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KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN TE AMSTERDAM.

PROCEEDINGS OF THE MEETING

of Saturday December 28, 1901.

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CONTENTS: "Contributions to the knowledge of VAN DER WAALS' ψ-surface. V. The dependence of the plait-point constants on the composition in binary mixtures with small proportions of one of the components". By W. H. KEESOM. (Communicated by Prof. H. KAMERLINGH ONNES), p. 293. — "On function and structure of the trunkdermatonia". (II). By Prof. C. WINKLER and Dr. G. VAN RIJNBERK, p. 308. — "The shape of an empiric isothermal of a binary mixture". By Dr. PH. A. KOHNSTAMM. (Communicated by Prof. J. D. VAN DER WAALS), p. 320. — "Factorisation of large numbers". (I). By F. J. VAES. (Communicated by Prof. P. H. SCHOUTE), p. 326, (with one plate). — "A formula for the volume of the prismoid". By Prof. JAN DE VRIES, p. 337. — "The dispersion of the magnetic rotation of the plane of polarisation in negatively rotating salt-solutions, II. Further measurements with potassium ferricyanide". By Dr. L. H. SIERTSEMA. (Communicated by Prof. H. KAMERLINGH ONNES), p. 339. — "A new law concerning the relation of stimulus and effect". By Prof. J. K. A. WERTHEIM SALOMONSON (Communicated by Prof. C. WINKLER, p. 341, (with one plate).

The following papers were read:

Physics. — W. H. KEESOM: "*Contributions to the knowledge of* VAN DER WAALS' *ψ-surface. V. The dependence of the plait-point constants on the composition in binary mixtures with small proportions of one of the components.*" (Communication N⁰. 75 from the Physical Laboratory at Leiden by Prof. H. KAMERLINGH ONNES).

§ 1. In § 2 of Communication N⁰. 59*a* (Proceedings June 1900 p. 276) KAMERLINGH ONNES has drawn attention to the question as to how far, for the study of VAN DER WAALS' ψ-surfaces, we can avail ourselves of the law of corresponding states by applying this to the homogeneous phases (stable and unstable) of mixtures of

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two normal substances, especially, in how far from an empirically correct representation of the isothermals (and thus of the ψ-lines), at different temperatures for a simple substance we can find the ψ-lines for mixtures of different composition x at one temperature, and hence also the unstable part of the ψ-surface. In Communication N°. 59*b* (in collaboration with REINGANUM) this method appeared permissible even with entirely arbitrary mixtures of carbon dioxide and methylchloride; also when the mixtures under observation differ only a little in composition, as when investigating the critical phenomena in a normal substance with small impurities, it promised to be very useful. For a long time (comp. Communication N°. 68, Proceedings March 1901 p. 630) investigations for this work have been made at the Leiden Laboratory, in which I have taken part by making some measurements. As the first part of them we may consider VERSCHAFFELT's measurements on the conduct of mixtures of carbon dioxide and hydrogen, in so far as they concern mixtures with a small proportion of the latter substance. They show, as VERSCHAFFELT [1]) has demonstrated in Communication N°. 65 that the law of corresponding states indeed is nearly applicable to these mixtures, and that by means of the said law, the critical temperature and pressure of the homogeneous mixtures can be determined.

In the following pages we will examine in the first place what may be derived from VAN DER WAALS' investigation of the mixtures, by the aid of the law of corresponding states, about the course in the pT-diagram of the plait-point curve of binary mixtures in the case that the proportion of one of the components of the mixture is very small. Then the formulae obtained are compared with VERSCHAFFELT's observations. Lastly by means of the law of corresponding states I have derived an expression for the variation of the plait-point volume with the composition.

§ 2. As a starting point some formulae given by VAN DER WAALS in the Proceedings May and June 1895, Arch. Néerl. t. XXX p. 266 and 278 are used, which formulae may be also derived using the property that in the plait-point:

$$\left(\frac{\partial^2 \zeta}{\partial x^2}\right)_{pT} = 0,$$

$$\left(\frac{\partial^3 \zeta}{\partial x^3}\right)_{pT} = 0,$$

where $\zeta = \psi + pv$, if ψ represents the free energy.

[1]) Arch. d. Sc. Néerl. (2) t. V p. 644. Comm. Phys. Lab. Leiden n°. 65.

The first of these equations states that the plait-point is situated on the spinodal line, the second that the isobar on the ψ-surface drawn through the plait-point, does not enter the plait.

VAN DER WAALS finds (Proceedings May 1895) for $x = 0$, a formula (5), which we write:

$$\left(\frac{dp}{dT}\right)_{pl} = \left(\frac{\partial p}{\partial T}\right)_v - \frac{MRT_k\left(\frac{\partial^2 p}{\partial v\,\partial T}\right)\left(\frac{\partial p}{\partial x}\right)_{vT}}{\left(\frac{\partial p}{\partial x}\right)^2_{vT} + MRT_k\left(\frac{\partial^2 p}{\partial x\,\partial v}\right)_T} \quad . \quad . \quad . \quad (1a)$$

where it is taken into account that at the critical point of a simple substance

$$\left(\frac{\partial^2 \varepsilon}{\partial v^2}\right)_T = T_k\left(\frac{\partial^2 p}{\partial v\,\partial T}\right).$$

Besides VAN DER WAALS finds an equation (9) (Proceedings June 1895) which we write:

$$\frac{dT_{pl}}{dx} = -\frac{\left(\frac{\partial p}{\partial x}\right)^2_{vT} + MRT_k\left(\frac{\partial^2 p}{\partial x\,\partial v}\right)_T}{MRT_k\left(\frac{\partial^2 p}{\partial v\,\partial T}\right)} \quad . \quad . \quad . \quad . \quad (1b)$$

for x equal to zero. From these two equations follows:

$$\frac{dp_{pl}}{dx} = \left(\frac{\partial p}{\partial x}\right)_{vT} - \left(\frac{\partial p}{\partial T}\right)_v \frac{\left(\frac{\partial p}{\partial x}\right)^2_{vT} + MRT_k\left(\frac{\partial^2 p}{\partial x\,\partial v}\right)_T}{MRT_k\left(\frac{\partial^2 p}{\partial v\,\partial T}\right)} \quad . \quad . \quad (1c)$$

Here $\frac{dT_{pl}}{dx}$ and $\frac{dp_{pl}}{dx}$ indicate the variation of the critical plait-point temperature and pressure with small admixtures, T_k is the critical temperature of the pure substance.

We may now naturally introduce the law of corresponding states into the equations given above. By means of

$$p = \pi\, p_{xk}\,; \qquad v = \omega\, v_{xk}\,; \qquad T = \tau\, T_{xk}$$

where p_{xk}, v_{xk} and T_{xk} respectively represent: critical pressure, volume and temperature of the mixture taken as homogeneous, and therefore :

$$\pi = f(\omega, \tau),$$

we find

$$\left(\frac{\partial p}{\partial x}\right)_{vT} = \pi \frac{dp_{xk}}{dx} - \frac{p_{xk}}{v_{xk}} \frac{dv_{xk}}{dx} \omega \left(\frac{\partial \pi}{\partial \omega}\right) - \frac{p_{xk}}{T_{xk}} \frac{dT_{xk}}{dx} \tau \left(\frac{\partial \pi}{\partial \tau}\right),$$

$$\left(\frac{\partial^2 p}{\partial x\, \partial v}\right)_T = \frac{1}{v_{xk}} \frac{dp_{xk}}{dx}\left(\frac{\partial \pi}{\partial \omega}\right) - \frac{p_{xk}}{v^2_{xk}} \frac{dv_{xk}}{dx}\left(\frac{\partial \pi}{\partial \omega}\right) - \frac{p_{xk}}{v^2_{xk}} \frac{dv_{xk}}{dx} \omega \left(\frac{\partial^2 \pi}{\partial \omega^2}\right) -$$

$$- \frac{p_{xk}}{T_{xk}\, v_{xk}} \frac{dT_{xk}}{dx} \tau \left(\frac{\partial^2 \pi}{\partial \omega\, \partial \tau}\right).$$

This becomes for $x = 0$, as then $\pi = \omega = \tau = 1$,

$$\left(\frac{\partial \pi}{\partial \omega}\right) = 0 \text{ and } \left(\frac{\partial^2 \pi}{\partial \omega^2}\right) = 0 \ :$$

$$\left(\frac{\partial p}{\partial x}\right)_{vT} = p_k \left\{\beta - \alpha \left(\frac{\partial \pi}{\partial \tau}\right)\right\}$$

$$\left(\frac{\partial^2 p}{\partial x\, dv}\right)_T = - \frac{p_k}{v_k} \alpha \left(\frac{\partial^2 \pi}{\partial \omega\, \partial \tau}\right)$$

in which we have called:

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

With these we have for equations (1*b*) and (1*c*):

$$\frac{1}{T_k} \frac{dT_{pl}}{dx} = \alpha - \frac{\left\{\beta - \alpha \left(\frac{\partial \pi}{\partial \tau}\right)\right\}^2}{C_4 \left(\frac{\partial^2 \pi}{\partial \omega\, \partial \tau}\right)} \quad . \ . \ . \ . \quad (2a)$$

$$\frac{1}{p_k} \frac{dp_{pl}}{dx} = \beta - \left(\frac{\partial \pi}{\partial \tau}\right) \frac{\left\{\beta - \alpha \left(\frac{\partial \pi}{\partial \tau}\right)\right\}^2}{C_4 \left(\frac{\partial^2 \pi}{\partial \omega\, \partial \tau}\right)} \quad . \ . \ . \ . \quad (2b)$$

if

$$C_4 = \frac{MRT_k}{p_k v_k},$$

which two equations also give immediately the slope of the plait-point curve in the Tp-diagram at the critical point of the pure substance. Hence we see that the variation of critical plait-point temperature and pressure due to the presence of small admixtures is entirely determined by the two quantities α and β.

From these two equations follows also that for very small values of x:

$$\frac{p_{pl} - p_{xk}}{T_{pl} - T_{xk}} = \left(\frac{dp}{dT}\right)_k \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

if $\left(\frac{dp}{dT}\right)_k$ is the $\frac{dp}{dT}$ for the saturated-vapourpressure curve of the simple substance at the critical point. In this way we again find the relation, given by VAN DER WAALS Proceedings Nov. '97, p. 298.

If therefore we connect in the pT-diagram the critical points of the homogeneous mixtures with the plait-points of these mixtures, these connecting lines at the critical point of the pure substance are parallel to the vapourpressure curve of the latter.

§ 3. In order to be able to compare these formulae with observations on mixtures $\left(\frac{\partial \pi}{\partial \tau}\right)$ and $C_4 \left(\frac{\partial^2 \pi}{\partial \omega \, \partial \tau}\right)$ are required.

$\left(\frac{\partial \pi}{\partial \tau}\right)$ can be determined in two ways. For according to a thesis of VAN DER WAALS $\left(\frac{\partial \pi}{\partial \tau}\right)$ at the critical point $= \left(\frac{\partial \pi}{\partial \tau}\right)_{coex}$, where π_{coex} represents the maximum vapourpressure. Prof. VAN DER WAALS was so kind as to communicate to me the following proofs for this thesis, as developed many years ago in his lectures.

1. MAXWELL's criterium at a coexistence pressure independent of the volume is given by

$$p_{coex} \, (v_d - v_v) = \int_{v_v}^{v_d} p \, dv,$$

where v_v and v_d refer respectively to liquid and vapour. By differentiating this with regard to T, we have

$$\left(\frac{dp}{dT}\right)_{coëx}(v_d - v_v) + p_{coëx}\left(\frac{dv_d}{dT} - \frac{dv_v}{dT}\right) = \int_{v_v}^{v_d}\left(\frac{\partial p}{\partial T}\right)_v dv + p_{coëx}\left(\frac{dv_d}{dT} - \frac{dv_v}{dT}\right)$$

or

$$\left(\frac{dp}{dT}\right)_{coëx} = \frac{1}{v_d - v_v}\int_{v_v}^{v_d}\left(\frac{\partial p}{\partial T}\right)_v dv$$

and in words: $\left(\frac{dp}{dT}\right)_{coëx}$ is the mean value of $\left(\frac{\partial p}{\partial T}\right)_v$ between the volumes v_v and v_d. At the critical temperature the mean value is the pressure-variation co-efficiënt itself or

$$\left\{\left(\frac{dp}{dT}\right)_{coëx}\right\}_{crit} = \left\{\left(\frac{\partial p}{\partial T}\right)_v\right\}_{crit}.$$

2. By integrating the isentropic relation

$$\left(\frac{\partial \eta}{\partial v}\right)_T = \left(\frac{\partial p}{\partial T}\right)_v \quad .$$

and by putting $(v_d - v_v)\left(\frac{dp}{dT}\right)_{coëx}$ instead of $\eta_d - \eta_v$ and proceeding as in 1°.

3. By using the pvT-surface.

At the critical point a tangent to this surface may be drawn parallel to the v-axis. The tangent-plane at the critical point is thus at right angles to the pT-plane, and its section is a straight line. Each curve on the pvT-surface which passes through the critical point and whose osculating plane at the critical point, while cutting the tangent plane to the pvT-surface at an angle, is not perpendicular to the pT-plane as is the case with the tangent plane to the pvT-surface, is projected on the pT-plane as a curve touching the above named section. Hence 1. the border curve, of which the osculating plane co-incides with the tangent plane to the pvT-surface at the critical point, 2. the section of the pvT-surface by a plane at right angles to the v-axis, 3. the isentropic line for the critical point, etc. All these lines have projections on the pT-plane, touching each other in the projection of the critical point and hence give $\left(\frac{dp}{dT}\right)$ values with different indices v, η, coëx., etc. which are equal to one another at the critical point.

Analytically we bring this into the following form. As for each point of the pvT-surface

$$dp = \left(\frac{\partial p}{\partial v}\right)_T dv + \left(\frac{\partial p}{\partial T}\right)_v dT$$

and as at the critical point $\left(\frac{\partial p}{\partial v}\right)_T$ is equal to zero, we obtain for each curve passing through that point

$$\frac{dp}{dT} = \left(\frac{\partial p}{\partial T}\right)_v.$$

We are uncertain of the equality only when the curve has an element in common with the isotherm. In this case the value of $\left(\frac{\partial p}{\partial v}\right)_T \frac{dv}{dT}$ must be more closely investigated. This strict investigation would therefore be also required for the border curve were this not rendered superfluous by the proofs 1 and 2. That the relation $\left(\frac{dp}{dT}\right)_{coëx} = \left(\frac{\partial p}{\partial T}\right)_v$ holds for the border curve must be ascribed to the circumstance that the latter lies in a cylinder surface, as mentioned above, which touches the pvT-surface at the critical point.

From a graphical representation of p as function of v in the neighbourhood of the critical point according to AMAGAT's data for the isothermals of carbon dioxide I found:

$$\left(\frac{\partial \pi}{\partial \tau}\right) = 7.3 \text{ and } C_4 \left(\frac{\partial^2 \pi}{\partial \omega\, \partial \tau}\right) = -32.2$$

putting the critical volume 0.00426 and $C_4 = 3.45$ while

$$\left(\frac{\partial \pi}{\partial \tau}\right) = 6.5$$

would follow from an extrapolation of AMAGAT's observations for the vapour pressures.

With this uncertainty in $\left(\frac{\partial \pi}{\partial \tau}\right)$ it may be well to investigate what would be yielded by different equations of state.

VAN DER WAALS' equation:

$$p + \left(\frac{a e^{\frac{T_k - T}{T_k}}}{v^2} \right) (v - b) = MRT$$

as well as CLAUSIUS':

$$\left\{ p + \frac{K}{T (v + nb)^2} \right\} (v - b) = MRT,$$

give:

$$\left(\frac{\partial \pi}{\partial \tau} \right) = 7, \qquad C_4 \left(\frac{\partial^2 \pi}{\partial \omega \, \partial \tau} \right) = - 32.$$

I would also have availed myself of the equation of state given by DIETERICI (DRUDE's Annalen Bd. 5 p. 51—88, May 1901), but found that there has crept an error into the derivation of this to which I draw attention in the following section.

§ 4. DIETERICI puts $p = \frac{RT}{v_a - b_a}$ in which v_a is derived from v by means of the equation:

$$\int_v^{v_a} \frac{dv}{v - b} = a \frac{v_k}{v} \frac{T_k^{3/2}}{T^{3/2}},$$

$$b_a = b_c - \frac{1}{4} \frac{b_c^2}{v}, \qquad b_c = \frac{2}{3} v_k,$$

where a is a constant to be calculated for each substance from the critical data, for instance for isopentane $a = 2.116$.

From these equations we find:

$$\frac{T}{p} \left(\frac{\partial p}{\partial T} \right)_v = 1 + \frac{3}{2} a \frac{v_k}{v} \frac{T_k^{3/2}}{T^{3/2}} \left\{ 1 - \frac{1}{9} \frac{v_k^2}{v_a^2} \right\}$$

which for the critical point becomes

$$\frac{T_k}{p_k} \left(\frac{\partial p}{\partial T} \right)_v = 1 + \frac{3}{2} a \left\{ 1 - \frac{1}{9} \frac{v_k^2}{v_a^2} \right\},$$

hence for isopentane $\frac{T_k}{p_k}\left(\frac{\partial p}{\partial T}\right)_v < 4.174$, which does not agree with the observations. Indeed DIETERICI wrongly supposes that his formulae also represent the correct isothermals for volumes smaller than the critical. [1])

He derives (l.c. p. 74) the following formula for $\frac{dp_s}{dT}$:

$$v_1\, v_2\, T^{3/2} \frac{dp_s}{dT} = 2.116\, v_k\, R T_k^{3/2},$$

where p_s represents the saturated vapourpressure and v_1 and v_2 the volumes of saturated liquid and vapour.

This formula gives at the critical point:

$$\frac{T_k}{p_k} \frac{dp_s}{dT} = 7.9.$$

According to the thermo-dynamic thesis laid down in § 3

$$\frac{dp_s}{dT} = \left(\frac{\partial p}{\partial T}\right)_v$$

at the critical point. Hence the two results contradict each other. The explanation may be found in the circumstance that DIETERICI has assumed that

$$\int_{v_1}^{v_2} \pi\, dv = J \,.\, \varrho$$

if

$$p + \pi = \frac{RT}{v-b}$$

and if ϱ is the internal latent heat of evaporation. This would be true if π were not a function of the temperature; as this is however the case with DIETERICI the internal latent heat of evaporation must be found from

$$J \,.\, \varrho = \int_{v_1}^{v_2} \left[T \left(\frac{\partial p}{\partial T}\right)_v - p \right] dv.$$

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[1]) See DANIEL BERTHELOT, Arch. Néerl. d. Sc. (2) t. V. p. 441.

Hence the circumstance that DIETERICI's formula for $\frac{dp_s}{dT}$ gives a good representation of the observations proves that his original equations do not do so. Hence his equation of state must be left out of consideration.

§ 5. The existing uncertainty about $\left(\frac{\partial \pi}{\partial \tau}\right)$ and $C_4 \left(\frac{\partial^2 \pi}{\partial \omega \, \partial \tau}\right)$, for a simple substance (when $\left(\frac{\partial \pi}{\partial \tau}\right)$ diminishes, probably $C_4 \left(\frac{\partial^2 \pi}{\partial \omega \, \partial \tau}\right)$ must also be diminished) is a great impediment in the application of our considerations to mixtures; we may, however, accept that we are not far wrong, when with VAN DER WAALS we put $\left(\frac{\partial \pi}{\partial \tau}\right) = 6.7$ and $C_4 \left(\frac{\partial^2 \pi}{\partial \omega \, \partial \tau}\right) = -32.2$.

§ 6. We will apply the equations (2) and (3) to the observations of VERSCHAFFELT. He gives (Communication n°. 47, Proceedings Febr. '99 and Communication n°. 65, Arch. Néerl. série II t. V p. 646) for two mixtures of carbon dioxide and hydrogen T_{pl} and p_{pl}, for three mixtures T_{xk} and p_{xk} as he has derived them by superimposing the logarithmic isothermal-systems, and also for carbon dioxide T_k and p_k as calculated by him from AMAGAT's isothermals

x	T_{pl}	p_{pl}	T_{xk}	p_{xk}
0	304.7	73.6	304.7	73.6
0.0494	300.4	91.85	287.8	68.1
0.0995	297.5	114.2	273.6	63.5
0.1990			248.7	54.8

To derive from this $\alpha = \frac{1}{T_k} \left(\frac{dT_{xk}}{dx}\right)_{x=0}$ when x is small, we may put $T_{xk} = T_k (1 + \alpha x + \alpha' x^2)$ and compute the co-efficients α and α' from the observations for $x = 0.0494$ and $x = 0.0995$. Thus we find $\alpha = -1.219$ $\beta = -1.645$. If on the contrary we compute α and β from the formulae accepted by VERSCHAFFELT (Communication n°. 65, Arch. Néerl. t. V p. 649) to represent T_{xk} and p_{xk} as functions of x:

$$T_{xk} = C'_1 \sqrt{\frac{K'_x}{b_x}}, \quad p_{xk} = C'_2 \sqrt{\frac{K_x}{b_x^3}}$$

where

$$\frac{K'_x}{K_{22}} = 1 - 1.40\,x + 0.18\,x^2, \quad \frac{b_x}{b_{22}} = 1 + 0.526\,x - 0.035\,x^2,$$

then we find:

$$\alpha = -0.963 \qquad \beta = -1.489.$$

It appears therefore that much uncertainty exists about the values of α and β. This must partly be ascribed to the uncertainty in the determination of T_{xk} and p_{xk} following the method of RAVEAU (from VERSCHAFFELT's quadratic formulae I calculate for $x = 0.0494$: $T_{xk} = 290.3°$ C., $p_{xk} = 68.35$ atm., while VERSCHAFFELT found $T_{xk} = 287.8°$ C. and $p_{xk} = 68.1$ atm.), and partly to the small number of observations, from which the variation of T_{xk} and p_{xk} with x must be derived.

However this may be, where the uncertainties in α and β are added to those in $\left(\frac{\partial \pi}{\partial \tau}\right)$ and $C_4 \left(\frac{\partial^2 \pi}{\partial \omega\, \partial \tau}\right)$ it is obvious that nothing can be derived from the comparison of the observations with the formulae (2*a*) and (2*b*). It is even easy to choose within the limits of uncertainty values for α, β, $\left(\frac{\partial \pi}{\partial \tau}\right)$, $C_4 \left(\frac{\partial^2 \pi}{\partial \omega\, \partial \tau}\right)$, that lead to results for $\frac{dT_{pl}}{dx}$ and $\frac{dp_{pl}}{dx}$, which are entirely at variance with the observations. With the selection we made, as stated above, of $\left(\frac{\partial \pi}{\partial \tau}\right) = 6.7$ and $C_4 \left(\frac{\partial^2 \pi}{\partial \omega\, \partial \tau}\right) = -32.2$ we should derive by means of the values of α and β, found from the quadratic formulae, in which VERSCHAFFELT expressed his observations:

$$\alpha = -0.963, \quad \beta = -1.49:$$

$$\frac{1}{T_k} \frac{dT_{pl}}{dx} = -0.20, \qquad \frac{1}{p_k} \frac{dp_{pl}}{dx} = 3.63,$$

which values might be made to agree with the form of the plait-point curve according to VERSCHAFFELT.

Of greater importance is the test of the relation (3), which not only for hydrogen but for every substance mixed with carbon dioxide will hold with x exceedingly small:

$$\frac{p_{pl} - p_{xk}}{T_{pl} - T_{xk}} = 1.61.$$

For we find for this proportion with

$$x = 0.0494 \quad : \quad 1.88\,,$$

$$x = 0.0995 \quad : \quad 2.12\,,$$

so that the value 1.61 for $x = 0$ will come near to the truth and therefore in this respect theory and observations confirm each other sufficiently.

§ 7. In the same way as we have considered $\frac{dp_{pl}}{dx}$ and $\frac{dT_{pl}}{dx}$, we can also consider $\frac{dv_{pl}}{dx}$ for $x = 0$, a quantity important with a view to the determination of the critical volume of a simple substance.

In the equation:

$$\frac{dv_{pl}}{dx} = \left(\frac{\partial v}{\partial p}\right)_{xT} \frac{dp_{pl}}{dx} + \left(\frac{\partial v}{\partial T}\right)_{px} \frac{dT_{pl}}{dx} + \left(\frac{\partial v}{\partial x}\right)_{pT} \quad . \quad . \quad . \quad (4)$$

the co-efficients $\left(\frac{\partial v}{\partial p}\right)_{xT}$, $\left(\frac{\partial v}{\partial T}\right)_{px}$ and $\left(\frac{\partial v}{\partial x}\right)_{pT}$ are all infinitely large for $x = 0$ and such that in the development their terms cancel one another. Therefore in the development of $\left(\frac{\partial v}{\partial p}\right)_{xT}$ etc. the finite terms, in that of $\frac{dp_{pl}}{dx}$ and $\frac{dT_{pl}}{dx}$ the terms with the first power of x must be kept.

As a starting point I have chosen the relations

$$\left(\frac{\partial^2 \zeta}{\partial x^2}\right)_{pT} = 0\,, \quad \left(\frac{\partial^3 \zeta}{\partial x^3}\right)_{pT} = 0$$

of § 2, which hold for the plait-point.

If in equation (4) we substitute the values $\frac{dp_{pl}}{dx}$ and $\frac{dT_{pl}}{dx}$ which we obtain by the differentiation of the above relations:

$$0 = \left(\frac{\partial^3 \zeta}{\partial x^2 \partial p}\right)_T \frac{dp_{pl}}{dx} + \left(\frac{\partial^3 \zeta}{\partial x^2 \partial T}\right)_p \frac{dT_{pl}}{dx},$$

$$0 = \left(\frac{\partial^4 \zeta}{\partial x^3 \partial p}\right)_T \frac{dp_{pl}}{dx} + \left(\frac{\partial^4 \zeta}{\partial x^3 \partial T}\right)_p \frac{dT_{pl}}{dx} + \left(\frac{\partial^4 \zeta}{\partial x^4}\right)_{pT},$$

while we write

$$\left(\frac{\partial \zeta}{\partial p}\right)_{xT} = v, \qquad \left(\frac{\partial \zeta}{\partial T}\right)_{vx} = -\eta,$$

we find:

$$\frac{dv_{pl}}{dx} = \left(\frac{\partial v}{\partial x}\right)_{pT} + \left(\frac{\partial^4 \zeta}{\partial x^4}\right)_{pT} \frac{\left(\frac{\partial v}{\partial p}\right)_{xT}\left(\frac{\partial^2 \eta}{\partial x^2}\right)_{pT} + \left(\frac{\partial v}{\partial T}\right)_{px}\left(\frac{\partial^2 v}{\partial x^2}\right)_{pT}}{\left(\frac{\partial^2 v}{\partial x^2}\right)_{pT}\left(\frac{\partial^3 \eta}{\partial x^3}\right)_{pT} - \left(\frac{\partial^2 \eta}{\partial x^2}\right)_{pT}\left(\frac{\partial^3 v}{\partial x^3}\right)_{pT}} . \quad (5)$$

To determine $\left(\frac{\partial v}{\partial x}\right)_{pT}$ with x small we may avail ourselves of the equation

$$\left(\frac{\partial^2 \zeta}{\partial x^2}\right)_{pT} = \left(\frac{\partial^2 \psi}{\partial x^2}\right)_{vT} + \left(\frac{\partial^2 \psi}{\partial x \partial v}\right)_T \left(\frac{\partial v}{\partial x}\right)_{pT} = 0.$$

We put

$$\psi = MRT\{(1-x)\,l\,(1-x) + x\,l\,x\} + \varphi$$

where therefore

$$\varphi = -\int^v p\,dv.$$

If we call

$$\left(\frac{\partial \varphi}{\partial x}\right)_{vT} = \varphi', \quad \left(\frac{\partial^2 \varphi}{\partial x^2}\right)_{vT} = \varphi'',$$

then

$$\left(\frac{\partial^2 \psi}{\partial x^2}\right)_{vT} = \frac{MRT}{x\,(1-x)} + \varphi''.$$

Hence

$$\left(\frac{\partial v}{\partial x}\right)_{pT} = \frac{MRT}{x(1-x)\left(\frac{\partial p}{\partial x}\right)_{vT}} + \frac{\varphi''}{\left(\frac{\partial p}{\partial x}\right)_{vT}} = \frac{MRT}{x\left(\frac{\partial p}{\partial x}\right)_{vT}} + \frac{MRT + \varphi''}{\left(\frac{\partial p}{\partial x}\right)_{vT}} +$$

$$+ \text{ terms with } x \text{ in the denominator.}$$

In a similar way we develop each of the differential quotients in (5), always retaining the terms of the highest order but one. We shall not repeat here the rather lengthy computations; it must be remarked that in the reduction of the differential quotients of η we have started from the fundamental form

$$d\varepsilon = Td\eta - pdv + \left(\frac{\partial \zeta}{\partial x}\right)_{pT} dx.$$

We obtain

$$T\left(\frac{\partial^2 \eta}{\partial x^2}\right)_{pT} = T\left(\frac{\partial p}{\partial T}\right)_{vx}\left(\frac{\partial^2 v}{\partial x^2}\right)_{pT} + \left(\frac{\partial^2 \varepsilon}{\partial x^2}\right)_{vT} +$$

$$+ 2\left(\frac{\partial^2 \varepsilon}{\partial x \partial v}\right)_T \left(\frac{\partial v}{\partial x}\right)_{pT} + \left(\frac{\partial^2 \varepsilon}{\partial v^2}\right)_{xT}\left(\frac{\partial v}{\partial x}\right)^2_{pT} \text{ [1]}$$

In the same way $\left(\frac{\partial^3 \eta}{\partial x^3}\right)_{pT}$ is determined by means of ε.

$\left(\frac{\partial^4 \zeta}{\partial x^4}\right)$ is expressed by means of differential quotients of ψ, where among others $\left(\frac{\partial^2 v}{\partial x^2}\right)_{pT}$ and $\left(\frac{\partial^3 v}{\partial x^3}\right)_{pT}$ occur. The equation $\left(\frac{\partial^3 \zeta}{\partial x^3}\right)_{pT} = 0$ gives a value for $\left(\frac{\partial^2 v}{\partial x^2}\right)_{pT}$ after which $\left(\frac{\partial^3 v}{\partial x^3}\right)_{pT}$ can be determined from the equations obtained by differentiating

$$p = f(v\, x\, T)$$

three times with regard to x, keeping T and p constant.

All this performed, we finally obtain:

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[1]) Comp. VAN DER WAALS, Continuitat II pag. 125.

$$\frac{dv_{pl}}{dx} = -\frac{MRT_k}{\left(\frac{\partial^3 p}{\partial v^3}\right)_T}\left[\frac{\left(\frac{\partial p}{\partial x}\right)^3_{vT}}{(MRT_k)^3} + \frac{\left(\frac{\partial^3 p}{\partial x\,\partial v^2}\right)_T}{MRT_k} + 3\,\frac{\left(\frac{\partial^2 p}{\partial x\,\partial v}\right)_T\left(\frac{\partial p}{\partial x}\right)_{vT}}{(MRT_k)^2} - \right.$$

$$\left. - \frac{\left(\frac{\partial^3 p}{\partial v^2 \partial T}\right)}{\left(\frac{\partial^2 p}{\partial v\,\partial T}\right)\left(MRT_k\right)^2}\left\{\left(\frac{\partial p}{\partial x}\right)^2_v + MRT_k\left(\frac{\partial^2 p}{\partial x\,\partial v}\right)_T\right\}\right]$$

If once more as in § 2 we introduce the law of corresponding states, this form may be reduced to:

$$\frac{1}{C_4}\,\frac{1}{v_k}\,\frac{dv_{pl}}{dx} = \frac{1}{C_4}(\alpha-\beta) - \frac{\beta - \alpha\left(\frac{\partial \pi}{\partial \tau}\right)}{C_4^3\left(\frac{\partial^3 \pi}{\partial \omega^3}\right).C_4\left(\frac{\partial^2 \pi}{\partial \omega\,\partial \tau}\right)} \times$$

$$\times \left[C_4\left(\frac{\partial^2 \pi}{\partial \omega\,\partial \tau}\right)\left\{\beta - \alpha\left(\frac{\partial \pi}{\partial \tau}\right)\right\}^2 - \right.$$

$$\left. - C_4^2\left(\frac{\partial^3 \pi}{\partial \omega^2\,\partial \tau}\right)\left\{\beta - \alpha\left(\frac{\partial \pi}{\partial \tau}\right)\right\} - 3\,C_4\left(\frac{\partial^2 \pi}{\partial \omega\,\partial \tau}\right)\alpha\right], \quad . \quad . \quad (2c)$$

where for $\alpha - \beta$ we may write: $\frac{1}{v_k}\,\frac{dv_{xk}}{dx}$.

In this formula two new constants occur, to be derived from the equation of state, viz.

$$C_4^3\left(\frac{\partial^3 \pi}{\partial \omega^3}\right) \text{ and } C_4^2\left(\frac{\partial^3 \pi}{\partial \omega^2 \partial T}\right).$$

According to VAN DER WAALS' formula with $ae^{\frac{T_k - T}{T_k}}$ for the molecular attraction (as well as for CLAUSIUS' formula) at the critical point

$$C_4^2\left(\frac{\partial^3 \pi}{\partial \omega^2\,\partial \tau}\right) = 256, \quad C_4^3\left(\frac{\partial^3 \pi}{\partial \omega^3}\right) = -\frac{512}{3}.$$

In consequence of the results found during the testing of the formulae (2*a*) and (2*b*) it is obvious that the observations do not yield sufficient data to test formula (2*c*), the more as higher differential quotients of π occur. For the comparison of observation and calculation formula (3) is for the present the most important.