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Chemistry. — "*On some phenomena, which can occur in the case of partial miscibility of two liquids, one of them being anomalous, specially water.*" By J. J. VAN LAAR. (Communicated by Prof. H. A. LORENTZ).

1. In the second part of his *Continuität* (1900)[1]) Prof. VAN DER WAALS has given the theory of the so called *longitudinal plait* on the ψ-surface, and in the last Chapter (§ 12, p. 175 sequ.) he gives moreover a special, ample discussion of this plait, in particular with regard to *anomalous* components. It is shown there, that for the appearance of certain complications, which can present themselves at this plait, one of the two components must be anomalous[2]).

In the following pages I shall try to explain the appearance of the different particular forms, which can present themselves, when one of the components is associative, specially when this anomalous component is *water*.

2. We begin to remember briefly the theory of the phenomenon of partial miscibility for binary mixtures of *normal* substances.

It is well known, that the total thermodynamic potential is represented by

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[1]) p. 41—45.

[2]) Also compare These Proceedings of Nov. 5, 1902.

$$Z = -\, \Sigma(n_1 k_1)\, T\,(log\, T - 1) + \Sigma(n_1(e_1{}^{`}{}_0) - T\, \Sigma(n_1(\eta_1)_0) -$$

$$-\int pdv + pv + RT\, \Sigma(n_1\, log\, n_1),$$

or

$$Z = \Sigma(n_1 C_1) - \left[\int pdv - RT\, \Sigma n_1\,.\, log\, \Sigma n_1 - pv\right] + RT\, \Sigma\left(n_1\, log\, \frac{n_1}{\Sigma n_1}\right).$$

Differentiating subsequently at constant T and p with respect to n_1 and n_2, we get:

$$\mu_1 = \frac{\partial Z}{\partial n_1} = C_1 - \frac{\partial \omega}{\partial n_1} + RT\, log\, \frac{n_1{}^{`}}{\Sigma n_1}$$

$$\mu_1 = \frac{\partial Z}{\partial n_2} = C_2 - \frac{\partial \omega}{\partial n_2} + RT\, log\, \frac{n_2}{\Sigma n_1}$$

where C_1 and C_2 are pure functions of the temperature, represented by

$$C_1 = -\, k_1 T\,(log\, T - 1) + (e_1)_0 - T(\eta_1)_0$$

$$C_2 = -\, k_2 T\,(log\, T - 1) + (e_2)_0 - T(\eta_2)_0$$

whereas the quantity ω is given by

$$\omega = \int pdv - RT\, \Sigma n_1\,.\, log\, \Sigma n_1 - pv\, .\quad\quad . \quad . \quad . \quad . \quad (1)$$

The meaning of the different quantities n_1, $(e_1)_0$, $(\eta_1)_0$, etc. etc. is supposed to be known.

We will substitute now the variables n_1 and n_2 by x, so that $n_1 = 1 - x$, $n_2 = x$ and $\Sigma n_1 = 1$. As ω is, just as Z, a *homogeneous* function of the *first* degree with respect to n_1 and n_2, we may write:

$$\mu_1 = C_1 - \left(\omega - x\,\frac{\partial \omega}{\partial x}\right) + RT\, log\,(1 - x)$$

$$\mu_2 = C_2 - \left(\omega + (1 - x)\frac{\partial \omega}{\partial x}\right) + RT\, log\, x$$

$$\quad\quad . \quad . \quad . \quad . \quad (2)$$

Now, when there is a plait on the Z-surface, the spinodal-curve, that is to say its projection on the T, x-plane, will be given by the condition $\dfrac{\partial^2 Z}{\partial x^2} = 0$, or also, p_1 being $= Z - x\dfrac{\partial Z}{\partial x}$, and

$$\mu_2 = Z + (1 - x)\frac{\partial Z}{\partial x},\ \text{by}\ \frac{\partial \mu_1}{\partial x} = 0\ \text{or}\ \frac{\partial \mu_2}{\partial x} = 0.$$

We therefore find for the equation of this curve in the T, x-plane:

$$x\,\frac{\partial^2 \omega}{\partial x^2} - \frac{RT}{1 - x} = 0,$$

or

$$RT = x\,(1 - x)\frac{\partial^2 \omega}{\partial x^2}.\quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

If we use the equation of VAN DER WAALS :

$$p = \frac{\Sigma n_1 \cdot RT}{v-b} - \frac{a}{v^2},$$

then we obtain.

$$\omega = \Sigma n_1 \cdot RT \, log \, (v - b) + \frac{a}{v} - RT \, \Sigma n_1 \cdot log \, \Sigma n_1 - pv \, ^1).$$

Supposing now, that in the case of liquids the external pressure p (or the vapour-tension) can be neglected with respect to the molecular pression $\frac{a}{v^2}$, the equation of VAN DER WAALS may be written :

$$\frac{a}{v^2} = \frac{\Sigma n_1 \cdot RT}{v-b},$$

and the expression for ω, when in the same manner pv is omitted by the side of $\frac{a}{v}$, passes into

$$\omega = \Sigma n_1 \cdot RT \, log \, \frac{\Sigma n_1 \cdot RT}{a/v^2} + \frac{a}{v} - RT \, \Sigma n_1 \cdot log \, \Sigma n_1 \, ,$$

or

$$\omega = \Sigma n_1 \cdot RT \, log \, \frac{RT}{a/v^2} + \frac{a}{v} \, ,$$

that is to say into

$$\omega = RT \, log \, \frac{RT}{a/v^2} + \frac{a}{v} \, ,$$

when $\Sigma n_1 = 1$. For $\frac{\partial^2 \omega}{\partial x^2}$ we find consequently :

$$\frac{\partial^2 \omega}{\partial x^2} = \frac{\partial^2}{\partial x^2} \left(\frac{a}{v} \right) - RT \frac{\partial^2}{\partial x^2} \, log \, \frac{a}{v^2} \, ,$$

by which the equation (3) of the projection of the locus of the points of inflection on the T, x-plane passes into

$$RT = x \, (1 - x) \left[\frac{\partial^2}{\partial x^2} \left(\frac{a}{v} \right) - RT \frac{\partial^2}{\partial x^2} \, log \, \frac{a}{v^2} \right],$$

or into

$$RT = \frac{x \, (1-x) \dfrac{\partial^2}{\partial x^2} \left(\dfrac{a}{v} \right)}{1 + x \, (1-x) \dfrac{\partial^2}{\partial x^2} \, log \, \dfrac{a}{v^2}} \qquad \cdots \cdots (4)$$

$^1)$ If $b = f(v)$, then $\int p dv$ still gives a term $RT \int \frac{db}{v-b}$. But this term may be regarded as independent of x, and so can be added to the temperature function C_1.

The term with $log \frac{a}{v^2}$ was introduced some time ago by VAN DER WAALS [1]); in the original theory this term was neglected, and so the equation (4) was simply $RT = x\,(1—x) \frac{\partial^2}{\partial x^2} \left(\frac{a}{v}\right)$.

In consequence of the relations $\frac{a}{v} = fRT_c$, $\frac{a}{v^2} = \gamma p_c$, where according to the variability of the liquid-volume v, the coefficients f and γ will still vary slowly with the temperature (f is the well known factor of the vapour-tension, which may be put circa 7), we can also write for (4):

$$T = \frac{fx\,(1—x) \dfrac{\partial^2 T_c}{\partial x^2}}{1 + x\,(1—x) \dfrac{\partial^2 \log p_c}{\partial x^2}} \quad \ldots \ldots \quad (4a)$$

We see, that only in the case, that the *critical pressures* of the two components *differ little*, the term with $\log p_c$ can be omitted. This will be also the case, when x is in the neighbourhood of 1 and 0. But in all other cases if would be inaccurate to omit à priori the designed term.

Further we write:

$$a = (1—x)^2\,a_1 + 2x\,(1—x)\,a_{12} + x^2\,a_2 \Big\}$$
$$v = (1—x)\,v_1 + xv_2 \qquad\qquad\qquad $$

since for liquids at low temperatures v can be supposed dependent on x in entirely the same manner as $b = (1—x)\,b_1 + xb_2$. The molecular volumes v_1 and v_2 must then be regarded, just as b_1 and b_2, as constant or as slowly varying with the temperature [2]). We then find after some reductions:

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[1]) These Proceedings, in Ternary Systems, specially IV, p. 96—100. (June 12, 1902); see also July 13, 1904, p. 145 sequ.

[2]) If we substitute in the case of liquids v by b, and then write $b = (1—x)\,b_1 + xb_2$, the difficulty arises, that in that way quantities of order $v-b$ are neglected against those of order v, and the question would present itself, if this is only upon very definite conditions *not* in contradiction with omitting p by the side of $\frac{a}{v^2}$. (This observation was kindly made to me by Prof. LORENTZ).

I hope to escape this difficulty by not substituting v by b, but by simply supposing the volume v *linearly* variable with x in the case of liquids at low temperatures; by writing therefore for v, analogous to the expression for b, $v = (1—x)\,v_1 + xv_2$. As I remarked, v_1 and v_2 still vary slowly with the temperature, whereas b_1 and b_2 of course would be perfectly constant. Now it

$$\frac{\partial^2}{\partial x^2}\left(\frac{a}{v}\right) = \frac{2}{v^3}(a_1 v_2{}^2 + a_2 v_1{}^2 - 2a_{12}v_1 v_2),$$

or — when we suppose for *normal* components the relation of BERTHELOT, viz. $a_{12} = \sqrt{a_1 a_2}$, as approximately exact:

$$\frac{\partial^2}{\partial x^2}\left(\frac{a}{v}\right) = \frac{2}{v^3}(v_2 \sqrt{a_1} - v_1 \sqrt{a_2})^2. \quad \ldots \ldots (5)$$

As the second member will be always *positive*, even if a_{12} might be $< \sqrt{a_1 a_2}$ [1]), the curve $T = f(x)$ will always turn its *convex* side to the x-axis.

We will now determine $\dfrac{\partial^2}{\partial x^2} \log \dfrac{a}{v^2}$. With $a_{12} = \sqrt{a_1 a_2}$ [2]) the expression for a becomes:

$$a = [(1-x)\sqrt{a_1} + x\sqrt{a_2}]^2,$$

so that

$$\log \frac{a}{v^2} = 2 \log \frac{(1-x)\sqrt{a_1} + x\sqrt{a_2}}{(1-x)v_1 + xv_2}.$$

Consequently we have:

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will be better justified to subsitute $\dfrac{a}{v}$ by fRT_c, than $\dfrac{a}{b}$ (and afterwards $\dfrac{a_1}{v_1}$ by fRT_1 and $\dfrac{a_2}{v_2}$ by fRT_2), where f will vary in the same manner as v with temperature. For it is easy to show, that the expression for the vapour-tension for a single substance at low temperatures is $\log \dfrac{a/v^2}{p} = \dfrac{a/v}{RT} - \displaystyle\int_l^v \dfrac{db}{v-b}$ (v is in the first two terms the liquid volume), whence we can deduce, in connexion with the empirical relation $\log \dfrac{p_c}{p} = f\left(\dfrac{T_c}{T} - 1\right)$, where f is circa 7, that $\dfrac{a}{v} = fRT_c$.

The error made by supposing v linearly variable with x, will certainly be much smaller than by putting $v = b$. In that way errors of at least 16% would be made, since $\dfrac{b}{v}$ will be nearly 5/6 for liquids in the neighbourhood of the melting-point.

The quantities v_1 and v_2 can now also immediately be substituted by the experimentally determined values in the liquid state.

[1]) See VAN DER WAALS, These Proceedings of Oct. 8, 1902, p. 294.

[2]) Although there is no sufficient reason for this relation, I have supposed it *approximately* exact, also because only in this case a simple expression could be obtained for $\dfrac{\partial^2}{\partial x^2} \log \dfrac{a}{v^2}$.

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$$\frac{\partial}{\partial x} \, log \, \frac{a}{v^2} = 2 \left[\frac{\sqrt{a_2} - \sqrt{a_1}}{\sqrt{a}} - \frac{v_2 - v_1}{v} \right],$$

and therefore

$$\frac{\partial^2}{\partial x^2} \, log \, \frac{a}{v^2} = 2 \left[\frac{(v_2 - v_1)^2}{v^2} - \frac{(\sqrt{a_2} - \sqrt{a_1})^2}{a} \right] \quad \ldots \quad (6)$$

This expression can be reduced to a different form, and then we find:

$$\frac{\partial^2}{\partial x^2} \, log \, \frac{a}{v^2} = \frac{2}{av^2} (v_2 \sqrt{a_1} - v_1 \sqrt{a_2}) \left[(v_2 \sqrt{a_1} - v_1 \sqrt{a_2}) + 2 v (\sqrt{a_2} - \sqrt{a_1}) \right],$$

whence it appears, that the factor $v_2 \sqrt{a_1} - v_1 \sqrt{a_2}$ occurs in the expression for $\frac{\partial^2}{\partial x^2} \, log \, \frac{a}{v^2}$ as well as in that for $\frac{\partial^2}{\partial x^2} \left(\frac{a}{v} \right)$.

Now when $v_2 \sqrt{a_1} = v_1 \sqrt{a_2}$ or $\frac{a_1}{v_1^2} = \frac{a_2}{v_2^2}$, when in other words the *critical pressures* of the two components are *equal*, then $\frac{\partial^2}{\partial x^2} \, log \, \frac{a}{v^2}$ becomes $= 0$.

But then *simultaneously* $\frac{\partial^2}{\partial x^2} \left(\frac{a}{v} \right)$ will be $= 0$, and the whole longitudinal plait will disappear, (at the same time the curve $T_c = f(x)$ will then pass into a straight line).

We see therefore, that for occurrence of the phenomenon of partial miscibility at attainable, that is too say at not to low temperatures, the *critical pressures* of the two components *must differ as much as possible*.

Now this is *not* the case for the greater part of *normal* substances, and that is the explanation of the well known fact, that for mixtures of normal substances the phenomenon of limitated miscibility has been so very rarely found at the common temperatures.

When we substitute (5) and (6) in the equation (4), then we find finally:

where

$$\left. \begin{array}{l} RT = 2 \, x \, (1 - x) \, \dfrac{(v_2 \sqrt{a_1} - v_1 \sqrt{a_2})^2}{v^3} : (1 + \Delta), \\[3mm] \Delta = 2 \, x \, (1 - x) \left[\dfrac{(v_2 - v_1)^2}{v^2} - \dfrac{(\sqrt{a_2} - \sqrt{a_1})^2}{a} \right] \end{array} \right\} \quad \ldots \quad (7)$$

This would be a pure parabola, if v and $1 + \Delta$ were independent of x.

3. We will now determine the values of x and T for the "*critical point of miscibility.*" For this the conditions $\frac{\partial \mu_1}{\partial x} = 0$ and $\frac{\partial^2 \mu_1}{\partial x^2} = 0$

combined must be satisfied, or — what is the same — the conditions

$$\frac{\partial \mu_1}{\partial x} = 0 \quad ; \quad \frac{dT}{dx} = 0,$$

as is obvious. Now from (7) follows, when $1 + \Delta$ is supposed independent of x, which will be certainly permitted, in consequence of the small values of Δ in the case of normal substances.

$$R\frac{dT}{dx} = \frac{2\,(v_2\,\sqrt{a_1} - v_1\,\sqrt{a_2})^2}{1+\Delta}\left\{\frac{1-2\,x}{v^3} - \frac{3\,x\,(1-x)}{v^4}(v_2 - v_1)\right\},$$

as $v = v_1 + x\,(v_2 - v_1)$. This expression becomes $= 0$, when

$$(1 - 2x)\,(1 + rx) - 3\,rx\,(1 - x) = 0,$$

where $r = \dfrac{v_2 - v_1}{v_1}$. This yields:

$$rx^2 - 2\,(r + 1)\,x + 1 = 0,$$

whence

$$x_c = \frac{1}{r}\left\{(r + 1) - \sqrt{r^2 + r + 1}\right\}.$$

When $r = 0$, that is to say when $v_1 = v_2$, then $x_c = 0.5$. At all events this will be *approximately* the case, if Δ should still be in any way dependent on x.

We will reduce now the equation (7) somewhat. With $a_1 = fRT_1v_1$ and $a_2 = fRT_2v_2$, where T_1 and T_2 are the critical temperatures of the components, these equations pass, after substituting x_c for x, into

$$RT_c = 2\,x_c\,(1 - x_c)\,\frac{[v_2\,\sqrt{fRT_1v_1} - v_1\,\sqrt{fRT_2v_2}]^2}{v_1^3\left(1 + x\,\dfrac{v_2 - v_1}{v_1}\right)^3} : (1 + \Delta_c)$$

$$\Delta_c = 2\,x_c\,(1 - x_c)\left\{\frac{(v_2 - v_1)^2}{v_1^2\left(1 + x\,\dfrac{v_2 - v_1}{v_1}\right)^2} - \frac{(\sqrt{T_2v_2} - \sqrt{T_1v_1})^2}{[\sqrt{T_1v_1} + x\{\sqrt{T_2v_2} - \sqrt{T_1v_1}\}]^2}\right\}$$

or with $T_2 = \theta T_1$ and $v_2 = \varphi v_1$ into

$$T_c = 2\,f\,x_c\,(1 - x_c)\,\frac{\varphi\,(\sqrt{\varphi} - \sqrt{\theta})^2}{(1 + (\varphi - 1)\,x_c)^3}\,T_1 : (1 + \Delta_c)$$

$$\Delta_c = 2\,x_c\,(1 - x_c)\left\{\frac{(\varphi - 1)^2}{(1 + (\varphi - 1)\,x_c)^2} - \frac{(\sqrt{\theta\varphi} - 1)^2}{(1 + (\sqrt{\theta\varphi} - 1)\,x_c)^2}\right\} \quad . \quad (8)$$

since $(\varphi - \sqrt{\theta\varphi})^2 = \varphi\,(\sqrt{\varphi} - \sqrt{\theta})^2$.

We shall illustrate these equations by an example. In order to find the critical point as high as possible, we will choose two

normal substances, of which the critical pressures differ as much as possible. We take therefore *ether* and *carbon disulphide*. The critical data are the following:

$$CS_2 \quad \bigg| \quad T_1 = 548° \quad ; \quad p_1 = 76 \; atm.$$
$$ether \quad \bigg| \quad T_2 = 467° \quad ; \quad p_2 = 35 \; atm.$$

In order to determine $\varphi = \dfrac{v_2}{v_1}$, we remark, that $v_1 = \dfrac{fR}{\gamma} \cdot \dfrac{T_1}{p_1}$, $v_2 = \dfrac{fR}{\gamma} \cdot \dfrac{T_2}{p_2}$, as for instance $\dfrac{a_1}{v_1} = fRT_1$ and $\dfrac{a_1}{v_1^2} = \gamma p_1$. We have therefore:

$$\frac{v_2}{v_1} = \frac{T_2}{p_2} \; : \; \frac{T_1}{p_1} = \frac{T_2}{T_1} \times \frac{p_1}{p_2},$$

that is to say $\underline{\varphi = \theta \, \pi}$, where the proportion $\dfrac{p_1}{p_2}$ is represented by π.

Now for the designed substances $\theta = 0,852$, $\pi = 2,17,$ so that we find $\varphi = 1,85$. Since $r = \varphi - 1$, the equation for x_c passes into

$$x_c = \frac{1}{\varphi - 1} (\varphi - \sqrt{\varphi^2 - \varphi + 1}), \quad \cdots \quad (9)$$

and hence we find for x_c the value $0,29$. Further $\sqrt{\theta} = 0,923$, $\sqrt{\varphi} = 1,36$, $f = 7$, and so (8) becomes:

$$T_c = \frac{14 \times 0,206 \times 1,85 \times 0,191}{(1,247)^3} \, 548 : (1 + \Delta_c),$$

or

$$T_c = \frac{1,019}{1,94} \, 548 : (1 + \Delta_c) = 288 : (1 + \Delta_c).$$

We have further:

$$\Delta_c = 0,412 \left\{ \frac{0,723}{1,555} - \frac{0,0650}{1,153} \right\} = 0,412 \times 0,409 = 0,169,$$

so that we find for $1 + \Delta_c$ the value $1,17$.

Hence T_c becomes $288 : 1,17 = 246 = \underline{- 27° C}$.

The critical point of the chosen substances lies therefore still a *thirty* degrees *beneath* the common zero of Celsius. And for the greater majority of other normal substances we will find for T_c still much smaller values — because the critical pressures will differ there in most of the cases less than in the case of ether and CS_2.

4. All that precedes now undergoes important modifications, when one of the two components is *anomalous*, specially *water*. For in the first place the *critical pressure* of the water is *very high*, not

less than 198 atm., so that it will differ much from the critical pressures of most of the other substances. And in the second place the value of v_1 is here so *extraordinarily variable* with the temperature. Water is in this respect exceptional in Nature, and gives therefore rise to very peculiar phenomena, which are not found with other substances, or not in that degree. Alcohol e.g. is also an anomalous substance, but neither is the variability ' of the molecular volume there particularly great, nor the critical pressure particularly high.

We know, that the variation of the molecular volume finds its cause in the decomposition of the *double molecules* with the temperature. Because v_1 gradually grows smaller and smaller, the quantity

$$(v_2\sqrt{a_1}-v_1\sqrt{a_2})^2,$$

which principally determines the value of T_c, will become greater and greater. And the initial value of that quantity is in the case of water as one of the components already higher than for mixtures of normal substances. This is connected with the high critical pressure of water, being 198 atm., whence can be calculated, that the critical pressure — if water continued to consist of only double molecules — would yet still amount to circa 66 atm., i.e. higher than that of most of the normal substances. [Of course the designed expression will increase with decreasing values of v, only when $\dfrac{\sqrt{a_1}}{v_1} > \dfrac{\sqrt{a_2}}{v_2}$,

that is to say, when the critical pressure of the first component is greater than that of the second. This condition will nearly always be satisfied, when we assume water as the *first* component].

As said, the decrease of v_1 is very considerable in the case of water. I remember, that I found some years ago [1]), that for 18 Gr. water $v_1 = 19,78$ ccm., when all the molecules are *double*; and only $= 11,34$ ccm. for 18 Gr., when all the molecules are *single*. When therefore the temperature increases from nearly $- 90°$ C., where all the molecules are double (supposing, that the water had not congealed long before), to circa 230° C., where all the molecules have become single, then v_1 will diminish down to nearly $^4/_7$ of its original value.

[In the same Memoir I showed, that in this fact lies also the explication — qualitative as well as quantitative — of the well-known phenomenon of maximum density at 4° C.]

Now the consequence of this variability of v_1 will be, that the second member of (7) — we will represent it (divided by R) in

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1) Z. f. Ph. Chemie **31** (Jubelband VAN 'T HOFF), p. 1—16, specially p. 13.

the following by K — will be no longer a constant for a definite value of x, but a function of temperature.

If we draw therefore (see fig. 1) the straight line OM, which divides into halves the angle of coordinates (OT is the axis of temperature, OA' that of the values of K) — then for mixtures of *normal* substances the point of intersection of the *straight* line $K =$ const., which runs consequently parallel with the T-axis, with the line OM will represent the temperature, corresponding in the T,x-projection of the spinodal curve with the chosen value of x. If this were x_c, then we should find in this manner T_c. That temperature will be — as we have shown on the preceding pages — extremely low.

On the other hand, in the case of *anomalous* mixtures, that is here: where one of the components is an associative substance, the straight line AA' will transform itself into *two straight* lines, joined by a *curve* (see fig. 2). The first straight line corresponds then with the temperatures, where all the molecules are double, that is therefore in the case of water below $-90°$ C.; the second straight line will correspond with the temperatures, where all the molecules have become single — so for water above $230°$ C. The joining curve will correspond with the temperatures between $-90°$ C. and $230°$ C., where the process of dissociation of the double molecules is going on.

Several cases can occur here, which presently we will briefly discuss.

5. We should now have to deduce an expression for RT and Δ, analogous to (7), but this time for the case that one of the substances is anomalous. The required considerations and calculations will not be reproduced here, however, because I shall do so in the more ample Memoir, which will soon be published in the *Archives Teyler*. We therefore will limit ourself to the communication of the final result, viz.

$$
\left.
\begin{aligned}
RT &= 2x(1-x)\left(1+\frac{1-\beta}{1+\beta}x\right)\frac{(v_2\sqrt{a_1}-v_{01}\sqrt{a_2})^2}{v^3} : (1+\Delta) \\
\Delta &= 2x(1-x)\left(1+\frac{1-\beta}{1+\beta}x\right)\left[\Sigma n_1\left\{\frac{(v_2-v_{01})^2}{v^2}-\frac{(\sqrt{a_2}-\sqrt{a_1})^2}{a}\right\}-\right. \\
&\quad -\left.(1-\beta)\left\{\frac{v_2-v_{01}}{v}-\frac{\sqrt{a_2}-\sqrt{a_1}}{a}\right\}\right].
\end{aligned}
\right\} (10)
$$

These expressions come in the place of the former expressions (7). Of course they are somewhat more complicated, but they have essentially the same form, as will be discussed amply in the designed Memoir. It will only be remarked, that $\Sigma n_1 = \frac{1+\beta}{2}+\frac{1-\beta}{2}x$,

where β is the degree of dissociation of the double molecules, that $v_{01} = \frac{1}{2}(1-\beta)v_0 + \beta v_1$, where v_0 is the molecular volume of the double molecules, and v_1 represents that of the single molecules, and then once more the relation $a_{12} = \sqrt{a_1 a_2}$ has been used, by which again the calculation of Δ was practically possible.

The expression for a reduced, in consequence of $a_0 = 4a_1$, $a_{01} = 2a_1$, $a_{02} = 2a_{12}$, to

$$a = (1-x)^2 a_1 + x^2 a_2 + 2x(1-x) a_{12}.$$

That for b or v to $v = (1-x)v_{01} + x v_2$, where v_{01} has the meaning as is indicated above. (The index 0 relates to the double molecules, the index 1 to the single molecules of the associative substance; the index 2 relates to the second, normal substance).

As is already briefly indicated above, it will be principally the factor $(v_2 \sqrt{a_1} - v_{01} \sqrt{a_2})^2$, on which the phenomenon, studied by us, depends. *The great variability of the quantity v_{01} with the temperature is the only cause* of all these peculiar phenomena of partial miscibility, occurring in the case of mixtures, when one of the components is anomalous, specially water.

That factor will increase more and more with the temperature, because v_{01} decreases in consequence of the continual formation of new single molecules from the dissociating double molecules — a single molecule being much smaller than half a double molecule. (compare § 4).

It is evident, that the denominator v^3 (by v_{01}) will equally diminish with the temperature, so that the value of the second member of (10) will increase still more. The variations of the other terms have comparatively but little influence.

6. What will now be the different forms of the plait — i. e. in the T,x representation — when the course of the curve $K = f(T)$ (see § 4) is continually modified with the different components added to the water? (We call attention to the fact, that K represents the second member of (10), divided by R, and that the following figures indicate therefore the *graphical* solution of the equation $T = K$ with respect to T).

a. The case of normal substances has already been considered by us. It is represented by fig. 1. The spinodal curve will have the same form as in fig. 2.

b. In fig. 2 the straight part of the curve $K = f(T)$, where K has the initial value K_1 (all molecules are still double), intersects the line OM in the point A; whereas the curved part, and the

second straight part, where K assumes the final value K_2 (all molecules have become single), lie wholly on the *right* of OM. The plait will consequently be identical with that of the preceding case — only with this difference, that the point A lies below $-90°$ C., where the dissociation of the double molecules begins, so that this point lies wholly *beyond* the region of attainable temperatures.

c. As soon as the value of K increases a little, we get the case of transition of fig. 3. The curve $K = f(T)$ *touches* now the line OM in B,C, and from this moment the *isolated* plait will begin to appear, extending itself above the just regarded normal plait, which lies in unattainable depth. Here it is only two coinciding critical points in the one point B,C.

d. When the value of K_1 is still a little greater, the case of fig.4 will present itself, where the line OM is intersected, besides in A, in still two other points B and C. The isolated plait above the normal one is formed now, with two critical points, a *lower* one in B and an *upper* one in C. Everywhere between B and C K is $> T$, just as below A, so that we are, in consequence of $\dfrac{\partial^2 Z}{\partial x^2} < 0$, in the unstable region, i. e. within the spinodal line of the plait.

This case — or the case of fig. 6 — is realised by a great number of substances, also in the case of *two* anomalous substances [1]).

α. In some cases the *upper* critical point is found, as in the case of water and $CO_{C_2H_5}^{CH_3}$ (Rothmund.), and of H_2O and *isobutyl-alcohol* (Alexejew); propably also in the case of water and *ether* (Klobbie and Alexejew), of H_2O and CO $(C_2H_5)_2$ (Rothmund), of H_2O and *ethyl-acetate* (Alexejew), and of H_2O and *amyl-alcohol* (Alexejew), in which latter cases, however, the point C was not reached. As to water and ether e.g., Klobbie has already found, that the values of x of the two coexisting liquid phases reapproach each other, when the temperature is lowered. That is an indication for the existence either of a lower critical point, lying still more down or of a contraction as in fig. 6.

β. In other cases it is only the *lower* critical point, that is observed, as in the case of water and *triethylamine* (Rothmund), water and *diethylamine* (Guthrie), and of water and *β-collidine* (Rothmund).

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[1]) Many anomalous substances namely can be regarded as normal ones, because the variation of v is so small; only in the case of water this variation is exceptionally great.

According to these observations the first mixture has its critical point (B) at nearly 18° C., the third at 6° C. [1]).

In the case of water and *nicotine*[2]) HUDSON (Z. f. Ph. Ch. **47**, p. 113) has observed the complete isolated plait. But here a hydrate is formed, being decomposed continually, when the temperature rises. The theory of the phenomenon remains however formally the same: everywhere, where a pretty considerable variaton in the value of v presents itself — whatever should be the cause of it — the existence of such a plait may be expected — as soon as the required conditions are satisfied.

Still another example is found in mixtures of *carbonic-acid* and *nitrobenzol* (BÜCHNER), which makes it probable, that CO_2 in *liquid* state is an associative liquid. Indeed, there exist important reasons in the thermal behaviour of that substance which would confirm that supposition.

ATEN has observed, that CH_3Cl and *pyridine* mix in every proportion, but that the *combination*, which is soon formed. is nearly unmixable with both components. In this case again there is found a *lower* critical point, for *both* plaits — i. e. for that, formed by CH_3Cl and the combination, and for that, formed by pyridine and the combination.

It is a matter of course that the existence of a *lower* critical point necessarily determines that of an *upper* one. With rise of temperature the *liquid* mixture approaches more and more to a *gaseous* one, where of course miscibility in every proportion takes place. (How the plait can transform itself there, and pass into the transversal plait, lies entirely without the plan of this inquiry).

Inversely we can *not* always conclude from the existence of an upper critical point to that of a lower one, because — even, when the connodal curve begins to. contract downward — the case of fig. 6 can occur.

But this is certain, that when an *upper* critical point is found at ordinary temperatures, we have *always* to deal with the point C, and not with A, the latter always lying (see fig. 2) in the case of mixtures of water and a normal (or anomalous) substance below — 90° C., and in the case of mixtures of two normal substances (compare § 3) at most some thirty degrees below 0° C.

Nearly always there may therefore be expected the case of fig. 4,

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[1]) KUENEN (Phil. Mag. [6] **6**, p. 637—653 (1903)) could however not confirm the existence of a lower critical point for diethylamine. In an earlier Memoir KUENEN has found also a *lower* critical point for mixtures of C_2H_6 and *ethyl-isopropyl-* and *butyl-alcohol.*

or that of fig. 6, when partial miscibility presents itself. The *normal* plait with the critical point in A will appear only in a great minority of cases, and can be regarded as highly exceptional. So the mixtures of water with *phenol* (ALEXEJEW), with *succinitrile* (SCHREINEMAKERS), with *aniline* (ALEXEJEW), with *isobutylic-acid* (id.), etc., etc. — which all present an upper critical point — will offer with great certainty examples of the very general case of fig. 6 or of that of fig. 4.

e. Fig. 5 again represents a transitory case, where the value of K_1 is still a little greater than in fig. 4. The two plaits — the normal one and the isolated one — will coincide from this moment into one *continual* plait.

f. This will be the case in fig. 6. It is observed for mixtures of water and *secondary butyl-alcohol* (ALEXEJEW). But, as we already remarked above, many observations with an upper critical point may belong just as well — whether the compositions of the two coexisting phases approach each other at lower temperatures or not — to this case as to that of fig. 4. The example mentioned belongs with certainty to the class of fig. 6, because it is observed, that the values of x after beginning to approach each other diverge again at still lower temperatures.

Fig. 7 shows, that the contraction at D, where the curve $K = f(T)$ comes into the neighbourhood of the line OM, gradually vanishes, so that the plait at last again will assume the *normal* form — only with this difference, however, that the critical point C of our quasi-normal plait will appear at higher temperatures than the critical point A of the real normal plait.

Remark. It will be superfluous to remark, that the *numerical* calculations by means of the formula (10) can be executed only then, when the conditions are satisfied, on which that expression is deduced. That will accordingly only be the case, when really p is to be omitted against $\dfrac{a}{v^2}$ (see § 2), that is to say at temperatures, which are not higher than circa half the critical temperature (in the ordinary meaning) of the mixture.

7. The question rises now, what will be the conditions to be satisfied, that the transitory cases of the figs. 3 and 5 may present themselves. Here too we only communicate the results of the calculations, that we have made on this subject. We found namely, that the *isolated* plait (fig. 4) is only possible, when the second (normal) substance has a *critical pressure between* circa 35 *and* 70 *atm.*, and

fig 1

fig 2

fig 3

fig 4

fig 5

fig 6

fig 7
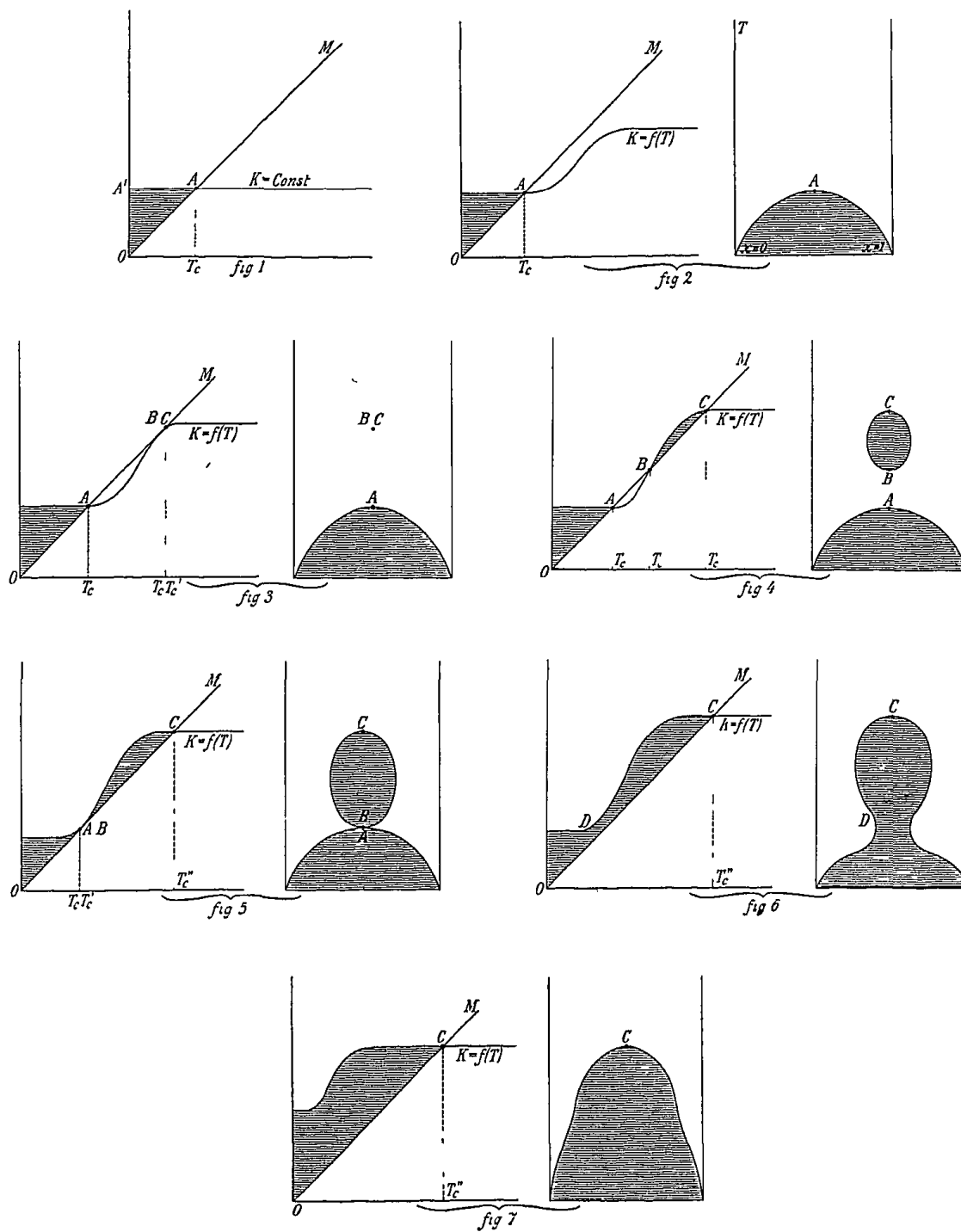
this nearly independent of the critical temperature of these substances (provided that the latter is .between $^1/_2$- and 1-time of that of the water).

All normal [1]) substances, which possess a *critical pressure above* $\pm$ 70 *atm.*, mix in every proportion with water; all such substances, having a *critical pressure below* $\pm$ 35 *atm.*, will form a *continual plait* (fig. 6).

To the first group of substances belong those with relatively *small molecular volume* (many anorganic substances and salts); to the second group those with relatively *great molecular volume* (many organic substances).

As to the factor $1 + \Delta = 1 + x(1 - x)\dfrac{\partial^2 \log p_c}{\partial x}$, the calculations have taught, that this factor at *higher* temperatures, where β comes into the neighbourhood of 1, can become very great, and also will be pretty strongly variable with x. So I found for that factor for $\beta = 1$ ($T = 230°$) the values 2,57, 2,54, 2,25, 1,94 and 1,70, resp. for $x = 0,1$, 0,2, 0,3, 0,4 and 0,5. But at such high temperatures the deduced formulae are not longer exact, p being in that case no longer to be neglected against $^a/_{v^2}$.

However, for *lower* temperatures, where β approaches 0, $1 + \Delta$ will not differ much from 1, and will be little dependent on x. At these temperatures — and for *these* temperatures the formulae are deduced — $1 + \Delta$ can, when not neglectable, yet be regarded as a constant factor. So I found for $1 + \Delta$ the values 1,08, 1,10, 1,10, 1,09 and 1,08, resp. for $x = 0,1$ unto 0,5.

Finally, I have applied the formula (10) for the case of *triethylamine* and water, and found that, whenever the critical pressure, viz. 30 atm., lies below the above designed limiting pressure of 35 atm., the appearance of a lower critical point at circa 18° C. is not in contradiction with the given theory. It must not be forgotten here, that when the temperature, where β is practically $= 0$, lies above $- 90°$ C., the limit in question also will lie below 35 atm.

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[1]) And as we have already seen above, also many *anomalous* substances, where the variability of v is small.