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**Physics.** — *"On the solid state."* VII. (Conclusion). By J. J. van Laar. (Communicated by Prof. H. A. Lorentz.)

**30.** We shall examine now to what modifications some formulae and results are subjected, when not *two* simple molecules, but several, e.g. $n$, associate to a compound molecule.

In the first place the formula for $\beta$, the degree of dissociation of the compound molecules. Now the calculation of I (These Proc XI p. 767—770) is modified as follows.

The condition of equilibrium:

$$- \mu_1 + n \mu_2 = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (a)$$

is reduced to:

$$(- C_1 + n C_2) - \left[ - \frac{\partial \Omega'}{\partial n_1} + n \frac{\partial \Omega'}{\partial n_2} \right] + RT \left( - \log c_1 + n \log c_2 \right) = 0,$$

after substitution of the values for $\mu_1$ and $\mu_2$ (see p. 767 loc. cit.).

In this equation $\Omega' = \int p dv - pv - RT \Sigma n_1 . \log \Sigma n_1$, $C_1$, $C_2$, $n_1$, $n_2$, $c_1$

and $c_2$ having the known meaning (see p. 767). Further:

$$\frac{\partial \Omega'}{\partial \beta} = \frac{\partial \Omega'}{\partial n_1} \frac{dn_1}{d\beta} + \frac{\partial \Omega'}{\partial n_2} \frac{dn_2}{d\beta} = - \frac{\partial \Omega'}{\partial n_1} + n \frac{\partial \Omega'}{\partial n_2},$$

because $n_1 = 1 - \beta$ and $n_2 = n\beta$, so that the equation of equilibrium passes into:

$$(- C_1 + n C_2) - \frac{\partial \Omega'}{\partial \beta} + RT \log \frac{c_2^n}{c_1} = 0,$$

or into

$$\log \frac{n^n \beta^n}{(1 - \beta)(1 + (n-1) \beta)^{n-1}} = \frac{(C_1 - n C_2) + \dfrac{\partial \Omega'}{\partial \beta}}{RT}, \quad . \quad . \quad (b)$$

because

$$c_1 = \frac{n_1}{n_1 + n_2} = \frac{1 - \beta}{1 + (n-1) \beta} \; ; \; c_2 = \frac{n_2}{n_1 + n_2} = \frac{n\beta}{1 + (n-1) \beta}$$

Now the value of $\dfrac{\partial \Omega'}{\partial \beta}$ may be calculated by means of the equation of state. From:

$$p = \frac{(1 + (n-1) \beta) RT}{v - b} - \frac{a}{v^2} \quad . \quad . \quad . \quad . \quad . \quad (c)$$

follows:

$$\int p dv = (1 + (n-1) \beta) RT \log (v-b) + \frac{a}{v},$$

because we know that the quantity $\beta$ must be kept constant during

this integration, as it refers to a mixture of the *definite* concentration $\beta$. (Only the condition of equilibrium $-\mu_1 + n\mu_2 = 0$ defines this value more closely). Hence we get for $\Omega'$:

$$\Omega' = (1 + (n-1)\,\beta)\,RT\,log\,\frac{v-b}{1+(n-1)\,\beta} + \frac{a}{v} - pv,$$

so that we get for $\dfrac{\partial \Omega'}{\partial \beta}$:

$$\frac{\partial \Omega'}{\partial \beta} = (n-1)\,RT\,log\,\frac{v-b}{1+(n-1)\,\beta} - (n-1)\,RT +$$

$$+ \frac{1+(n-1)\,\beta}{v-b}\,RT\left(\frac{\partial v}{\partial \beta} - \frac{db}{d\beta}\right) - \frac{a}{v^2}\frac{\partial v}{\partial \beta} - p\frac{\partial v}{\partial \beta}.$$

We have, namely, assumed the quantity $a$ to be independent of $\beta$. For:

$$a = n_1^2 a_1 + 2n_1 n_2 a_{12} + n_2^2 a_2$$

passes with $n_1 = 1 - \beta$, $n_2 = n\beta$, $a_{12} = \dfrac{a_1}{n}$, $a_2 = \dfrac{a_1}{n^2}$ into:

$$a = [(1-\beta)^2 + 2\,(1-\beta)\,\beta + \beta^2]\,a_1 = a_1,$$

i.e. independent of $\beta$. ($a$ and $a_1$ both refer to an $n$-fold "molecular" quantity). In consequence of the equation of state all the terms with $\dfrac{\partial v}{\partial \beta}$ vanish, so that:

$$\frac{\partial \Omega'}{\partial \beta} = (n-1)\,RT\,log\,\frac{RT}{p + ^a/_{v^2}} - (n-1)\,RT - (p + ^a/_{v^2})\,\Delta b, \quad . \quad (d)$$

is left, because
$b = n_1 b_1 + n_2 b_2 = (1-\beta)\,b_1 + n\beta b_2 = b_1 + \beta\,(-b + nb_2) = b_1 + \beta\Delta b$.
So the quantity $\Delta b = -b_1 + nb_2$ again represents the variation of volume, when a compound molecule breaks up into $n$ simple molecules. We know particularly from my last paper on the solid state that it depends entirely on the quantity $\Delta b$ whether this state exists or not. As soon as $\Delta b$ becomes $= 0$, there is no solid state any longer.

Then substitution of $(d)$ into $(b)$ and introduction of the values of $C_1$ and $C_2$ gives:

$$log\,\frac{n^n \beta^n}{(1-\beta)\,(1+(n-1)\,\beta)^{n-1}} = \frac{1}{RT}\left[-\,T\,(log\,T - 1)\,(k_1 - nk_2) + \right.$$

$$+ [(e_1)_0 - n\,(e_2)_0] - T\,[(\eta_1)_0 - n\,(\eta_2)_0] + (n-1)\,RT\,log\,RT -$$

$$\left. - (n-1)\,RT\,log\,(p + ^a/_{v^2}) - (n-1)\,RT - (p + ^a/_{v^2})\,\Delta b\right],$$

or also:

$$log \frac{\beta^n}{(1-\beta)(1+(n-1)\beta)^{n-1}} = (log\,T-1)\frac{-k_1+nk_2}{R} - \frac{-(e_1)_0+n(e_2)_0}{RT} +$$

$$+ \frac{-(\eta_1)_0+n(\eta_2)_0}{R} + (n-1)\,log\,R + (n-1)\,log\,T - (n-1) - log\,n^n -$$

$$- (n-1)\,log\,(p+{}^a/_{v^2}) - \frac{p+{}^a/_{v^2}}{RT}\,\Delta b.$$

If we now put:

$$-\frac{-k_1+nk_2}{R} + \frac{-(\eta_1)_0+n(\eta_2)_0}{R} + (n-1)\,log\,R - (n-1) - log\,n^n = log\,c$$

$$\frac{-k_1+nk_2}{R} = \gamma\,; \qquad -(e_1)_0 + n\,(e_2)_0 = q_0 \qquad\qquad \Big\}\,,(e)$$

we get:

$$log\frac{\beta^n}{(1-\beta)(1+(n-1)\beta)^{n-1}} = log\,c + \gamma\,log\,T - \frac{q_0}{RT} +$$

$$+ (n-1)\,log\,T - (n-1)\,log\,(p+{}^a/_{v^2}) - \frac{p+{}^a/_{v^2}}{RT}\,\Delta b,$$

Hence finally :

$$\frac{\beta^n}{(1-\beta)(1+(n-1)\beta)^{n-1}} = \frac{cT^{\gamma+(n-1)}\,e^{-\frac{q_0}{RT}}\,e^{-\frac{p+{}^a/_{v^2}}{RT}\Delta b}}{(p+{}^a/_{v^2})^{n-1}} \qquad . \quad (28)$$

For $n=2$ this equation passes into formula (2) on p. 770 l.c. The only difference is after all this that in the general case the exponent of $T$ is found to be $\gamma+(n-1)$ instead of $\gamma+1$; that in the denominator $(p+{}^a/_{v^2})^{n-1}$ is found instead of $p+{}^a/_{v^2}$, and that the first member has become what (28) gives instead of $\frac{\beta^2}{(1-\beta)(1+\beta)}$.

**31.** In this connection we may devote a few words to the dimensions of the constant $c$. If we have a quantity of substance $m$ times as great, the 1st member in (28) remains unchanged, as $\beta$ and $n$ are *numbers*. Also $T$, and hence $T^{\gamma+(n-1)}$, because $\gamma$ is likewise a number. For in the expression for $\gamma$ (see above) $k_1$ and $k_2$ become $m$ times as great, but also $R$ becomes $m$ times as great. The exponent $q_0/RT$ remains unchanged for the same reason. For $q_0$ and $R$ become both $m$ times greater. Further $\frac{p+{}^a/_{v^2}}{RT}\Delta b$ is also

$$= \frac{1+(n-1)\beta}{v-b}\,\Delta b$$ according to the equation of state, and so remains again unchanged, as $\Delta b$ and $v-b$ become both $m$ times greater.

Finally $p + a/v^2$ does not change in the denominator either, as $a$ and $v^2$ become both $m^2$-times greater and $p$ remains unchanged, of course. So it follows from this that the constant $c$ must necessarily be independent of the quantity of the considered substance, and consequently must not contain linearly the quantities $v$ or $R$. In how far is this in harmony with what $(e)$ gives for $c$?

Apart from terms which apparently do not change when the quantity of substance becomes $m$-times as great, the terms:

$$\frac{-(\eta_1)_0 + n(\eta_2)_0}{R} + (n-1) \log R,$$

are left, in which particularly at first sight, the term with $\log R$ looks strange.

On closer consideration of the so-called entropy constants $\eta_0$, however, we see that it is not strange at all. For when calculating the entropy of a perfect gas, we arrived at the expression:

$$s - s_0 = k \log \frac{T}{T_0} + R \log \frac{v}{v_0},$$

by integration between the limits $v_0$ and $v$, $T_0$ and $T$ ($v_0$ and $T_0$ arbitrary initial states). Hence

$$s = (s_0 - k \log T_0 - R \log v_0) + k \log T + R \log v,$$

and in this $\eta_0$, the entropy constant was written for $s_0 - k \log T_0 - R \log v_0$; i. e. $\eta_0$ is properly speaking $= \eta'_0 - R \log v_0$, and so:

$$\frac{-(\eta_1)_0 + n(\eta_2)_0}{R} + (n-1) \log R = \frac{-(\eta'_1)_0 + n(\eta'_2)_0}{R} -$$

$$- (n-1) R \log v_0 + (n-1) \log R,$$

in which now in the fraction of the second member both the numerator $-(\eta'_1)_0 + n(\eta'_2)_0$ and the denominator $R$ become $m$-times larger, so that we may write:

$$\log c = \log c_0 + (n-1) \log \frac{R}{v_0},$$

which entirely solves the apparent contradiction. In consequence of $R$ and $v_0$ the quantity $c$ now remains really unchanged, when the quantity of substance is increased or decreased.

**32.** Let us now examine in the second place what takes place with the formula for the pressure of coexistence liquid-solid, as we derived it in V (These Proc., Oct. 1910) p. 454—458. In this we shall assume that both in the liquid phase and in the solid phase only $n$-fold molecules are present $\dots$ in the liquid phase only to a

slight amount, in the solid phase to a very great amount, as we saw before; only in the neighbourhood of critical points the concentrations approach each other.

As the functions of the temperature $C_1$ in the two members cancel each other the condition of equilibrium, viz.: (see also IV p. 133—135; These Proc. June 1909):

$$(\mu_1)_{liq} = (\mu_1)_{solid}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (a)$$

i.e. the equality of the molecular potentials of the compound molecules [then naturally $(\mu_2)_l = (\mu_2)_{sol.}$ in the two cases because of $\mu_1 = n\mu_2$], passes into:

$$\left(\frac{\partial \Omega'}{\partial n_1} - RT \log c_1\right)_{liq.} = (id.)_{solid} \quad . \quad . \quad . \quad . \quad . \quad (b)$$

From the expression for $\Omega'$, derived in § 30, viz.

$$\Omega' = \Sigma n_1 . RT \log \frac{v-b}{\Sigma n_1} + \frac{a}{v} - pv,$$

follows:

$$\frac{\partial \Omega'}{\partial n_1} = RT \log \frac{v-b}{\Sigma n_1} - RT - \frac{\Sigma n_1 . RT}{v-b} b_1 + \frac{2a_1}{v},$$

because the terms with $\dfrac{\partial v}{\partial n_1}$ vanish in consequence of the equation of

state, while $\dfrac{\partial b}{\partial n_1} = b_1$ and $\dfrac{\partial a}{\partial n_1} = 2a_1$. For from $a = n_1^2 a_1 + 2n_1 n_2 a_{12} + n_2^2 a_2$

follows

$$\frac{\partial a}{\partial n_1} = 2n_1 a_1 + 2n_2 a_{12} = 2\left((1-\beta) + \frac{n\beta}{n}\right) a_1 = 2a_1,$$

as $a_{12} = \dfrac{a_1}{n}$. So we get:

$$\frac{\partial \Omega'}{\partial n_1} = RT \log \frac{RT}{p + a/v^2} - RT - b_1\left(p + a/v^2\right) + \frac{2a}{v},$$

writing again $a$ for $a_1$ (see § 30). In consequence of this the relation $(b)$ passes after division by $RT$ into:

$$\log \frac{p + a/v^2}{p + a/v'^2} + \frac{b_1}{RT}\left(\frac{a}{v^2} - \frac{a}{v'^2}\right) - \frac{2a}{RT}\left(\frac{1}{v} - \frac{1}{v'}\right) + \log\left[\frac{1-\beta}{1+(n-1)\beta} \cdot \frac{1+(n-1)\beta'}{1-\beta'}\right] = 0,$$

when the solid phase is indicated by accentuated quantities. So we get finally:

$$\log\left[\frac{p + a/v'^2}{p + a/v'^2} \frac{1-\beta}{1+(n-1\beta} \frac{1+(n-1)\beta'}{1-\beta'}\right] = \frac{a}{RT}\left[2\left(\frac{1}{v} - \frac{1}{v'}\right) - b_1\left(\frac{1}{v^2} - \frac{1}{v'^2}\right)\right], \quad . \quad (29)$$

quite in accordance with (19) in V, p. 455. Only, $1 + (n-1)\beta$ is

substituted for $1+\beta$. As $\beta$ is mostly near 1, $\beta'$ on the other hand mostly near 0, we shall again transform (29) by means of (28). From (28) follows viz:

$$log\,(1-\beta) = log\left[(p+a/_{v^2})^{n-1}\,\frac{\beta^n}{(1+(n-1)\beta)^{n-1}}\right] - log\,\theta + \frac{p+a/v^2}{RT}\,\Delta b,$$

when the temperature function $cT^{\gamma+(n-1)}e^{-\frac{q_0}{RT}}$ is indicated by $\theta$. Hence:

$$log\,(p+a/v^2)\,\frac{1-\beta}{1+(n-1)\beta} =$$

$$= n\,log\left[(p+a/v^2)\,\frac{\beta}{1+(n-1)\beta}\right] - log\,\theta + \frac{p+a/v^2}{RT}\,\Delta b, \quad . \quad . \quad . \quad (c)$$

and (29) reduces to

$$n\,log\left[\frac{p+a/v^2}{p+a/v'^2}\,\frac{\beta}{1+(n-1)\beta}\,\frac{1+(n-1)\beta'}{\beta'}\right] =$$

$$= \frac{a}{RT}\left[2\left(\frac{1}{v}-\frac{1}{v'}\right)-b_1\left(\frac{1}{v^2}-\frac{1}{v'^2}\right)-\Delta b\left(\frac{1}{v^2}-\frac{1}{v'^2}\right),$$

because $log\,\theta$ has the same value in the two phases, and is accordingly cancelled. Now $b_1 + \Delta b = nb_2$, hence also:

$$n\,log\left[\frac{v+a/_{v^2}}{p+a/v'^2}\,\frac{\beta}{1+(n-1)\beta}\,\frac{1+(n-1)\beta'}{\beta'}\right] =$$

$$= \frac{a}{RT}\left[2\left(\frac{1}{v}-\frac{1}{v'}\right)-nb_2\left(\frac{1}{v^2}-\frac{1}{v'^2}\right)\right], \quad . \quad . \quad . \quad (29^a)$$

analogous to $(19^a)$ in $V$, p. 456.

If only for the *liquid state* we substitute the 2$^{\text{nd}}$ member of $(c)$ for the 1$^{\text{st}}$ member in (29), we get:

$$log\left[\frac{v+a/_{v^2})^n}{p+a/v'^2}\,\frac{\beta^n}{(1+(n-1)\beta)^n}\,\frac{1+(n-1)\beta'}{1-\beta'}\,\frac{1}{cT^{\gamma+(n-1)}}\right] =$$

$$= \frac{a}{RT}\left[2\left(\frac{1}{v}-\frac{1}{v'}\right)-b_1\left(\frac{1}{v^2}-\frac{1}{v'^2}\right)\right] + \frac{(p+a/v^2)\,(-\Delta b)-q_0}{RT}, \quad . \quad (29^b)$$

analogous to $(19^b)$ in V, loc. cit.

The relation (29) can be profitably used when $\beta$ and $\beta'$ are both near 0; $(29^a)$ when they are both near 1; and $(29^b)$, when $\beta$ is in the neighbourhood of 1, $\beta'$ on the other hand not very far from 0 — as will in reality occur most frequently. If in the last case $\beta = 1$, $\beta' = 0$, $v = nb_2$, $v' = b_1$ may be put (this is the case at some distance from a critical point), we may write $-\dfrac{1}{b_1}\left(\dfrac{-\Delta b}{nb_2}\right)$ for

$$2\left(\frac{1}{v} - \frac{1}{v'}\right) - b_1\left(\frac{1}{v^2} - \frac{1}{v'^2}\right) = \left(\frac{1}{v} - \frac{1}{v'}\right)\left(2 - b_1\left(\frac{1}{v} + \frac{1}{v'}\right)\right)$$ If we

add to this $-\dfrac{\Delta b}{v^2} = -\dfrac{\Delta b}{(nb_2)^2}$ the sum becomes (see also p. 457 loc. cit.)

$\dfrac{-\Delta b}{b_1 \; nb_2}$, and $(29^h)$ reduces to;

$$log\left[\frac{\left(p + \frac{a}{(nb_2)^2}\right)^n}{p + a/b_1{}^2}\frac{1}{n^n c T'+(n-1)}\right] = \frac{a}{RT}\frac{-\Delta b}{b_1 \; nb_2} + \frac{p(-\Delta b)-q_0}{RT}.$$

Now:

$$p_0 = \frac{q_0}{-\Delta b} - \frac{a}{vv'} = \frac{q_0}{-\Delta b} - \frac{a}{b_1 . nb_2},$$

as before [see II p. 35, formula (10); These Proc. May 1909], when namely the coexistence curve solid-liquid is *retrogressive* (for $\Delta b$ negative), so that a pressure of coexistence $p_0$ becomes possible for $T = 0$. The second member of the preceding equation becomes then

$$= \frac{-\Delta b}{RT} (p - p_0),$$ and we get:

$$p - p_0 = \frac{RT}{-\Delta b}\left[log\left(\frac{\left(p + \frac{a}{(nb_2)^2}\right)^n}{p + a/b_1{}^2}\frac{1}{n^n c}\right) - (\gamma + (n-1)) log\; T\right], \quad . \quad (30)$$

quite analogous to (20), but $\left(p + \dfrac{a}{(nb_2)^2}\right)^n$ substituted for $\left(p + \dfrac{a}{(2b_2)^2}\right)^2$, $n^n$ for $2^2$, and $\gamma + (n-1)$ for $\gamma + 1$.

If we put again:

$$log\left[\frac{\left(p + \frac{a}{(nb_2)^2}\right)^n}{p + a/b_1{}^2}\frac{1}{n^n c}\right] = C,$$

in which $C$ may be considered constant (i. e. independent of $p$) by approximation at some distance from a critical point (p. 457 loc. cit.), (30) passes into:

$$p - p_0 = \frac{RT}{-\Delta b}\left[C - (\gamma + (n-1)) log\; T\right], \quad . \quad . \quad . \quad (31)$$

analogous to (21) on p. 458 loc. cit. Just as before, $T_0$, i. e. the temperature of the triple point can be found from this, by putting $p = 0$. (See also p. 460 loc. cit.).

33. Let us now repeat the calculation on p. 461, viz. that of $T_0/T_c$, which relation is of great importance for the theory of the solid state. Let us viz. put in $(29^a)$:

.

$$\beta = 1, \quad \beta' = 0, \quad p = 0, \quad v = nb_2, \quad v' = b_1,$$

we get:

$$n \log \left( \frac{b_1^2}{n^2 b_2^2} \frac{1}{n\beta'} \right) = \frac{a}{RT_0} \left( \frac{1}{nb_2} - \frac{1}{b_1} \right) \left[ 2 - nb_2 \left( \frac{1}{nb_2} + \frac{1}{b_1} \right) \right] =$$

$$= \frac{a}{RT_0} \frac{-\Delta b}{b_1 \cdot nb_2} \left( 1 - \frac{nb_2}{b_1} \right) = \frac{a}{RT_0} \frac{(-\Delta b)^2}{b_1^2 \cdot nb_2},$$

from which

$$RT_0 = \frac{a}{nb_2} \left( \frac{\Delta b}{b_1} \right)^2 : n \log \left( \frac{b_1^2}{n^2 b_2^2} \frac{1}{n\beta'} \right) \quad . \quad . \quad . \quad (32)$$

Of course this expression also holds for $\Delta b$ positive, if only a triple point occurs, and this lies far enough from any critical point to justify the just mentioned suppositions. The value of $T_0$ to be calculated from (31) only holds for the case $\Delta b$ negative, for only then there is a pressure of coexistence $p_0$ at $T = 0$. Moreover $T_0$ cannot be explicitly solved from (31). On the other hand in (32) the quantity $\beta'$ occurs, of which we only know that it will be near 0. But as we shall see, all the same some inferences may be made concerning $T_0$ or rather concerning the relation $T_0/T_c$.

If we suppose that at the critical temperature (vapour-liquid) the molecules have become single for the greater part, $T_c$ can be calculated from:

$$RT_c = \frac{8}{27} \frac{a_2}{b_2} = \frac{8}{27} \frac{a_1 : n^2}{b_2} = \frac{8}{27n} \frac{a}{nb_2} . [1])$$

Hence $\dfrac{27n}{8} RT_c$ can be written for $\dfrac{a}{nb_2}$, in consequence of which (32) becomes:

$$\frac{T_0}{T_c} = \frac{27}{8} \left( \frac{\Delta b}{b_1} \right)^2 : \log \left( \frac{b_1^2}{n^2 b_2^2} \cdot \frac{1}{n\beta'} \right) \quad . \quad . \quad . \quad (32a)$$

Formula $(32a)$ differs in this from $(27a)$ on p. 461 loc. cit. that apart from the substitution of $(nb_2)^2$ for $(2b_2)^2$, the numerator $2\beta'$ has now changed into $n\beta'$. This is very essential, and brings the value of $T_0/T_c$ into the neighbourhood of the experimental value $1/2$, without such a large value of $\Delta b$ being required for this. We saw in V p. 461 that $\beta'$ would still have to be $= 0.37$ for $\dfrac{\Delta b}{b_1} = -1/2$, to bring the ratio $T_0/T_c$ to $1/2$ for $n = 2$. Only for still greater values of $\Delta b$, $\beta'$, might have been slightly smaller This is no longer the case now.

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[1]) Also from $(1 + (n-1)\beta) RT_c = \dfrac{8}{27} \dfrac{a}{b}$, which passes into $nRT_c = \dfrac{8}{27} \dfrac{a_1}{nb_2}$ with $\beta = 1$. ($a$ is viz. independent of $\beta$ and $= a_1$ for an $n$ fold molecular quantity).

If we, namely put $T_0'/T_1 = {}^1/_2$, $(32^a)$ becomes, when $b_1 + \Delta b$ is substituted for $nb_2$ in it:

$$\frac{1}{2} = \frac{27}{8}\left(\frac{\Delta b}{b_1}\right)^2 : log\left(\frac{1}{\left(1 + \frac{\Delta b}{b_1}\right)^2 \frac{1}{n\beta'}}\right).$$

So we get:

$$log\left(\frac{1}{(1 + x)^2}\frac{1}{n\beta'}\right) = \frac{27}{4}x^2,$$

when $x$ is written for the ratio $\Delta b : b_1$. From this we calculate then the following values of $n\beta'$ for $x = -0,5$, $-0,3$ and $-0,1$:

| | | | |
|---|---|---|---|
| $x = -0,5$ | $log\dfrac{4}{n\beta'} = \dfrac{27}{16}$ ; | $log^{10} = 0,733$ | $n\beta' = 0,74$ |
| $x = -0,3$ | $log\dfrac{1}{0,49n\beta'} = \dfrac{243}{400}$ ; | $log^{10} = 0,264$ | $n\beta' = 1.11$ |
| $x = -0,1$ | $log\dfrac{1}{0,81n\beta'} = \dfrac{27}{400}$ ; | $log^{10} = 0,0293$ | $n\beta' = 1,15$ |
| $(x = 0)$ | $log\dfrac{1}{n\beta'} = 0$ ; | $log^{10} = 0$ | $(n\beta' = 1)$ |

So if $\beta'$ is not to be greater than e.g. 0,07 (see p. 462 loc. cit.), $n$ must be at least $= 11$ for $x = -0,5$; at least $= 16$ for $x = -03$, at least $= 17$ for $x = -0,1$, this number verging to about 14 according as $x$ approaches to 0. In his first paper on Quasi association in liquids (These Proc. June 1910 p. 129) VAN DER WAALS found already $n > 6$; so it is by no means remarkable that we find $n > 10$ (for negative values of $\Delta b$, so for retrogressive melting-point lines), the more so as we have included not only the liquid state, but more particularly the *solid* state, in our considerations.

Repeating the above calculation for *positive* values of $\Delta b$, we find for $x = 0,5$, 0,3 and 0,1 successively:

| | | |
|---|---|---|
| $x = 0,5$ | $log\dfrac{1}{2.25n\beta'} = \dfrac{27}{16}$ | $n\beta' = 0,082$ |
| $x = 0,3$ | $log\dfrac{1}{1,69n\beta'} = \dfrac{243}{400}$ | $n\beta' = 0,322$ |
| $x = 0,1$ | $log\dfrac{1}{1,21n\beta'} = \dfrac{27}{400}$ | $n\beta' = 0,770$ |
| $(x = 0)$ | $log\dfrac{1}{n\beta'} = 0$ | $(n\beta' = 1$ |

So here the conditions are still more favourable, as we already found in VI p. 644; These Proc. of Dec. 1910. For $\beta' = 0.07$ $n$ must be at least $= 2$ for $x = 0.5$; for $x = 0.3$ at least $= 5$; for $x = 0.1$ at least $= 11$; which would again approach to 14 for $x = 0$.

If we now suppose that in reality $\pm \Delta b$ will probably always be $< 1/2$, and if we assume e. g. 0,1 as mean value, then from this would follow $n = 17$, resp. 11 − let us say 14 on an average, a very plausible value, also in connection with van der Waals' investigations.

**34.** To the foregoing remarks a great deal might be added. In reality the relations will probably not be so simple as we have thought them in what precedes; particularly in the easily mobile liquid state — where the situation of the compound molecules is not fixed as in the solid state — all possible combinations will be conceivable. double molecules, triple, quadruple etc. And all this in ratios which depend on the constants of the substance, and moreover on the temperature and pressure. In the solid state, on the other hand, probably one kind of multiple molecules will prevail. But this would simply render the above computations somewhat more complicated, the essential part will remain the same. Accordingly I have not entered into the calculation for a special case, e. g. $n = 10$. The main point is, and remains that on account of association, both in the liquid and in the solid state, the occurrence of this latter state follows from this as a necessary consequence for not too low values of $\Delta b$. The considerations and calculations of the foregoing papers have taught us this. At certain high pressures the isotherms *turn back once more*, and this is repeated for the second time at low pressures, after which they finally rise to $p = \infty$. And we have seen *critical points* appear both in the case $\Delta b$ negative, and in that where $\Delta b$ is positive (see specially V and VI, which J shall not discuss any further here).

So the whole theory of the solid state rests on *two* suppositions : that of the *association* and that of the *variation of volume* ($\Delta b$) with the association. The former supposition is now universally accepted, though van der Waals continues to speak of "Quasi" association. Yet he applies the thermo-dynamic conditions of equilibrium to it already in his 1st paper (p. 121—123), which strictly speaking only hold for "real" association. Hence I have never understood quite clearly, why quasi association is spoken of — unless it should be that quasi association specially appears under the exclusive influence of the molecular forces and that in the expression for the variation

of energy

$$\Delta E = \beta \left( q_0 + \gamma RT \right) + \left( p + \frac{a}{v^2} \right) \Delta V$$

the quantity $q_0 = 0$. But then, this is a very special case, which is probably only reached by approximation in reality. In any case $\gamma$ cannot be $= 0$ even then, and even though the "internal" variation of energy $= 0$ at the absolute zero-point, it is not at the ordinary temperatures (because of the term $\gamma RT$).

And where for water, acetic acid etc. (also in the vapour) real association is assumed, it is no more than consistent in my opinion to assume this "real" association in *all* cases by analogy.

Whether we consider the matter from a kinetic or from a thermodynamical point of view, we always come to the same results, in my opinion. If at a certain moment we could fix the state in the whirl of the molecular movements — we should always see a certain number of groups, where two molecules are in each other's immediate neighbourhood (and stay there for some time, however short it be); where three, four, or more molecules happen to be together, etc., etc.[1]). In the same way the real association is thought also thermodynamically. The principle of the "mobile equilibrium" involves that a certain number of the formed double molecules break up again into simple molecules in a certain time etc. And the known thermodynamic principles are applied to the "state of equilibrium" which has set in in this way.

So association; but besides variation of volume caused by the association. For again : without assigning some value to $\Delta b$, we do *not* arrive at the *solid* state. The theory developed in V and VI has proved this convincingly in my opinion.

And now it is, indeed remarkable, that in his theory of quasi-association VAN DER WAALS does assume contraction in the value of $a$ — which is supposed constant in our theory (see above) — but no change in the value of $b$.[2]).

No doubt VAN DER WAALS will have had a good reason for this contraction in the value of $a$, — the matter, however, has not

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[1]) In connection with this we may refer e. g. to the theory of "Schwarmbildung" of v. SCHMOLUCHOWSKI.

[2]) See these Proc. June 1910, p. 119—121 (with regard to $b$ p. 121); also Nov. 1910, p. 494. With reference to the value of $b$, VAN DER WAALS owns that $\Delta b$ will not be $= 0$, and even makes the supposition that $\Delta b$ will probably be nearly always positive. (But then what about the melting-point lines running to the left ?). Notwithstanding this he assumes provisionally $\left( \frac{db}{dx} \right)_v = 0$.

become clear to me. The grounds alleged by van der Waals for this p. 119—120, have not been able to convince me and at any rate the supposition $k = \frac{1}{3}$ is arbitrary. It might be asked with some justice how great the value of $n$ will have to be for contraction to take place in the molecular attraction, and below what this contraction need *not* be reckoned with (e. g. for $n = 2$, see p. 119 loc. cit. : "It is true") In any case the future will show whether, and if so in how far a change should be made also in the value of $a$ — also with regard to the *solid* state. For there is reason to assume that — in consequence of the immobility of the molecule groups — the molecular attraction in the solid state may be different from that in the liquid state.

**35.** In conclusion I will still discuss here an important question, which is in close connection with the foregoing, and which I thought about already years ago: I refer to the dependence of the quantity $b$ on the temperature and the volume.

In a third paper van der Waals once more discusses the critical quantities fully, and the changes to which they are subjected in consequence of the variability of $b$ with $v$. The influence of the temperature is disregarded in this important investigation. I also occupied myself with these questions already before — though it be on a more moderate scale — and handled the question in a perfectly analogous way. I need only refer to an article in the Arch. Teyler of 1901 [1]), where I derived the quite general formula for $v_c$ as a function of $b_c$, $\left(\dfrac{db}{dv}\right)_c = b'_c$ and $\left(\dfrac{d^2b}{dv^2}\right)_c = b''_c$ (see p. 2), and also that for $p_c$, $RT_c$, and $\mu = \dfrac{p_c v_c}{RT_c}$ (p. 7 formulae (9), (10) and (11)). But particularly to a paper in the same Archives of 1905: Quelques remarques sur l'équation d'état, where on p. 47 et seq. I gave analogous considerations to those van der Waals gave later on p. 117—119 of his first paper (June 1910) on the Quasi association, and more extensively in his last paper of April 1911 (p. 1211 et seq.) [2]).

Two things have particularly struck me in this last paper. First of all that on p. 1214 with too great modesty van der Waals calls his theoretical formula $log \dfrac{p_k}{p} = f\left(\dfrac{T_k}{T} - 1\right)$ an *empirical* formula.

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[1]) Sur l'influence des corrections à la grandeur $b$ etc.

[2]) The formula (II) on p. 1214 for $v_c$ agrees with that already cited on p. 2 of my paper of 1901.

For this formula can very easily — as far as its *form* is concerned — be derived from the equation of state combined with MAXWELL's theorem. But in the second place that in virtue of considerations on the value of $\left(\dfrac{db}{dv}\right)_c$ and $\left(\dfrac{d^2b}{dv^2}\right)_c$ on p. 1221—1229 loc. cit. he arrives at the empirical formula (in the neighbourhood of the critical point):

$$\frac{b}{b_q} = 1 - a\left(\frac{b_q}{v}\right)^n. \qquad \qquad (a)$$

p. 1227, where then $n = 4\frac{1}{3}$ is found.

Now in virtue of considerations — which are in close connection with the theory of association, developed by me in connection with the solid state in the six preceding papers — I think we have to arrive at the result, that the dependence of the quantity $b$ on $v$ in the neighbourhood of the critical point is represented better by the relation:

$$\frac{b}{b_q} = 1 - \varphi\left(\frac{b_q}{v-b}\right)^2, \qquad \qquad (b)$$

and this led by the following theoretical considerations.

In order to arrive at the form of the function $b = f(v, T)$ in the equation of state $(p + {}^a/_{v^2})(v-b) = RT$, we can, namely, follow two different courses.

The *first* course, which is generally followed, is this that the problem is considered from a purely *kinetic* point of view. According to the method of MAXWELL, BOLTZMANN, V. D. WAALS, KORTEWEG, LORENTZ, REINGANUM, and others the vicissitudes of every molecule separately are followed, the effects of collisions etc. etc. To shorten the calculations we can also make use of the theorem of the *Virial* (CLAUSIUS). By often laborious calculations we arrive in this way at the formula of approximation

$$b = 4b_q\left(1 - \frac{17\,b_q}{32\,v} + \text{etc.}\right),$$

the coefficient ${}^{17}/_{32}$ of which has afterwards proved to be $= {}^3/_8$. The calculation of the following coefficients becomes practically about infeasible. In this molecular forces are still left entirely out of consideration. If we wanted to include them into the considerations, the calculations become still much more complicated, and the temperature also appears as influencing factor. (REINGANUM).

So the above formula gives the "apparent" change of $b$, when the volume decreases. We leave aside here a "real" diminution, fully discussed by VAN DER WAALS some years ago.

But there is still a *second* method, which leads to the purpose quicker and more accurately in my opinion, viz. the *thermodynamic* method. What can hardly be taken into account in the first method: attraction, the staying together for some time of the molecules, formation of so-called clusters of molecules, etc. is here implicitly *directly* reckoned with.

The thermodynamic (or statistic) method simply briefly summarizes, what the kinetic method would be able to reach only in a very circuitous way. The thermodynamic method does not occupy itself with the vicissitudes of every molecule separately, but only directs its attention to the most probable *final state* of the system. And the collisions and the temporary molecule aggregations considered in the kinetic theory are — from a thermodynamic point of view — nothing but the double, triple, quadruple etc. molecules, the varying quantities of which are only functions of $v$ and $T$.

It is this method which more than ten years ago I wanted to apply to the solution of this problem, and I repeatedly discussed it orally, but I abandoned the attempt, because at the time the solution was sought in an entirely different — in my opinion — impracticable direction. I am now perfectly justified in using the qualification "impracticable", as I myself am more or less competent to judge about it.

There is, however, one difference between the two methods. The kinetic method gives some *quantitive* results, which the thermodynamic method would never be able to give. E. g. that for $v = \infty$ the volume $v$ must be diminished by *four*-times the molecular volume, to enable us to find the correct value for the pressure. For this is a question which is in connection with the collision of molecules considered as *perfectly elastic spheres*.

But the corrections which were applied later on for the overlapping of two, three, and more "distance spheres", can also be obtained thermodynamically, in my opinion, by examining how many double, triple etc. molecules are temporarily formed. It is true that we do not arrive at the quantitative value of the coefficients $\alpha$, $\beta$, etc. of before, but yet at quantities corresponding with them. Where, namely, these coefficients $\alpha$, $\beta$, etc. were calculated from the consideration of segments cut off from purely geometrical *spheres*, now the quantities $\Delta_1 b$, $\Delta_2 b$, etc. are entered into the calculation, i.e. the variation of the molecular volume in consequence of the formation of double, triple, etc. molecules. These last quantities remain purely empirical, and can be considered kinetically as the apparent change of $4b$ for *simple* molecules, when two, three etc. of them get into

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each others' neighbourhood — i. e. as far as their effect on the *pressure* is concerned, in consequence of the "efficient" diminution of the available volume. I do not know, if I have expressed myself clearly enough, but the attentive reader cannot fail to feel the analogy of the two methods.

The thermodynamic method, however, has this advantage that also the influence of the mutual attraction of the molecules, of the variation of energy in the formation of multiple molecule groups etc. can now easily be taken into consideration.

We will not enter here into the accurate solution of this important problem, in which we are also confronted by pretty great difficulties, but only give an approximating expression, which may be used· in the neighbourhood of the critical point.

**36.** Let us imagine instead of $n_1$ simple melecules $n_2$ double, $n_3$ triple, $n_4$ quadruple ones etc. all the molecules to be $n$-fold on an average. Then according to (28) of § 30, when we replace

$$p + {^a/_{v^2}} \text{ by } \frac{(1 + (n-1)\beta)RT}{v-b} \text{ in it:}$$

$$\frac{\beta^n}{(1-\beta)(1+(n-1)\beta)^{n-1}} = \frac{cT^{\gamma+-} \ e^{-\frac{q_0}{RT}} \ e^{-\frac{1+(n-1)\beta}{v-b}\Delta b}}{(1+(n-1)\beta)^{n-1}(RT)^{n-1}} (v-b)^{n-1} \ ,$$

holds, so that we get ($c' = c : R^{n-1}$)

$$\frac{\beta^n}{1-\beta} = c'T^\gamma(v-b)^{n-1} \ e^{-\frac{q_0}{RT}} \ e^{-\frac{1+(n-1)\beta}{v-b}\Delta b} \ .$$

If now in the neighbourhood of the critical point $\beta$ is put near 1. i. e. if the multiple molecules are nearly all dissociated to simple ones, and if we further assume $q_0 = 0$ (see § 34), we get by approximation:

$$\frac{1}{1-\beta} = c'T^\gamma(v-b)^{n-1} \ e^{-\frac{n\Delta b}{v-b}} \ .$$

In this the association factor $n$ (at the critical point) can be put independent of $v$ and $T$; in general this is, of course, not the case, as *on an average* a smaller number ($n$) of molecules will be associated to a compound molecule at high temperature and great volume than at lower temperature and smaller volume.

So if we represent the temperature function $(c'T'^)^{-1}$ by $a'$ [1]), we get:

$$1 - \beta = a' \frac{e^{-\frac{n\Delta b}{v-b}}}{(v-b)^{n-1}}.$$

Hence for $b = b_1 + \beta \Delta b$ — or as $\Delta b = -b_1 + nb_2$, $b = nb_2 - (1-\beta)\Delta b$ — we find:

$$b = nb_2 - a'\Delta b \frac{e^{-\frac{n\Delta b}{v-b}}}{(v-b)^{n-1}}.$$

As $\dfrac{\Delta b}{v-b}$ is about $= \dfrac{\Delta b}{b}$ at the critical point, and will therefore be comparatively small, we may put $e^{-\frac{n\Delta b}{v-b}}$ independent of $v$ as a further approximation, and write simply:

$$b = nb_2 - a \frac{\Delta b}{(v-b)^{n-1}},$$

when $a'e^{-\frac{n\Delta b}{v-b}}$ is represented by $a$. The apparent contradiction in the dimensions of the fraction $a\Delta b : (v-b)^{n-1}$ with that of $nb_2$ vanishes when we consider that $c' = c : R^{n-1}$, and that therefore $a'$ and $a$ still contain the factor $R^{n-1}$.

As for $v = \infty$ at any rate $b = nb_2$, we may write for $nb_2$ also $b_q$, and so we get by approximation in the neighbourhood of the critical temperature:

$$b = b_q \left[ 1 - \varphi \left( \frac{b_q}{v-b} \right)^{n-1} \right], \quad \ldots \ldots \quad (33)$$

in which, therefore, $\varphi = \dfrac{a\Delta b}{b_q^{\,n}}$.

From (33) the approximate expression:

$$b' = \frac{db}{dv} = (n-1)\, \varphi \left( \frac{b_q}{v-b} \right)^n, \quad \ldots \ldots \quad (33^a)$$

now follows easily for $T_c$, when $\dfrac{d(v-b)}{dv} = 1 - b' = 1$ is put as first approximation ($b'_c$ is about $= 0,07$).

Finally we find, also at $T_c$:

$$-v_c b'' = -v_c \frac{d^2 b}{dv^2} = n\,(n-1)\, \varphi \frac{v_c}{b_q} \left( \frac{b_q}{v-b} \right)^{n+1}. \quad \ldots \quad (33^b)$$

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[1]) If we do not put $q_0 = 0$, the factor $e^{-\frac{q_0}{RT}}$ is added to $c'T'^$.

So for the relation $\dfrac{-v_c b_c''}{b_c'}$ is found :

$$\dfrac{-v_c b_c''}{b_c'} = n\,\dfrac{v_{c_-}}{v_c - b_c} \quad . \quad . \quad . \quad . \quad . \quad . \quad (33^c)$$

Now at the critical point about

$$v_c = 2{,}20\,b_c \quad ; \quad -v_c b_c'' = 0{,}38 \quad ; \quad b_c' = {}^1/_{14} = 0{,}07$$

so that we get:

$$\dfrac{0{,}38}{0{,}07} = \dfrac{2{,}20}{1{,}20}\,n\,,$$

hence

$$5{,}32 = 1{,}83\,n\,,$$

so that for $n$ a value is found which is only slightly below 3. If we take the value $0{,}39$ for $-v_c b_c''$ (van der Waals gives even the value $\dfrac{f-4}{f} = \dfrac{2{,}8}{6{,}8} = 0{,}41$ on p. 1227 loc. cit.), we find accurately $n = 3$. Hence it seems that in the neighbourhood of the critical point the slight number of complex molecules which still remain, are on an average associations of *triple* molecules.

Hence we may write for $T_c$ by approximation:

$$\dfrac{b}{b_q} = 1 - \varphi\left(\dfrac{b_g}{v-b}\right)^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad (34)$$

I shall have to conclude now; the fuller discussion of this interesting problem, only just alluded to in §§ 35 and 36, I must postpone to a further occasion.

*Clarens*, April 22nd 1911.

**Chemistry.** — *"Action of sunlight on allocinnamic acid."* By Dr. A. W. K. de Jong at Buitenzorg.

Some time ago (Ber. **35**, 2908 [1902]) Riiber found that ordinary cinnamic acid, in the solid condition, is converted by the action of sunlight into *a*-truxillic acid. A number of other compounds possessing a 4-ring have been obtained in a similar manner.

Among the acids obtained by the splitting of the coca alkaloids occurs, besides *a*-truxillic acid, also a structure-isomer, *β*-truxillic acid. It seemed to me very probable that this compound might form from *allo*cinnamic acid, which always occurs among the split off acids.

The *allo*cinnamic acid, used in this investigation, was prepared from the split off acids; it melted at 41°—42°, the melting point of Erlenmeyer's *iso*cinnamic acid. It was readily soluble in both petro-