Citation:

Johannes Diderik van der Waals, The derivation of the formula which gives the relation between the concentration of coexisting phases for binary mixtures, in:
KNAW, Proceedings, 7, 1904-1905, Amsterdam, 1905, pp. 156-162

Physics. — *"The derivation of the formula which gives the relation between the concentration of coexisting phases for binary mixtures."* By Prof. J. D. VAN DER WAALS.

(Communicated in the meeting of June 25, 1904).

Already in my molecular theory (Cont. II, p. 10) I derived a formula for the concentration in coexisting phases of binary mixtures. This formula has the following form:

$$\left\{MRT\,l\frac{x}{1-x}+MRT\frac{\frac{db}{dx}}{v-b}-\frac{\frac{da}{dx}}{v}\right\}_1=\left\{MRT\,l\frac{x}{1-x}+MRT\frac{\frac{db}{dx}}{v-b}-\frac{\frac{da}{dx}}{v}\right\}_2$$

In the case that the second phase is a rarefied gasphase, the second member is simplified to $MRT\,l\frac{x}{1-x}$ and we find:

$$MRT\,l\frac{x_1}{1-x_1}\,\frac{1-x_2}{x_2}=\left\{\frac{\frac{da}{dx}}{v}-MRT\frac{\frac{db}{dx}}{v-b}\right\}_1 \quad . \; . \; . \; . \quad (1)$$

From this I have drawn the conclusion that the circumstance that two coexisting phases have the same concentration can only occur for mixtures, for which a minimum value of the quantity $\frac{a_x}{b_x}$ occurs, and so a minimum value for the critical temperature. For the limiting case, with exceedingly low values of T, the mixture for which $\frac{a_x}{b_x}$ has a minimum value, would be exactly the mixture, for which the value of x is the same in the two phases; but for increasing values of T this concentration shifts to the side of the substance with the lowest value of the size of the molecules. (Cont. II, p. 19 and p. 120).

Afterwards I have derived in "Ternary Systems" for equation (1) the following equation:

$$l\frac{x_1}{1-x_1}\,\frac{1-x_2}{x_2}=-\frac{f}{T}\frac{dT_k}{dx}+\frac{1}{p_k}\frac{dp_k}{dx}, \quad . \; . \; . \; . \quad (2)$$

which also holds only approximately for the case that the second phase is a rarefied gas-phase. For the derivation of (2) I have not directly used the equation of state, but I have considered the well-known formula for the vapour-pressure $-l\frac{p}{p_k}=f\frac{T_k-T}{T}$ as sufficiently accurate for liquid volumes which are not much smaller than that of the pressure of coincidence (pressure of the saturated vapour for the unsplit mixture).

Equation (2) however, can also be found directly from the equation of state. It was to be expected that this was possible, because as I have shown in "The liquid state and equation of condition"[1]) the formula for the vapour may be derived from this equation. If we want to find also for the factor f the real value of about 7, it is necessary to consider b as function of the volume. This not only renders the derivation very complicate, but it places us before the unsolved question: in how far is the decrease of b with the volume to be ascribed to real or quasi diminution?

I have therefore confined myself for the moment to examining what follows for the form of (2) from the equation of state, when b is put independent of the volume.

We have then to reduce:

$$\frac{MRT\dfrac{db}{dx}}{v-b}-\frac{\dfrac{da}{dx}}{v}.$$

We write for this successively:

$$\frac{MRT\dfrac{db}{dx}}{v-b}-\frac{\dfrac{da}{dx}}{v}=\left(p+\frac{a}{v^2}\right)\frac{db}{dx}-\frac{1}{v}\frac{da}{dx}=$$

$$=p\frac{db}{dx}-\frac{d\dfrac{a}{b}}{dx}+\left(\frac{a}{v^2}-\frac{a}{b^2}\right)\frac{db}{dx}-\left(\frac{1}{v}-\frac{1}{b}\right)\frac{da}{dx}.$$

Now for $a\dfrac{db}{dx}\left(\dfrac{1}{v^2}-\dfrac{1}{b^2}\right)-\left(\dfrac{1}{v}-\dfrac{1}{b}\right)\dfrac{da}{dx}$ we may write:

$$\frac{a(v-b)}{bv}\left\{\frac{1}{a}\frac{da}{dx}-\frac{v+b}{v}\frac{1}{b}\frac{db}{dx}\right\}=\frac{a(v-b)}{bv}\left\{\frac{1}{a}\frac{da}{dx}-\frac{2}{b}\frac{db}{dx}-\left(1-\frac{b}{v}\right)\frac{1}{b}\frac{db}{dx}\right\}$$

and as according to the equation of state $\dfrac{a(v-b)}{bv}$ is equal to

$$\frac{a(v-b)}{bv}=MRT+(MRT-vp)\frac{v-b}{b}$$

we find after some reductions:

$$\frac{MRT\dfrac{db}{dx}}{v-b}-\frac{\dfrac{da}{dx}}{v}=p\frac{db}{dx}-\frac{d\dfrac{a}{b}}{dx}+MRT\frac{dl\dfrac{a}{b^2}}{dx}+\frac{v-b}{b}(MRT-vp)\frac{dl\dfrac{a}{b^2}}{dx}+$$
$$+\frac{v-b}{b}\frac{1}{b}\frac{db}{dx}[MRT-p(v-b)]\quad.\quad.\quad.\quad.\quad.\quad.\quad.\quad.\quad.\quad.\quad.\quad.\quad(3)$$

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[1]) These Proc. VI. p. 123.

We may also write the second member of (3) as follows:

$$p\left\{\frac{db}{dx}-\frac{v}{b}(v-b)\frac{d\,l\dfrac{a}{b^2}}{dx}-\frac{(v-b)^2}{b^2}\frac{db}{dx}\right\}-$$

$$-\frac{d\dfrac{a}{b}}{dx}+MRT\frac{d\,l\dfrac{a}{b^2}}{dx}+MRT\frac{v-b}{v}\frac{d\log\dfrac{a}{b}}{dx}\quad .\ .\ .\ .\quad (4)$$

In order to examine the general value of the quantity which is to be reduced, we have to distinguish two cases. The first case, that $v-b$ is small and $p(v-b)$ may be neglected compared with MRT. In this case (4) may be simplified to:

$$p\frac{db}{dx}-\frac{d\dfrac{a}{b}}{dx}+MRT\frac{d\,l\dfrac{a}{b^2}}{dx}.$$

The second would hold for high pressures, then the value of $p(v-b)$ approaches to MRT, when v approaches to b. In this case (4) is simplified to:

$$p\frac{db}{ax}-\frac{d\dfrac{a}{b}}{dx}.$$

As we assume coexistence with a rarefied gasphase we have only to deal with the first case. In the second there would not even be question of coexistence with a second phase. We find now for the formula, giving the relation for the concentration of the two phases:

$$l\frac{x_1}{1-x_1}\frac{1-x_2}{x_2}=\left(\frac{1}{MRT}\frac{d\dfrac{a}{b}}{dx}-\frac{d\,l\dfrac{a}{b^2}}{dx}\right)_1\quad .\ .\ .\ .\quad (5)$$

in which $p\dfrac{db}{dx}$ is neglected, or rather where it is cancelled by an almost equal value, which would occur in the second member of the equation given at the beginning of this paper.

Let us put:

$$MRT_k=\frac{8}{27}\frac{a}{b}$$

and

$$p_k=\frac{1}{27}\frac{a}{b^2},$$

then (5) assumes the form of:

$$l\frac{x_1}{1-x_1}\frac{1-x_2}{x_2}=\left(\frac{27}{8}\frac{1}{T}\frac{dT_k}{dx}-\frac{dp_k}{p_k dx}\right)_1.$$

The factor $\frac{27}{8}$ is in perfect concordance with the factor which occurs in the formula of the vapour pressure, when we put the quantity b independent of the volume. I have shown before that it must be about doubled, when we assume variability for b — or rather the factor $\frac{27}{8}$ is not increased, but the assumption of the smaller value of b comes to doubling the factor, when we substitute the value of T_k for $\frac{a}{b}$. Without carrying out the elaborate calculations, which in our case might be the consequence of assumption of the variability of b, I think to be justified in concluding to the doubling of that factor as a sufficiently approximated value. Then we find back exactly the same value as I had found in "Ternary Systems", viz.

$$l\frac{x_1}{1-x_1}\frac{1-x_2}{x_2}=\left(\frac{f}{T}\frac{dT_k}{dx}-\frac{1}{p_k}\frac{dp_k}{dx}\right)_1, \quad . \quad . \quad . \quad . \qquad (6)$$

in which formula f may put about 7.

As $\frac{T_k}{8\times 273p_k}=b$, we may put for $\frac{dlp_k}{dx}$:

$$\frac{d\,log\,T_k}{dx}-\frac{d\,log\,b}{dx}.$$

Hence (6) becomes:

$$l\frac{x_1}{1-x_1}\frac{1-x_2}{x_2}=\left(\frac{f}{T}-\frac{1}{T_k}\right)\frac{dT_k}{dx}+\frac{1}{b}\frac{db}{dx} \quad , \quad . \quad . \quad . \qquad (7)$$

From the form (7) we derive, that only when $\frac{db}{dx}=0$, and so when the molecules of the mixed substances are of the same size, the concentration of the coexisting phases is the same for the mixture with minimum critical temperature. If the size of the molecules is not the same $x_1=x_2$ for the mixture for which

$$\left(\frac{f}{T}-\frac{1}{T_k}\right)\frac{dT_k}{dx}=-\frac{1}{b}\frac{db}{dx} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (8)$$

If $\frac{db}{dx}$ is positive, as is the case for mixtures of acetone and ether (ether as second component), then $x=x_2$ for a mixture for which $\frac{dT_k}{dx}$ is negative. Then the concentration where x_1 and x_2 are equal and therefore also the maximum pressure in the p, x line has shifted to the side of the component with the smallest molecule. If we multiply both members of (8) by T, the shifting proves to increase for increasing value of T, and so we arrive at a conclusion, to which I came already before, viz. that the concentration of the maximum value of p in the p, x curve is sufficiently the same as that of the mixture with minimum critical temperature only for the very lowest values of T. It only appears that already at ordinary temperatures the shifting mentioned above may be rather considerable. A consequence of this is, that the shifting between the ordinary temperatures and $T = T_k$ may be only slight. This shifting is however the greater as the difference in the size of the molecules is the more considerable, and as the decrease in critical temperature takes place the more slowly.

Now that we have found an approximate value for μ'_x, we can immediately derive from it an approximate value for μ''_x, a quantity which must be known, if in the equation:

$$v_{21}\, dp = (x_2 - x_1) \left(\frac{\partial^2 \zeta}{\partial x_1^2}\right)_{pT} dx_1 + \frac{w_{21}}{T}\, dT$$

the factor of dx_1 is to be considered as known. We have viz.

$$\left(\frac{\partial^2 \zeta}{\partial x_1^2}\right)_{pT} = MRT \left\{ \frac{1}{x_1(1-x_1)} + \mu''_x \right\}$$

We find then:

$$\mu''_x = -\frac{1}{MRT} \frac{d^2 \frac{a}{b}}{dx^2} + \frac{d^2\, l \frac{a}{b^2}}{dx^2},$$

or

$$\mu''_x = -\frac{f}{T} \frac{d^2 T_k}{dx^2} + \frac{d^2 l p_k}{dx^2}.$$

So for small vapour pressure the equation:

$$\frac{1}{p} \left(\frac{dp}{dx_1}\right)_T = (x_2 - x_1) \left\{ \frac{1}{x_1(1-x_1)} - \frac{f}{T} \frac{d^2 T_k}{dx_1^2} + \frac{d^2 l p_k}{dx^2} \right\}$$

holds approximately.

In general the quantity $\frac{d^2 T_k}{dx_1^2}$ will be positive, and this is certainly so when there is a minimum value for T_k; the value of the other term may change this of course. But as a rule μ''_{x_1} will be found negative for normal substances.

In the value of the quantity $\frac{T}{p}\left(\frac{dp}{dT}\right)_{x_1}$ only one of the two parts of μ'_{x_1} occurs, viz. $\frac{f}{T}\frac{dT_k}{dx_1}$ and not the other part $\frac{dlp_k}{dx_1}$. So only the part depending on T is kept. In different ways the value of this quantity may be found. It is easily found from the equation, occurring in Cont. II p. 146, slightly reduced, viz:

$$\frac{p}{MRT}=\{(1-x_1)+x_1\,e^{\mu'_{x_1}}\}\,e^{\mu_{x_1}-x_1\mu'_{x_1}-1}$$

From this form we derive, keeping x_1 constant:

$$\frac{dp}{pdT}-\frac{1}{T}=\frac{x_1\,e^{\mu'x_1}\dfrac{d\mu_{x_1}}{dT}}{1-x_1+x_1\,e^{\mu'_{x_1}}}+\frac{d\,(\mu_{x_1}-x_1\,\mu_{x_1}-1)}{dT}$$

for which we may write:

$$\frac{dp}{pdT}-\frac{1}{T}=x_2\,\frac{d\mu'_{x_1}}{dT}+\frac{d\,(\mu_{x_1}-x_1\,\mu'_{x_1})}{dT}$$

or

$$\frac{dp}{pdT}-\frac{1}{T}=(x_2-x_1)\frac{d\mu'_{x_1}}{dT}+\frac{d\mu_{x_1}}{dT}\,.$$

For $\frac{d\mu'_{x_1}}{dT}$ we find $\frac{f}{T^2}\frac{dT_k}{dx}$, and for $\frac{d\mu_{x_1}}{dT}$ we get the value $\frac{f}{T^2}T_k-\frac{1}{T}$.

Hence:

$$\left(\frac{Tdp}{pdT}\right)_{x_1}=\frac{f}{T}\left\{T_{k_1}+(x_2-x_1)\frac{dT_{k_1}}{dx_1}\right\}$$

Multiplying the second member by MRT, we find w_{21}. For w_{21} we find then 2 terms, the first $MRf\,T_k$ representing the heat of evaporation, when the mixture x_1 evaporated as an unsplit substance, and therefore the vapour phase would have the same concentration as the liquid phase. The second part $\frac{f}{T}(x_2-x_1)\frac{dT_k}{dx_1}$ denotes the modification, which is the consequence of the circumstance, that the vapour phase has another concentration than the liquid phase. This modification can be very considerable in certain cases, viz. when x_2-x_1 is very large. If T_k should depend linearly on x, then $T_{k_1}+(x_2-x_1)\frac{dT_{k_1}}{dx_1}=T_{k_2}$ and for T_{k_2} we might write in that case, denoting the components of the mixture by a and b: $T_{k_2}=T_{k_a}(1-x_2)+T_{k_b}x_2$. (Cont. II, p. 155) or $\frac{T}{p}\left(\frac{dp}{dT}\right)_{x_1}=(1-x_2)\frac{T}{p_a}\frac{dp^a}{dT}+$ $+\,x_2\frac{T}{p_b}\frac{dp_b}{dT}$. Then $w_{21}=M_a\,r_a\,(1-x_2)+M_b\,r_b\,x_2$, and the process of mixing in the liquid state will take place without heat of mixing.

If the graphical representation of T_k as function of x, is a curve (Cont. II, p. 45), lying everywhere above the tangent, which is the case when $\frac{a_1}{b_1^2}+\frac{a_2}{b_2^2}-\frac{2a_{12}}{b_1 b_2}$ is positive, then $T_{k_1}+(x_2-x_1)\frac{dT_{k_1}}{dx_1}$ is smaller than T_{k_2}.

If we draw a tangent to the curve in the point x_1, this tangent cuts the ordinate of x_2 in a point which lies lower than the curve, and the distance from that point of intersection to the curve is a measure for the quantity of heat required for mixing the condensed vapour with the liquid phase considered. As μ''_x consists of two terms, the latter of which is only negative, when the mixing in the liquid state is attended by absorption of heat, we are not justified in expecting that this latent heat of mixing alone determines the sign of μ''_x.

Physics. — "*On Px-curves of mixtures of acetone and ethyl-ether and of carbon tetrachloride and acetone at* 0° *C.*" By G. C. GERRITS. (Communicated by Prof. J. D. VAN DER WAALS).

(Communicated in the meeting of June 25, 1904).

The imperfect concordance found by CUNAEUS [1]) between the relation deduced by VAN DER WAALS [2]) in his theory between the vapour tension over a mixture of two liquids, the molecular concentration of the vapour and that of the liquid, induced us to take up the investigation once more according to the same method as had been used by CUNAEUS and with the same substances, acetone and ethyl-ether. Afterwards also mixtures of carbon tetrachloride and acetone were examined.

It had viz. appeared, that improvements might be applied to the method of investigation.

By means of the determination of the refractivity of the vapour, both of the simple substances and of the mixtures, the molecular concentration of the vapour was determined by means of the law of BIOT and ARAGO.

This determination of the refractivity was made according to the method of Lord RAYLEIGH [3]) also followed by CUNAEUS [4]).

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[1]) CUNAEUS, Proefschrift, Amsterdam, 1900, blz. 47—51.

[2]) VAN DER WAALS, Arch. Néerl. 24, blz. 44; Continuität des gasf. und flüss. Zustandes II, blz. 137.

[3]) RAYLEIGH, Proc. Roy. Institution, Vol. XV, Part. 1, pag. 1; Proc. Roy. Soc. Vol. 59, blz. 201.

[4]) CUNAEUS, Proefschrift, blz. 4—6. Proc.