{,}17\, x + 1{,}58\, x^2\right)$$
$$p_{xk} = p_k \left(1 - 1{,}62\, x + 2{,}45\, x^2\right) \quad . \quad . \quad . \quad . \quad (16)$$
$$v_{xk} = v_k \left(1 + 0{,}62\, x - 0{,}95\, x^2\right), \; [1)]$$

while from (14') would follow:

$$v_{xk} = v_k \left(1 + 0{,}45\, x + 0{,}08\, x^2\right).$$

Although the agreement between the two expressions for v_{xk} is not quite satisfactory, it yet by no means indicates that the law of corresponding states does not hold; it may very well be a result of the uncertainty of the critical data of the homogeneous mixtures, chiefly of the v_{xk}'s. Besides from the second formula for v_{xk} I find:

for $x = 0{,}05$ $v_{xk} = 0{,}00432$ and for $x = 0{,}1$ $v_{xk} = 0{,}00441$, and these values deviate from those determined directly ($0{,}00434$ and $0{,}00444$) not more than the amount of the error that can be made in these determinations. Besides, since the law of corresponding states does not hold entirely with pure substances, it is not likely to do so for mixtures.

3. *The p, v, x, diagram for mixtures with a small value of x, at a temperature differing little from T_k.*

We shall now consider different mixtures at the same temperature T; the system of isothermals in the p, v, x diagram, at that temperature is represented by the equation of state (13), where, however, T must now be taken as constant and x as variable. We will now put this equation in another and more suitable form.

Among all the mixtures there is one for which the critical temperature would be T if this mixture remained homogeneous; the composition x_{Tk} of this mixture, and also the critical elements p_{Tk} and v_{Tk} are determined by equation (14). (In this equation we must put· $T_{xk} = T$, $x = x_{Tk}$, $p_{xk} = p_{Tk}$ and $v_{xk} = v_{Tk}$).
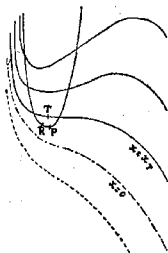
Hence we find to a first approximation

$$x_{Tk} = \frac{T - T_k}{\alpha\, T_k}, \quad p_{Tk} = p_k + \frac{p_k \beta}{\alpha\, T_k}(T - T_k), \quad v_{Tk} = v_k + \frac{v_k(\alpha - \beta)}{\alpha\, T_k}(T - T_k). \, (17)$$
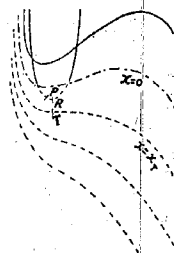
It will be seen that to a first approximation the value x_{Tk} is either positive or negative according as $T - T_k$ and α have the same or opposite signs, that is to say

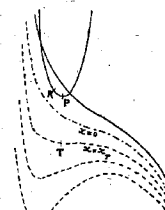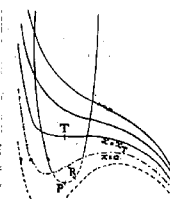|	$\alpha > 0$	$\alpha < 0$
$T > T_k$	$x_{Tk} > 0$; figs. 1 and 7	$x_{Tk} < 0$, figs. 3, 5, 9 and 11
$T < T_k$	$x_{Tk} < 0$; figs. 2 and 8	$x_{Tk} > 0$; figs. 4, 6, 10 and 12

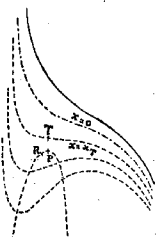[2)] Comp. also KEESOM, *loc. cit.*, p. 12.

$m_{01} > 0 \quad > 0, \; RT^2_k\, k_{11}\, a < m^2_{01}. \; T > T_l.$

Fig. 1.

$m_{01} > 0, \; a > 0, \; RT^2_k\, k_{11}\, a < m^2_{01}, \; T < T_k.$

Fig. 2.

$m_{01} > 0, \; a < 0, \; RT^2_k\, k_{11}\, a < m^2_{01}, \; T > T_k.$

Fig. 3.

$m_{01} > 0, \; a < 0, \; RT^2_k\, k_{11}\, a < m^2_{01}, \; T < T_l.$
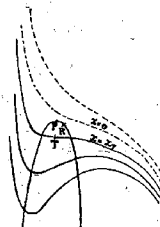
Fig. 4.

$m_{01} > 0, \; a < 0, \; RT^2_k\, k_{11}\, a > m^2_{01}, \; T > T_l.$

Fig. 5.

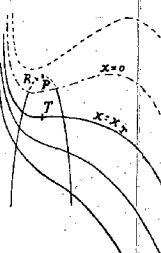$m_{01} > 0, \; a < 0, \; RT^2_k\, k_{11}\, a > m^2_{01}, \; T < T_k.$

Fig. 6.

$m_{01} < 0, \; a > 0, \; RT^2_k\, k_{11}\, a < m^2_{01}, \; T > T_k.$

Fig. 7.

$m_{01} < 0, \; a > 0, \; RT^2_k\, k_{11}\, a < m^2_{01}, \; T < T_l.$

Fig. 8.

$m_{01} < 0, \; a < 0, \; RT^2_k\, k_{11}\, a < m^2_{01}, \; T > T_k.$

Fig. 9.

$m_{01} < 0, \; a < 0, \; RT^2_k\, k_{11}\, a < m^2_{01}, \; T < T_k.$
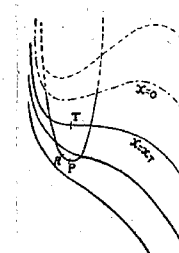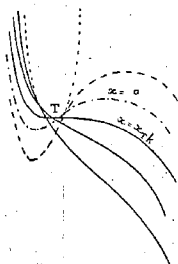
Fig. 10.

$m_{01} < 0, \; a < 0, \; RT^2_k\, k_{11}\, a > m^2_{01}, \; T > T_k.$

Fig. 11.

$m_{01} < 0, \; a < 0, \; RT^2_k\, k_{11}\, a > m^2_{01}, \; T < T_k.$
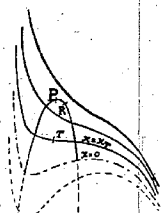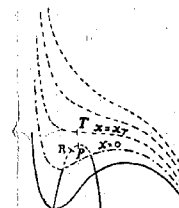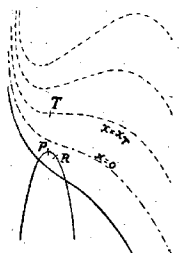
Fig. 12.

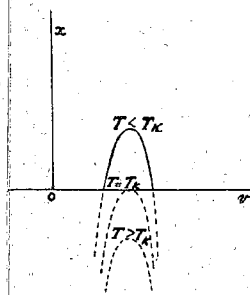$m_{01} = 0, \; a < 0, \; T < T_k, \; m_{01} < 0.$
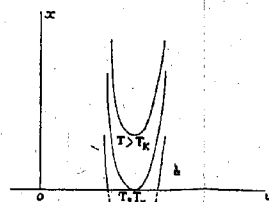
Fig. 13.

Fig. 14.

Fig. 15.

Although from a physical point of view x can only take positive values, in these considerations even the case $x_{Tk} < 0$ is not impossible; for the point p_{Tk}, v_{Tk} has only a mathematical meaning.

In general, equation (13) may now be written thus:

$$p = m_0 + m_1 (v - v_{Tk}) + m_2 (v - v_{Tk})^2 + m_3 (v - v_{Tk})^3 + \ldots, \quad . \quad (18)$$

where m_0, m_1 etc. are functions of x which can be developed in powers of $x - x_{Tk}$; for instance:

$$m_0 = m_{00} + m_{01} (x - x_{Tk}) + m_{02} (x - x_{Tk})^2 + \ldots \quad . \quad . \quad (18')$$

The co-efficients m are functions of the temperature which is here considered constant; it will be obvious that $m_{00} = p_{Tk}$, while m_{10} and $m_{20} = 0$. By equalization of (18) with (13) we can express all the m's in the k's, and in KAMERLINGH ONNES' α's and β's; for we find:

$$m_{n0} = k_{n0} - \frac{k_{n0}}{T_k \alpha} [n\alpha - (n + 1) \beta] (T - T_k) + \ldots .$$

$$m_{n1} = - k_{n0} [n\alpha - (n + 1)\beta] - k_{n1} T_k \alpha - (n + 1) k_{(n+1)0} (\alpha - \beta) v_k + \ldots, \text{etc. (19)}$$

so that to a first approximation:

$$m_{30} = k_{30}, \quad m_{40} = k_{40}, \ldots .$$

$$m_{01} = p_k \beta - k_{01} T_k \alpha, \quad m_{11} = - k_{11} T_k \alpha, \quad m_{21} = - k_{21} T_k \alpha - 3 k_{30} v_k (\alpha - \beta), \text{etc. (19')}$$

HARTMAN [1]) has given a diagrammatical representation of the p, v, x diagram. This representation completely resembles a p, v, T diagram; but this resemblance is not necessary. It follows directly from the p, v, T diagram that k_{01} is positive, while k_{11} and k_{30} are negative; in the p, v, x diagram m_{30} is negative, but according to (19), m_{01} and m_{11} may be either positive or negative. The circumstance $m_{01} < 0$ does not indeed influence the general shape of the diagram; it indicates that the isothermals of the mixtures lie below those of the pure substance as is the case at the upper limit ($x = 1$) of HARTMAN's representation [2]). But while in the p, v, T diagram the isothermals with maximum and minimum pressure occur under the critical, the opposite may be the case in the p, v, x diagram, if m_{01} and m_{11} have the same sign. The four cases which may now present themselves, leaving out very particular values of the coefficients, are given in the following table:

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[1]) Thesis for the doctorate, Leiden 1899, p. 6; Journ. of Phys. Chem., 5, 425, 1901.

[2]) From a mathematical point of view we may imagine the p, v, x diagram to be continued outside the limits $x = 0$ and $x = 1$. It is also obvious that x, if differing little from 1, means the same as x infinitely small and that $x > 1$ means the same as $x < 0$.

22

	$m_{01} > 0$ or $\dfrac{\beta}{\alpha} > \dfrac{T_k}{pk} k_{01}$	$m_{01} < 0$ or $\dfrac{\beta}{\alpha} < \dfrac{T_k}{pk} k_{01}$
$m_{11} > 0$ or $\alpha > 0$	figs. 1 and 2 [1])	figs. 7 and 8
$m_{11} < 0$ or $\alpha < 0$	figs. 3, 4, 5 and 6	figs. 9, 10, 11 and 12.

HARTMAN's diagram represents at the lower limit the case $m_{01} > 0$ and $m_{11} < 0$, at the superior $m_{01} < 0$ and $m_{11} > 0$. The case $\alpha > 0$ will in general occur when the second is less volatile than the first substance; this for instance is the case when methyl chloride is added to carbon dioxide [2]). On the other hand we shall find the case $\alpha < 0$ when the second substance is the more volatile, when for instance hydrogen is added to carbon dioxide (comp. formulae 16) or carbon dioxide to methyl chloride [3]).

A p, v, x diagram based on observations has, so far as 1 know, not yet been published. A diagram of this kind which I have drawn from my measurements on mixtures of carbon dioxide and hydrogen perfectly resembles the p, v, T diagram after HARTMAN, so that in the neighbourhood of pure carbon dioxide we must have $m_{01} > 0$ and $m_{11} < 0$; according to formula (16) α is really negative, while with $k_{01} = 1,61$ (comp. KEESOM *loc. cit.*, p. 14) I find $m_{01} = 454$, and positive. For carbon dioxide with a small quantity of methyl chloride [4]) $\alpha = 0,378$ and $\beta = 0,088$, and hence $m_{01} < 0$ and $m_{11} > 0$; and for methyl chloride with a small quantity of carbon dioxide, $\alpha = -0,221$ and $\beta = 0,281$ so that $m_{01} > 0$ and $m_{11} < 0$. At temperatures between the critical temperatures of the two pure substances, the p, v, x diagram for mixtures of carbon dioxide and methyl chloride will probably correspond to HARTMAN's drawing.

While two neighbouring isothermals $(T, T + dT)$ never intersect in the p, v, T diagram (the $\left(\dfrac{\partial p}{\partial T}\right)_v$ never being zero) this may be the case in the p, v, x diagram for two neighbouring mixtures

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[1]) Figs. 1—13 represent diagrammatically p, v, x curves for infinitely small values of x and $T-T_k$, such as they appear in reality for finite values of x and $T-T_k$. They are moreover theoretically extended into the imaginary region $x < 0$. All lines lying within the region of negative x are dotted; the isothermal $x = 0$ is represented by a dot-dash line. The line $x = x_{Tk}$ (erroneously marked x_r in figs. 1—12) would be the critical isotherm of the homogeneous mixture.

[2]) Comp. KAMERLINGH ONNES and REINGANUM, *loc. cit.*, p. 35.

[3]) *Ibidem.*

[4]) Comp. KEESOM, Comm. n⁰. 79, p. 8.

(v and $x + dx$). If this point of intersection is situated at a finite distance from the point p_{Tk}, v_{Tk}, it lies outside the limits we are considering; but if it lies infinitely near this point, then it practically co-incides with it; then $m_{01} = 0$ and all the isothermals in the neighbourhood will intersect each other approximately at the point p_{Tk}, v_{Tk}. This case is shown in fig. 13, where I have also supposed $\alpha < 0$ and $T < T_k$. The isothermals intersect in pairs, and the curve formed by all the points of intersection of two consecutive isothermals, also passes through the critical point (p_{Tk}, v_{Tk}); this is represented in fig. 13. The connecting line of the points of contact envelops the isothermals; its equation is found by eliminating x from equation (18) and from $\dfrac{\partial p}{\partial x} = 0$, where we also put $m_{01} = 0$; hence we find to the first approximation :

$$p - p_{Tk} = -\frac{1}{4} \frac{m^2_{11}}{m_{02}} (v - v_{Tk})^2.$$

This parabola is turned upwards (as in fig. 13) if m_{02} is negative.

4. The ψ-surface.

In order to find from equation (18) the phases co-existing at the temperature T, I shall make use of the properties of the ψ-surface of van der Waals. The equation of that surface is:

$$\psi = -\int p dv + RT\left[x \log x + (1-x) \log (1-x) \right],$$

where R is the gas constant for a gramme molecule, hence the same quantity for all substances. Neglecting the linear functions of x, we may write:

$$\psi = - m_0 (v - v_{Tk}) - \frac{1}{2} m_1 (v - v_{Tk})^2 - \frac{1}{3} m_2 (v - v_{Tk})^3 - \frac{1}{4} m_3 (v - v_{Tk})^4 + \ldots$$

$$+ RT\left[x \log x + \frac{1}{2} x^2 + \frac{1}{6} x^3 + \ldots \right] \quad . \quad . \quad , \quad . \quad . \quad . \quad . \quad . \quad . \quad (20)$$

5. The co-existing phases.

The co-existing phases are now determined by the co-existence conditions :

$$\left(\frac{\partial \psi}{\partial v}\right)_2 = \left(\frac{\partial \psi}{\partial v}\right)_1 , \quad \left(\frac{\partial \psi}{\partial x}\right)_2 = \left(\frac{\partial \psi}{\partial x}\right)_1 \quad \text{and} \quad \mu_2 = \mu_1 , \quad . \quad (21)$$

if μ represents the thermodynamic potential :

$$\mu = \psi - v \frac{\partial \psi}{\partial v} - x \frac{\partial \psi}{\partial x} .$$

22*

ead of the third condition I find it however better to use an-
which follows from all three, viz.

$$M_2 = M_1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (21')$$

$$M = \psi - (v - v_{Tk}) \frac{\partial \psi}{\partial v} - (x - x_{Tk}) \frac{\partial \psi}{\partial x} .$$

responding to a former transformation now I write

$$\tfrac{1}{2}(v_2 + v_1) - v_{Tk} = \Phi \quad \text{and} \quad \tfrac{1}{2}(v_2 - v_1) = \varphi$$

ually

$$\tfrac{1}{2}(x_2 + x_1) - x_{Tk} = \Xi \quad \text{and} \quad \tfrac{1}{2}(x_2 - x_1) = \xi,$$

consider the infinitely small quantities Φ, φ, Ξ and ξ as func-
of the same variable, viz. $p_1 - p_{Tk}$. Thus I find to the first
imation [1])

$$- \frac{1}{2m_{30}} \left[\frac{1}{3} \frac{m^3_{01}}{R^2 T^2} + \frac{m_{01} m_{11}}{RT} + \frac{2}{3} m_{21} - \frac{4}{5} \frac{m_{40}}{m_{30}} \left(\frac{m^2_{01}}{RT} + m_{11} \right) \right] \frac{p_1 - p_{Tk}}{m_{01}}$$
$$- \frac{m_{01}}{2RT m_{30}} \left[\frac{1}{3} \frac{m^2_{01}}{RT} + m_{11} - \frac{4}{5} \frac{m_{01} m_{40}}{m_{30}} \right] x_{Tk} \quad . \quad . \quad . \quad (22)$$

$$\varphi^2 = -\frac{1}{m_{30}} \left[\frac{m^2_{01}}{RT} + m_{11} \right] \frac{p_1 - p_{Tk}}{m_{01}} - \frac{m^2_{01}}{RT m_{30}} x_{Tk}, \quad . \quad . \quad (23)$$

$$\Xi = \frac{p_1 - p_{Tk}}{m_{01}}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (24)$$

$$\xi = \frac{m_{01}}{RT} \varphi \left[\frac{p_1 - p_{Tk}}{m_{01}} + x_{Tk} \right]; \quad . \quad . \quad . \quad . \quad (25)$$

v_{Tk} and p_{Tk} may be replaced by their expression (17).

6. *The plaitpoint.*

ie plaitpoint the co-existing phases become identical. If we
it the elements of the plaitpoint by x_{Tpl}, p_{Tpl} and v_{Tpl} then

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four equations from which I derive the relations (22)—(25) are :

$$= \left(\frac{\partial \psi}{\partial x} \right)_1, \ M_2 = M_1, \ \left(\frac{\partial \psi}{\partial v} \right)_2 = \left(\frac{\partial \psi}{\partial v} \right)_1, \ \text{and} \ p_1 \doteq -\tfrac{1}{2} \left[\left(\frac{\partial \psi}{\partial v} \right)_2 + \left(\frac{\partial \psi}{\partial v} \right)_1 \right]$$

first equations contain the expression $log \frac{x_2}{x_1}$; as all the other terms are

small, this must also be the case with $log \frac{x_2}{x_1}$, in other words, the ratio $\frac{x_2}{x_1}$

only infinitely little from 1 ; ξ must therefore be of a higher order than Ξ,

so $log \frac{x_2}{x_1}$ may be developed in a series in powers of $\dfrac{\xi}{\Xi + x_{Tk}}$.

at that point $\psi = r_{Tpl} - v_{Tk}$, $\varphi = 0$, $\Xi = x_{Tpl} - x_{Tk}$ and $\xi = 0$, while $p_1 = p_{Tpl}$; thus we obtain, from the equations (22), (23) and (24),

$$x_{Tpl} = \frac{RTm_{11}}{m^2{}_{01} + RTm_{11}} x_{Tk}, \quad \ldots \quad \ldots \quad (26)$$

$$p_{Tpl} = p_{Tk} - \frac{m^3{}_{01}}{m^2{}_{01} + RTm_{11}} x_{Tk}, \quad \ldots \quad (27)$$

and

$$v_{Tpl} = v_{Tk} + \frac{m_{01}}{2m_{30}(m^2{}_{01} + RTm_{11})} \left[\frac{2}{3} m_{01}m_{21} - \frac{1}{3} \frac{m^2{}_{01}m_{11}}{RT} - m^2{}_{11} \right] x_{Tk} \text{ [1]}(28)$$

If x_{Tk}, p_{Tk}, and v_{Tk} are replaced by their expressions (17), the elements of the plaitpoint are thereby determined to the first approximation as functions of the temperature T, RTm_{11} may then be replaced by $RT_k m_{11}$.

From equations (26) and (27) follows immediately:

$$\frac{p_{Tpl} - p_{Tk}}{x_{Tpl} - x_{Tk}} = m_{01} \quad \ldots \quad , \quad \ldots \quad \ldots \quad (29)$$

In order to see how this relation holds for mixtures of carbon dioxide and hydrogen I consider the temperature 27,10° C. at which the mixture $x = 0,05$ has its plaitpoint $(p_{Tpl} = 91,85 \text{ atm.})$, at that temperature $x_{Tk} = 0,011$ and $p_{Tk} = 72,4$ atm. so that $\dfrac{p_{Tpl} - p_{Tk}}{x_{Tpl} - x_{Tk}} = 500$, in good agreement with the value 454 which I have found for m_{01}.

It follows from equation (26) that x_{Tpl} can be positive or negative. As $x_{Tk} < 0$ is not impossible, this is equally the case with x_{Tpl}. It is true that from a purely physical point of view the ψ-surface, only exists between the limits $x = 0$ and $x = 1$ (in our case $x > 0$), but from a mathematical point of view we can imagine this surface to extend also beyond those limits [2]. If we consider a temperature lying above the critical temperatures of the two components of a mixture, then there are, exceptional cases excluded (HARTMAN's 3d type), no co-existing phases, that is to say the real ψ-surface does not show a plait, although formula 26 shows that there is a plait-

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[1] If we take the value of x_{Tk} from the equation (26), insert it in (27) and (28), and finally introduce the k's, α's and β's, the formulae (27) and (28) become KEESOM's formulae (2b) and (2c) (Comm. n°. 75), while (26) corresponds to KEESOM's formula (2a).

[2] Outside the limits $x = 0$ and $x = 1$ ψ is imaginary owing to the presence of terms with $log\ x$ and $log\ (1-x)$. Although this is the case the co-existing phases beyond those limits are real, as the co-existence conditions contain the necessarily real expressions $log\ \dfrac{x_2}{x_1}$ and $log\ \dfrac{1-v_2}{1-x_1}$.

point on the imaginary part of it. If the temperature is lower than the critical temperatures of the two components the plait occurs between the limits $x = 0$ and $x = 1$, but, except for mixtures of the second type, according to formula 26 the plaitpoint lies outside these limits. Hence the case is physically not without significance, but the plaitpoint cannot be observed.

Equation (26) may be written:

$$x_{Tpl} = \frac{RT_k \, k_{11}}{RT^2_k \, k_{11}a - m^2_{01}} \, (T - T_k) , \quad \cdots \quad (26')$$

and this form shows that x_{Tpl} will be positive or negative as $T - T_k$ and $RT^2_k \, k_{11}a - m^2_{01}$ have different or the same signs. $RT^2_k \, k_{11}a > m^2_{01}$ is only possible if $a < 0$; $RT^2_k \, k_{11}a < m^2_{01}$ will always be the case if $a > 0$, but may occur with $a < 0$. The different cases that may occur are shown in the following table.

	$RT^2_k \, k_{11} \, a > m^2_{01}$	$RT^2_k \, k_{11} \, a < m^2_{01}$	
		$a > 0$	$a < 0$
$T > T_k$	$0 > x_{Tk} > x_{Tpl}$ figs. 5 and 11	$x_{Tk} > x_{Tpl} > 0$ figs. 1 and 7	$x_{Tpl} > 0 > x_{Tk}$ figs. 3 and 9
$T < T_k$	$x_{Tpl} > x_{Tk} > 0$ figs. 6 and 12	$0 > x_{Tpl} > x_{Tk}$ figs. 2 and 8	$x_{Tk} > 0 > x_{Tpl}$ figs. 4 and 10

7. *The border curve in the p, v, x diagram at the temperature T.*

Along the border curve $v = v_{Tk} + \Phi \pm \varphi$, so that the equation of the border curve may be written

$$0 = (v - v_{Tk})^2 - 2 \, \Phi \, (v - v_{Tk}) + \Phi^2 - \varphi^2 \quad \cdots \quad (30)$$

where Φ and φ must be replaced by the expressions as functions of p_1. To the first approximation we can take therefor the expressions (22) and (23) and neglect Φ^2; the equation (30) then represents a parabola of the second degree. The apex of this parabola does not, as in the $p, v,$ diagram of a simple substance co-incide with the critical point (p_{Tk}, v_{Tk}), but with the plaitpoint.

Along that parabola

$$\frac{d^2p}{dv^2} = -\frac{2 \, m_{01} \, m_{30} RT_k}{m^2_{01} + RT_k m_{11}} = \frac{2 \, m_{01} \, k_{30} \, RT_k}{RT^2_k \, k_{11}a - m^2_{01}} \quad \cdots \quad (31)$$

This expression is either positive or negative; that is to say that the border curve may be turned with its convex side towards the v-axis, while in the p, v, diagram for a simple substance the border curve is always concave to the v-axis. $\dfrac{d^2p}{dv^2}$ will be positive if m and $RT^2_k k_{11} \alpha - m^2{}_{01}$ have different signs, and will be negative in the other case :

	$RT^2_k\, k_{11}\, \alpha > m^2{}_{01}$	$RT^2_k\, k_{11}\, \alpha < m^2{}_{01}$
$m > 0$	figs. 5 and 6	figs. 1—4
$m_{01} < 0$	figs. 11 and 12	figs. 7—10

8. *The projection of the connodal line on the x, v plane.*

The equation of this curve has been given by KORTEWEG [1]). In connection with our preceding formulae it is most easily derived from equation (30) by expressing p in terms of x and v by means of the equation of state (18). I shall now bring it in a form analogous to (30).

The border curve intersects the isothermal of the mixture x at two points (p'_1, v'_1), and (p'_2, v'_2) which indicate the phases where the condensation begins and ends. I again make :

$$\tfrac{1}{2}(v'_2 + v'_1) - v_{Tk} = \Phi', \quad \tfrac{1}{2}(v'_2 - v'_1) = \varphi'$$
$$\tfrac{1}{2}(p'_2 + p'_1) - p_{Tk} = \Pi' \text{ and } \tfrac{1}{2}(p'_2 - p'_1) = \pi',$$

and consider the four infinitely small quantities Φ', φ', Π' and π' as functions of x.

By expressing that the two points are situated on the isothermal (18) and on the border curve (30), I obtain four equations from which the relations we want can be derived. In this way I obtain to the first approximation,

$$\Phi' = -\frac{1}{2m_{30}}\left[\frac{1}{m_{01}}\left(\frac{m^2{}_{01}}{RT}+m_{11}\right)^2 - \frac{2}{3}\frac{m^3{}_{01}}{R^2T^2}+\frac{2}{3}\,m_{21} - \frac{4m_{40}}{5m_{30}}\left(\frac{m^2{}_{01}}{RT}+m_{11}\right)\right]x +$$
$$+ \frac{1}{2m_{30}}\left[\frac{m_{11}}{m_{01}}\left(\frac{m^2{}_{01}}{RT}+m_{11}\right)+\frac{2}{3}m_{21}-\frac{4m_{11}m_{40}}{5\,m_{30}}\right]x_{Tk} \quad . \quad . \quad . \quad . \quad (32)$$

$$\varphi'^2 = -\frac{1}{m_{30}}\left[\frac{m^2{}_{01}}{RT}+m_{11}\right]x + \frac{m_{11}}{m_{30}}\,x_{Tk}, \quad . \quad . \quad . \quad (33)$$

$$\Pi' = m_{01}(x - x_{Tk}), \quad . \quad . \quad . \quad . \quad . \quad . \quad (34)$$

and

$$\pi' = m_{11}(x - x_{Tk})\,\varphi'. \quad . \quad . \quad . \quad . \quad . \quad . \quad (35)$$

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[1]) Wien. Ber. 98, 1159, 1889.

Now we may again write for the equation of the connodal line

$$0 = (v - v_{Tk})^2 - 2 \, \Phi' (v - v_{Tk}) + \Phi'^2 - \varphi'^2. \quad . \quad . \quad . \quad (36)$$

To the first approximation along this curve

$$\frac{d^2x}{dv^2} = - \frac{2m_{30} \, RT_k}{m^2_{01} + RT_k \, m_{11}} = \frac{2k_{30} \, RT_k}{RT^2_k \, k_{11}a - m^2_{01}} \quad . \quad . \quad . \quad (37)$$

and this expression has the opposite sign to $RT^2_k \, k_{11} \, a - m^2_{01}$. Here therefore we distinguish only two cases.

1. $RT^2_k \; k_{11} \; a > m^2_{01}; \; \dfrac{d^2x}{dv^2} < 0,$ i. e. the connodal line turns its concave side towards the v-axis (fig. 14);

2. $RT^2_k \; k_{11} \; a < m^2_{01}; \; \dfrac{d^2x}{dv^2} > 0$ and the connodal line is convex to the v-axis (fig. 15).

9. *The critical point of contact.*

The characteristic of the critical point of contact is that there the two phases with which the condensation begins and ends coincide. If x_{Tr}, p_{Tr} and v_{T_i} represent the elements of that point we have there

$$\Phi' = v_{Tr} - v_{Tk}, \; \varphi' = 0, \; \Pi' = p_{T_i} - p_{Tk}, \pi' = 0 \text{ and } x = x_{Tr}.$$

and from (33) it follows that

$$x_{Tr} = \frac{RT_k \, m_{11}}{m^2_{01} + RT_k \, m_{11}} \, x_{Tk}, \quad . \quad . \quad . \quad . \quad . \quad (38)$$

that is to say to the first approximation the composition at the critical point of contact is the same as at the plaitpoint (cf. 26) The different cases which may occur now follow.

1. $RT^2_k \, k_{11} \, a > m^2_{01}$ (fig. 14).

a). $T > T_k$; x_{Tr} is negative and there is no connodal line inside the region that can be observed. This corresponds to the position of the border curve in figs. 5 and 11.

b) $T = T_k$, $x_{T_i} = 0$ and the formula (30) represents a connodal line which touches the v-axis.

c) $T < T_k$; $x_{T_i} > 0$ and there is a connodal line in the region of positive x, (see also figs. 6 and 12).

2. $RT^2_k \, k_{11} \, a < m^2_{01}$ (fig. 15).

a) $T > T_k$; $x_{Tr} > 0$ and the connodal line lies entirely within the region that can be observed; (figs. 1, 3. 7 and 9).

b) $T = T_k$; $x_{Tr} = 0$ and the connodal line touches the v-axis;

c) $T < T_k$; $x_{Tr} > 0$ and the connodal line can only be completed

by prolonging it in the region of the negative x (fig. 2, 4, 8 and 10).
Equation (34) gives :

$$p_{T_r} = p_{T_k} + m_{01}(x_{T_r} - x_{T_k}) = p_{T_l} - \frac{m^3_{01}}{m^2_{01} + RT_k m_{11}} x_{T_k}, \quad . \quad (39)$$

so that also to the first approximation $p_{T_r} = p_{T_l}$ (comp. equation 27).
And from the equation (32) we derive in connection with (38)·

$$v_{Tr} = v_{T_k} + \frac{1}{3} \frac{m^2_{01}}{m_{30}(m^2_{01} + RT_k m_{11})} \left(m_{21} + \frac{m_{01} m_{11}}{RT_k} \right) x_{T_k}, \quad . \quad (40)$$

from which by comparison with (28) we find

$$v_{T_r} - v_{T_{pl}} = \frac{1}{2} \frac{m_{01} m_{11}}{RT_k m_{30}} x_{T_k} = -\frac{1}{2} \frac{k_{11} m_{01}}{RT_k k_{30}} (T - T_k) \quad . \quad (41)$$

The difference $v_{T_r} - v_{T_{pl}}$ may be positive or negative, that is to
say the critical point of contact may be situated on the vapour or
on the liquid branch of the border curve (or of the connodal line).
In the first case, as it is well-known, we have retrograde conden-
sation of the first type for all mixtures comprised between x_{T_r} and
$x_{T_{pl}}$, in the second case retrograde condensation of the second type :

$T > T_k$	$v_{T_r} < v_{T_{pl}}$; r. c. II, figs. 1,3 and 5	$v_{T_r} > v_{T_{pl}}$; r. c. I; figs. 7,9 and 11
$T < T_k$	$v_{T_r} > v_{T_{pl}}$; r. c. I; figs. 2, 4 and 6	$v_{T_r} < v_{T_{pl}}$; r.c.II; figs.8,10 and 12

Expressing that the plaitpoint and the critical point of contact lie
on the connodal line and subtracting the equations thus obtained
we find to the second approximation·

$$x_{T_r} - x_{T_{pl}} = \frac{1}{4} \frac{m^2_{01} m^2_{11}}{RT_k m_{30} (m^2_{01} + RT_k m_{11})} x^2_{T_k}; \quad . \quad (42)$$

this expression is positive if $RT^2_k k_{11} a > m^2_{01}$ (fig. 14), and negative
if $RT^2_k k_{11} a < m^2_{01}$ (fig. 15). In the same way we find by means
of the border curve

$$p_{T_r} - p_{T_{pl}} = -\frac{1}{4} \frac{m^3_{01} m^2_{11}}{RT_k m_{30} (m^2_{01} + RT_k m_{11})} x^2_{T_k} \quad . \quad (43)$$

so that

	$m_{01} > 0$	$m_{01} < 0$
$RT^2_k k_{11} a > m^2_{01}$	$p_{T_r} < p_{T_{pl}}$, figs. 5 and 6	$p_{T_r} > p_{T_{pl}}$; figs. 11 and 12
$RT^2_k k_{11} a < m^2_{01}$	$p_{T_r} > p_{T_{pl}}$; figs. 1—4	$p_{T_r} < p_{T_{pl}}$; figs. 7—10

(To be continued).