

Physics. — “*On the Heat of Mixing of Normal and Associating Liquids.*” By Dr. J. J. VAN LAAR. (Communicated by Prof. H. A. LORENTZ).

(Communicated at the meeting of September 30, 1922).

1. In connection with a study by J. R. KATZ (published in „Verlag der Wis- en Natuurk. Afdeeling Kon. Akad. v. Wetensch.” Vol. XXXI, nos 5/6, p. 333—336) I wish to make a few remarks on the heat of mixing of liquids, also in reference to the quantity a/v^2 (or a/b^2).

Different authors, among others VAN DER WAALS and myself, made use of approximations some time ago, which seemed permissible; but which gave no account, not even in approximation, of the heat-effect, which is sometimes very slight, especially for normal substances. For here the case presented itself that the neglected quantities $(v-b)^2$ by the side of v^2 , p by that of a/v^2 would give a term of higher order of magnitude in the results than that which results from the not neglected part. The latter term appears to be of the order of magnitude $(b_2\sqrt{a_1}-b_1\sqrt{a_2})^2$, whereas that of the neglected part — yielding a term with $(p + a/v^2) \Delta v$ — is of the order $b_2\sqrt{a_1}-b_1\sqrt{a_2}$, on account of Δv ; hence, when the difference of the critical pressures of the components is small, the neglected part will have a much greater value than the not neglected part.

And besides: While the first part — referring to the change of the potential energy without reference to the contraction — will always be *positive*, the second (neglected) part — which is in connection with the *volume contraction* Δv — is nearly always *negative*. In “quasi-ideal” mixtures of two liquids (i.e. liquids the critical pressures of which are about equal), the effect will nearly always be *negative* (i.e. heat is *liberated*), and not *positive*, as the earlier theoretical derivation indicated. In liquids the critical pressures of which are not about equal, sometimes differ even considerably, it will entirely depend on circumstances (relation of the a 's and b 's inter se, value of the mixing ratio x) whether the result will be positive or negative.

In associated components, where Δv can become much greater than in mixtures of normal components (generally the critical pressures also differ much more from each other), the above ratios will

be more greatly accentuated, and the negative term with $(p + a/v^2)\Delta v$ will predominate still more.

Already BAKHUIS ROOZEBOOM — now about twenty years ago — drew my attention to the insufficiency of the approximative expression, but at the time we attributed this to other causes ¹⁾, thinking that — especially in quasi-ideal mixtures — the possible volume-contraction would probably be quite negligible. Not until 1912, when in a letter my friend Prof. KREMANN at Graz put a question to me on this subject, was I led to carry out the perfectly accurate calculation of the quantity Δv ²⁾.

In what follows I may be allowed to give the exact theory, first of all of mixtures of normal components. Here too the perfectly accurate derivation appears to be by no means more difficult or longer than the approximated derivation, and the result is almost equally simple. The same thing is found here as before with the exact derivation of the equations of the spinodal and the plaitpoint line ³⁾. There the perfectly accurate results are even simpler than the earlier approximated expressions.

2. Heat of mixing of normal components.

From the well-known expression for the total energy

$$e = e' + kT - \frac{a}{v} + pv,$$

in which the energy constant e' is $= n_1 e'_1 + n_2 e'_2$, and the heat capacity at constant (infinitely great) volume $k = n_1 k_1 + n_2 k_2$, we find for the pure components:

$$\left. \begin{aligned} e_1^{\circ} &= e'_1 + k_1 T - \frac{a_1}{v_1^{\circ}} + pv_1^{\circ} \\ e_2^{\circ} &= e'_2 + k_2 T - \frac{a_2}{v_2^{\circ}} + pv_2^{\circ} \end{aligned} \right\}$$

For the *integral* heat of mixing of n_1 gr. mol. of one component and n_2 gr. mol. of the other component the expression

¹⁾ Inaccuracy of VAN DER WAALS' equation of state; non-validity of BERTHELOT'S assumption $\alpha_{12} = \sqrt{a_1 a_2}$, etc. But since then I have got more than ever convinced of the absolute validity (in liquids) of the said equation and B's assumption. Of course a and b then have *other* values than in the gaseous state, but this need, of course, not be considered here.

²⁾ Later inserted summarized in his valuable — unfortunately too little known — book: "Die Eigenschaften der binären Flüssigkeitsgemische etc." (Sammlung (HERZ) chemischer Vorträge Bd. 23, Stuttgart, Enke, 1916); see p. 170—171.

³⁾ These Proc. Vol. VII, p. 646; Vol. VIII, p. 33.

$$w = - \left(\frac{a}{v} - n_1 \frac{a_1}{v_1^0} - n_2 \frac{a_2}{v_2^0} \right) + p (v - n_1 v_1^0 - n_2 v_2^0) \quad (\alpha)$$

is at once found from

$$w = e - (n_1 e_1^0 + n_2 e_2^0).$$

Now

$$\frac{a}{v} = \frac{a}{v_0} + \left(\frac{a}{v} - \frac{a}{v_0} \right) = \frac{a}{v_0} - \frac{a}{v v_0} \Delta v,$$

in which $v_0 = n_1 v_1^0 + n_2 v_2^0$, and $v - v_0 = \Delta$ is written. Further $a = (n_1 \sqrt{a_1} + n_2 \sqrt{a_2})^2$, and from this follows:

$$\frac{a}{v_0} = \left(n_1 \frac{a_1}{v_1^0} + n_2 \frac{a_2}{v_2^0} \right) - n_1 n_2 \frac{(v_2^0 \sqrt{a_1} - v_1^0 \sqrt{a_2})^2}{v_0 v_1^0 v_2^0}.$$

Hence:

$$w = n_1 n_2 \frac{(v_2^0 \sqrt{a_1} - v_1^0 \sqrt{a_2})^2}{v_0 v_1^0 v_2^0} + \left(p + \frac{a}{v v_0} \right) \Delta v \quad (1)$$

Remarks. a. Formerly ¹⁾ the following equation was written:

$$\frac{a}{v} = \frac{a}{v} + \left(\frac{a}{v^2} (v-b) + p(v-b) - (n_1 + n_2) RT \right),$$

on account of the equation of state. This gives:

$$\frac{a}{v} = \frac{a}{v^2} (2v-b) + p(v-b) - (n_1 + n_2) RT = \frac{a}{b} \left(1 - \left(\frac{v-b}{v} \right)^2 \right) + p(v-b) - (n_1 + n_2) RT,$$

hence:

$$e = e' + \left(k + (n_1 + n_2) R \right) T - \frac{a}{b} \left(1 - \frac{(v-b)^2}{v^2} \right) + pb,$$

for which $e = e' + k' T - a/b$ was written — with an apparently perfectly justifiable neglect of some terms. Then we get:

$$w = n_1 n_2 \frac{(b_2 \sqrt{a_1} - b_1 \sqrt{a_2})^2}{b b_1 b_2}.$$

It is seen that the very essential term $\frac{a}{v v_0} \Delta v$ is omitted.

b. We might also have written:

$$\frac{a}{v} = n_1 \frac{a_1}{v_1} + n_2 \frac{a_2}{v_2} - n_1 n_2 \frac{(v_2 \sqrt{a_1} - v_1 \sqrt{a_2})^2}{v v_1 v_2},$$

in which $v_1 = \frac{\partial v}{\partial n_1}$ and $v_2 = \frac{\partial v}{\partial n_2}$. For according to a property of the

¹⁾ Cf. among others Zeitschr. f. physik. Ch. 63, p. 219 (1908).

homogeneous functions of the first degree with regard to n_1 and n_2 , we have $v = n_1 v_1 + n_2 v_2$. And further according to (a):

$$w = n_1 n_2 \frac{(v_2 \sqrt{a_1} - v_1 \sqrt{a_2})^2}{v v_1 v_2} + n_1 \left(\frac{a_1}{v_1 v_1^0} - \frac{a_1}{v_1} \right) + n_2 \left(\frac{a_2}{v_2 v_2^0} - \frac{a_2}{v_2} \right) + p (n_1 (v_1 - v_1^0) + n_2 (v_2 - v_2^0)),$$

or also

$$w = n_1 n_2 \frac{(v_2 \sqrt{a_1} - v_1 \sqrt{a_2})^2}{v v_1 v_2} + \left(p + \frac{a_1}{v_1 v_1^0} \right) n_1 \Delta v_1 + \left(p + \frac{a_2}{v_2 v_2^0} \right) n_2 \Delta v_2, \quad (1^a)$$

which expression will at once appear to be useful.

Here is $v_1 - v_1^0 = \Delta v_1$ and $v_2 - v_2^0 = \Delta v_2$ and evidently we have $\Delta v = v - v_0 = (n_1 v_1 + n_2 v_2) - (n_1 v_1^0 + n_2 v_2^0) = n_1 \Delta v_1 + n_2 \Delta v_2$.

For the differential heats of mixing $w_1 = \frac{\partial w}{\partial n_1}$ and $w_2 = \frac{\partial w}{\partial n_2}$ we now have from (1^a):

$$w_1 = n_2 \frac{(v_2 \sqrt{a_1} - v_1 \sqrt{a_2})^2}{v_1 v_2} \frac{\partial}{\partial n_1} \left(\frac{n_1}{v} \right) + \left(p + \frac{a_1}{n_1 v_1^0} \right) \Delta v_1,$$

$$\text{or as } \frac{\partial}{\partial n_1} \left(\frac{n_1}{v} \right) = \frac{v - n_1 v_1}{v^2} = \frac{n_2 v_2}{v^2} :$$

$$w_1 = n_2^2 \frac{(v_2 \sqrt{a_1} - v_1 \sqrt{a_2})^2}{v^2 v_1} + \left(p + \frac{a_1}{v_1 v_1^0} \right) \Delta v_1$$

Likewise

$$w_2 = n_1^2 \frac{(v_2 \sqrt{a_1} - v_1 \sqrt{a_2})^2}{v^2 v_2} + \left(p + \frac{a_2}{v_2 v_2^0} \right) \Delta v_2 \quad \left. \begin{array}{l} \dots \\ \dots \end{array} \right\} \quad (2)$$

¹⁾ In these differentiations many parts have not been taken into account. For in general v_1 and v_2 are still functions of n_1 and n_2 . But as the neglected parts in w_1 and w_2 can always be represented by $z_1 = \frac{\partial z}{\partial n_1}$ and $z_2 = \frac{\partial z}{\partial n_2}$, in which z , just as w , will always be a homogeneous function of the first degree with respect to n_1 and n_2 , necessarily $n_1 z_1 + n_2 z_2$ will have to be $= 0$, $n_1 w_1 + n_2 w_2$ already being $= w$ according to (2). Now also $n_1 z_1 + n_2 z_2 = z$, hence z is identically $= 0$, hence also z_1 and z_2 .

It would indeed not be difficult to show directly the disappearance of the parts z_1 and z_2 , which have been left out of account. As to z_1 , we get the result:

$$\frac{1}{v} \left(n_1 \frac{a_1}{v_1} + n_2 \frac{a_2}{v_2} \right) \left(n_1 \frac{\partial v_1}{\partial n_1} + n_2 \frac{\partial v_2}{\partial n_1} \right),$$

in which the last factor will disappear in consequence of $\frac{\partial v_2}{\partial n_1} = \frac{\partial v_1}{\partial n_2}$, as v_1 is a homogeneous function of the 0th degree with respect to the molecular numbers n_1 and n_2 .

For liquids p may of course always be cancelled against the so much greater molecular pressure a/v^2 .

We will just mention that the earlier — inaccurate — expressions were:

$$w_1 = n_2 \frac{(b_2 \sqrt{a_1} - b_1 \sqrt{a_2})^2}{b^2 b_1} ; \quad w_2 = n_1 \frac{(b_2 \sqrt{a_1} - b_1 \sqrt{a_2})^2}{b^2 b_2}.$$

3. Volume contraction with normal components.

We must now try to find an expression for Δv , and then also for Δv_1 and Δv_2 , in order to be able to substitute in (1) and (2), and to form an opinion of the order of magnitude of the different parts. As

$$\Delta v = v - v_0 = v - (n_1 v_1^0 + n_2 v_2^0),$$

we have also:

$$\Delta v = b - (n_1 b_1 + n_2 b_2) + (v - b) - n_1 (v_1^0 - b_1) - n_2 (v_2^0 - b_2).$$

Now $b = n_1 b_1 + n_2 b_2$, hence after application of the equation of state, there remains:

$$\Delta v = \frac{(n_1 + n_2) RT}{p + a/v^2} - \frac{n_1 RT}{p + a_1/v_1^0{}^2} - \frac{n_2 RT}{p + a_2/v_2^0{}^2},$$

i.e. with neglect of p :

$$\Delta v = RT \left[(n_1 + n_2) \frac{v^2}{a} - n_1 \frac{v_1^0{}^2}{a_1} - n_2 \frac{v_2^0{}^2}{a_2} \right],$$

or

$$\Delta v = \frac{RT}{a a_1 a_2} \left[(n_1 + n_2) (n_1 v_1^0 + n_2 v_2^0)^2 a_1 a_2 - n_1 v_1^0{}^2 a a_2 - n_2 v_2^0{}^2 a a_1 \right] + \frac{RT}{a} (n_1 + n_2) \left(2 \Delta v (n_1 v_1^0 + n_2 v_2^0) + (\Delta v)^2 \right),$$

as $v = (n_1 v_1^0 + n_2 v_2^0) + \Delta v$. In consequence of this, with $a = (n_1 \sqrt{a_1} + n_2 \sqrt{a_2})^2$:

$$\Delta v = \frac{(n_1 + n_2) RT}{a} \left(2 \Delta v (v - \Delta v) + (\Delta v)^2 \right) = \frac{RT}{a a_1 a_2} \left[(n_1 + n_2) (n_1 v_1^0 + n_2 v_2^0)^2 a_1 a_2 - (n_1 v_1^0{}^2 a_2 + n_2 v_2^0{}^2 a_1) (n_1 \sqrt{a_1} + n_2 \sqrt{a_2})^2 \right],$$

which, worked out with neglect of Δv by the side of $2v$, and putting $n_1 + n_2 = 1$ at RT , gives:

$$\Delta v \left(1 - \frac{2 RT}{a/v} \right) =$$

$$\begin{aligned}
&= \frac{RT}{a a_1 a_2} n_1 n_2 \left[\left\{ n_1 v_1^{\circ 2} + 2(n_1 + n_2) v_1^{\circ} v_2^{\circ} + n_2 v_2^{\circ 2} \right\} a_1 a_2 - \right. \\
&\quad \left. - \left\{ n_1 v_2^{\circ 2} a_1^2 + 2(n_1 v_1^{\circ 2} a_2 + n_2 v_2^{\circ 2} a_1) \sqrt{a_1 a_2} + n_2 v_1^{\circ 2} a_2^2 \right\} \right] \\
&= \frac{RT}{a a_1 a_2} n_1 n_2 \left[n_1 \left\{ v_1^{\circ} a_2 \sqrt{a_1} \left((v_1^{\circ} + 2v_2^{\circ}) \sqrt{a_1} - 2v_1^{\circ} \sqrt{a_2} \right) - v_2^{\circ 2} a_1^2 \right\} + \right. \\
&\quad \left. + n_2 \left\{ v_2^{\circ} a_1 \sqrt{a_2} \left((v_2^{\circ} + 2v_1^{\circ}) \sqrt{a_2} - 2v_2^{\circ} \sqrt{a_1} \right) - v_1^{\circ 2} a_2^2 \right\} \right] \\
&= \frac{RT}{a a_1 a_2} n_1 n_2 \left[n_1 \left\{ 2v_1^{\circ} a_2 \sqrt{a_1} (v_2^{\circ} \sqrt{a_1} - v_1^{\circ} \sqrt{a_2}) + a_1 (v_1^{\circ 2} a_2 - v_2^{\circ 2} a_1) \right\} + \right. \\
&\quad \left. + n_2 \left\{ 2v_2^{\circ} a_1 \sqrt{a_2} (v_1^{\circ} \sqrt{a_2} - v_2^{\circ} \sqrt{a_1}) + a_2 (v_2^{\circ 2} a_1 - v_1^{\circ 2} a_2) \right\} \right] \\
&= \frac{RT}{a a_1 a_2} n_1 n_2 (v_1^{\circ} \sqrt{a_2} - v_2^{\circ} \sqrt{a_1}) \left[n_1 \left\{ (v_1^{\circ} \sqrt{a_2} + v_2^{\circ} \sqrt{a_1}) a_1 - 2v_1^{\circ} a_2 \sqrt{a_1} \right\} + \right. \\
&\quad \left. + n_2 \left\{ - (v_1^{\circ} \sqrt{a_2} + v_2^{\circ} \sqrt{a_1}) a_2 + 2v_2^{\circ} a_1 \sqrt{a_2} \right\} \right].
\end{aligned}$$

For the form between [] we may further write:

$$\begin{aligned}
&n_1 a_1 (v_1^{\circ} \sqrt{a_2} + v_2^{\circ} \sqrt{a_1}) - n_2 a_2 (v_1^{\circ} \sqrt{a_2} + v_2^{\circ} \sqrt{a_1}) - 2n_1 v_1^{\circ} a_2 \sqrt{a_1} + 2n_2 v_2^{\circ} a_1 \sqrt{a_2} \\
&= -n_1 a_1 (v_1^{\circ} \sqrt{a_2} - v_2^{\circ} \sqrt{a_1}) - n_2 a_2 (v_1^{\circ} \sqrt{a_2} - v_2^{\circ} \sqrt{a_1}) + \\
&\quad + 2a_1 \sqrt{a_2} (n_1 v_1^{\circ} + n_2 v_2^{\circ}) - 2a_2 \sqrt{a_1} (n_1 v_1^{\circ} + n_2 v_2^{\circ}),
\end{aligned}$$

so that we finally get:

$$\Delta v \left(1 - \frac{2RT}{a/v} \right) = \frac{RT}{a a_1 a_2} n_1 n_2 (v_1^{\circ} \sqrt{a_2} - v_2^{\circ} \sqrt{a_1}) \left[\begin{array}{l} \\ \underline{\underline{2v_2^{\circ} (\sqrt{a_1} - \sqrt{a_2}) \sqrt{a_1 a_2} - (n_1 a_1 + n_2 a_2) (v_1^{\circ} \sqrt{a_2} - v_2^{\circ} \sqrt{a_1})}} \end{array} \right] \quad (3)$$

This almost quite exact result (only p has been neglected, and in the 1st member Δv by the side of $2v$) shows that Δv will be of the order $\sigma = v_1^{\circ} \sqrt{a_1} - v_2^{\circ} \sqrt{a_1}$, so that w consists of two parts, of which the first is of the order σ^2 (cf. equation (1)), the second of the order σ . When the critical pressures differ little, σ is very small, and of the small heat of mixing w the second part (neglected before) will certainly predominate.

In the case that the *critical pressures differ little*, expression (3) can be considerably simplified. For then $v_1^{\circ} \sqrt{a_2} - v_2^{\circ} \sqrt{a_1} = 0$ can be put between [], and there remains:

$$\Delta v \left(1 - \frac{2RT}{a/v}\right) = \frac{2RT}{a/v_0} n_1 n_2 \left(1 - \frac{v_2^0 \sqrt{a_1}}{v_1^0 \sqrt{a_2}}\right) \frac{v_1^0 \sqrt{a_2} (\sqrt{a_1} - \sqrt{a_2})}{\sqrt{a_1 a_2}}.$$

But because then $\sqrt{a_2} = \frac{v_2^0}{v_{10}} \sqrt{a_1}$, $\sqrt{a_1} - \sqrt{a_2} = \frac{v_1^0 - v_2^0}{v_1^0} \sqrt{a_1}$,

$$\text{hence } \Delta v \left(1 - \frac{2RT}{a/v}\right) = \frac{2RT}{a/v_0} n_1 n_2 \left(1 - \sqrt{\frac{p_{k_1}}{p_{k_2}}}\right) (v_1^0 - v_2^0). \quad (3a)$$

As for ordinary substances in liquid state (below the boiling-point) $a/v = 7RT_k$, and in the second member $v_0 = v$ may be put, we find with $T/T_k = m$:

$$\Delta v = \frac{2/7 m}{1 - 2/7 m} n_1 n_2 \left(1 - \sqrt{\frac{p_{k_1}}{p_k}}\right) (v_1^0 - v_2^0). \quad (3b)$$

If e.g. $m = 1/2$, we have with $n_1 = 1-x$, $n_2 = x$ for Δv the value $1/6 x(1-x)(1-\sqrt{})(v_1^0 - v_2^0)$, so that the *maximum* contraction (at $x = 1/2$) becomes $1/24(1-\sqrt{})(v_1^0 - v_2^0)$ — hence very small and of the order $1-\sqrt{}$.

With regard to the *sign* of Δv it may be pointed out that $b_1 > b_2$, e.g. $b_1 = \theta b_2$ corresponds with $v_1^0 > v_2^0$. Then a_1 is approximately $= \theta^2 a_2$, so that a_1/b_1 becomes $= \theta a_2/b_2$, or $T_{k_1} > T_{k_2}$. But from this it ensues that p_{k_1} is generally somewhat greater than p_{k_2} , in consequence of which $1-\sqrt{}$ becomes negative. And the reverse when v_1^0 should be $< v_2^0$. The quantity Δv will, therefore, nearly always be *negative*, in other words volume contraction will take place.

With regard to the differential variations of volume $\Delta v_1 = v_1 - v_1^0 = \frac{\partial(\Delta v)}{\partial n_1}$ and $\Delta v_2 = v_2 - v_2^0 = \frac{\partial(\Delta v)}{\partial n_2}$, from the approximated expression (3a) follows, when a/v is considered constant in the correction term of the 1st member:

$$\Delta v_1 \left(1 - \frac{2RT}{a/v}\right) = 2RT n_2 (1-\sqrt{}) (v_1^0 - v_2^0) \frac{\partial}{\partial n_1} \left(\frac{n_1 v_0}{a}\right).$$

In approximation $v_1^0 \sqrt{a_2} = v_2^0 \sqrt{a_1}$ was taken, so that $\sqrt{a_1}$ is $= \frac{v_1^0}{v_2^0} \sqrt{a_2}$, and $\sqrt{a} = n_1 \sqrt{a_1} + n_2 \sqrt{a_2} = \sqrt{a_2} \left(n_1 \frac{v_1^0}{v_2^0} + n_2\right) = \frac{v_0}{v_2^0} \sqrt{a_2}$.

In consequence of this $\frac{\partial}{\partial n_1} \left(\frac{n_1 v_0}{a}\right)$ becomes $= \frac{\partial}{\partial n} \left(\frac{n_1 v^0 v_2^0}{a_2 v_0^2}\right) = \frac{v_2^0}{a_2} \frac{\partial}{\partial n_1} \left(\frac{n_1}{v_0}\right)$, in which $\frac{\partial}{\partial n_1} \left(\frac{n_1}{v_0}\right) = \frac{v_0 - n_1 v_1^0}{v_0^2} = \frac{n_2 v_2^0}{v_0^2}$. Hence we have

$\frac{\partial}{\partial n_1} \left(\frac{n_1 v_0}{a} \right) = n_2 \frac{v_2^0 v_1^0}{v_0^2 a} = n_2 \frac{v_2^0}{a}$; therefore with the same approximation as (3a):

$$\text{and } \left. \begin{aligned} \Delta v_1 \left(1 - \frac{2RT}{a/v} \right) &= \frac{2RT}{a/v_2^0} n_2^2 (1-V) (v_1^0 - v_2^0) \\ \Delta v_2 \left(1 - \frac{2RT}{a/v} \right) &= \frac{2RT}{a/v_1^0} n_1^2 (1-V) (v_1^0 - v_2^0) \end{aligned} \right\} \dots (4a)$$

We now duly get again $n_1 \Delta v_1 + n_2 \Delta v_2 = \Delta v_1$, because $n_1 n_2^2 \frac{v_2^0}{a} + n_2 n_1^2 \frac{v_1^0}{a} = n_1 n_2 \frac{v_0}{a}$:

4. Substitution of (3^b) in (1).

We get for w , after substitution of (3^a) in (1), with omission of the external pressure p :

$$w = n_1 n_2 \frac{(v_2^0 \sqrt{a_1 - v_1^0 \sqrt{a_2}})^2}{v_0 v_1^0 v_2^0} + \frac{a^{1/7} m}{v v_0 1 - 2/7 m} n_1 n_2 \frac{v_1^0 \sqrt{a_2 - v_2^0 \sqrt{a_1}} (v_1^0 - v_2^0)}{v_1^0 \sqrt{a_2}}$$

or

$$w = n_1 n_2 \left[\frac{(v_2^0 \sqrt{a_1 - v_1^0 \sqrt{a_2}})^2}{v_0 v_1^0 v_2^0} - \frac{2/7 m}{1 - 2/7 m} \frac{(v_2^0 \sqrt{a_1 - v_1^0 \sqrt{a_2}}) (v_1^0 - v_2^0) \sqrt{a}}{v v_1^0 v_2^0} \right],$$

when $v_2^0/v_0 \sqrt{a}$ is substituted for $\sqrt{a_2}$. With $m = 1/2$ and $v = v_0$, this passes into

$$w = \frac{n_1 n_2}{v_0 v_1^0 v_2^0} (v_2^0 \sqrt{a_1 - v_1^0 \sqrt{a_2}}) \left[(v_2^0 \sqrt{a_1 - v_1^0 \sqrt{a_2}}) - \frac{1}{6} (v_1^0 - v_2^0) \sqrt{a} \right] \dots (5b)$$

The factor $1/6$ is, of course, somewhat different, when $m = T/T_c$ is not $= 1/2$. When the critical pressures are equal, the foregoing factor is $= 0$, hence also the total heat of mixing. But when these pressures do not differ too much, the first term between [] will all the same be small with regard to the second, and in approximation

$$w = - \frac{1}{6} \frac{n_1 n_2}{v_0 v_1^0 v_2^0} (v_2^0 \sqrt{a_1 - v_1^0 \sqrt{a_2}}) (v_1^0 - v_2^0) \sqrt{a} \dots (5c)$$

may be written.

But however this be, we shall always be allowed to write:

$$w = n_1 n_2 \frac{\beta}{v_0 v_1^0 v_2^0} ; \quad w_1 = n_2^2 \frac{\beta}{v_0^2 v_1^0} ; \quad w_2 = n_1^2 \frac{\beta}{v_0^2 v_2^0},$$

or, as $v_0 = n_1 v_1^0 + n_2 v_2^0 = (1-x) v_1^0 + x v_2^0 = v_1^0 + x(v_2^0 - v_1^0) =$

$= v_1^0 (1 + rx)$, when $\frac{v_2^0 - v_1^0}{v_1^0} = r$ (hence $\frac{v_2^0}{v_1^0} = 1 + r$) is put, and

with $\frac{\beta}{(v_1^0)^2} = \alpha$:

$$w = x(1-x) \frac{\alpha}{(1+rx)(1+r)}; w_1 = \frac{x^2 \alpha}{(1+rx)^2}; w_2 = \frac{(1-x)^2 \alpha}{(1+rx)^2(1+r)}, \quad (6)$$

the old expressions, but in which α has now a somewhat different value than before, and will also be dependent on the temperature (through m).

When in approximation

$$w = \frac{\alpha}{v v_0} \Delta v = \frac{\alpha}{v^2} \Delta v$$

is written for (1) with omission of the first part, which is generally much smaller, we get approximately:

$$\frac{w}{\Delta v} = \frac{\alpha}{v^2} \dots \dots \dots (7)$$

If the critical pressures of different substances do not diverge too much, also the values of α/v^2 do not lie far apart in mixtures of different pairs of substances, and we shall find values of at least the same order of magnitude for the quotient $\frac{w}{\Delta v}$; a result to which also Mr. KATZ came experimentally in his latest paper (loc.cit.)¹⁾ — at least as far as volume-contraction and heat of imbibition of amorphous and crystalline swelling substances is concerned. That the ratios there are quite analogous to those of liquid mixtures is owing to this, that when one of the components is *solid*, it must first be reduced to the liquid state, whence the pure heat of melting of this components is simply added to w . But if Δv predominates, also *this* heat might be omitted with respect to the second part.

At any rate we shall never find exactly α/v^2 for $w/\Delta v$, because the omitted part can never be entirely disregarded. For this reason also the values of $w/\Delta v$ will differ somewhat, even with almost equal values of α/v^2 , which was also found by KATZ.

¹⁾ The curves of Fig. 1 and 2 are no hyperbolae, but *oblique parabolae*, as according to (6) w is $= \frac{x(1-x)}{1+rx} \frac{\alpha}{1+r}$. If r were $= 0$ ($v_2^0 = v_1^0$), the curve of the integral heat of mixing (i.e. $1-x$ gr. mol. of I + x gr. mol. of II) would be a pure parabola. If, however, v_2^0 is not $= v_1^0$, the top of the parabola will have been displaced somewhat to the side of the component with the smallest molecular volume, as is easy to verify. From $\partial w/\partial x = 0$ we find $x = 1/(1 + \sqrt{1+r})$, which gives $x = 1/2$ for $r = 0$, but $x < 1/2$ for $r > 0$. ($v_2^0 > v_1^0$).

The values of a/v_2 in our above formulae always refer exclusively to the *liquid mixture*, even for *solid* components, for as we already remarked above: this solid component must first be thought liquid, so that after all we have always to do with *liquid* mixtures.

Now that through the formulae derived by us above, the *absolute* values of w and Δv are known, which Mr. KATZ so eagerly desired, the problem has become clearer. Also when the components should be associated, everything remains essentially the same, as I will shortly show in a concluding paper. But then the preponderating influence of Δv will still be more pronounced, in consequence of the great variation of volume on dissociation of the double molecules.

And finally as regards the "important as yet undiscovered principles of the laws that govern molecular attraction" — I believe that this principle too was solved long ago¹⁾. This subject will also be discussed more fully in our concluding paper.

Tavel sur Clarens (Suisse), September 1922.

¹⁾ Compare my papers in These Proc. Vol. XVIII N^o. 8, p. 1220—1235, and following numbers; in the Journ. de Ch. physique **14**, p. 1 et seq. (1916); in the Z. f. anorg. und allg. Chemie **104**, p. 57—156 (1918); in the Ch. Weekbl. of 1918 (p. 1124); in These Proc. Vol. XXI N^o. 5, p. 644—655, and the J. de Ch. ph. **16**, 411 (1919), which possibly have escaped Mr. KATZ's notice.
