**Physics**. — *"On the Critical Quantities in the Case of Association, when the Molecular Attraction is considerably Increased on Dissociation of the Molecules to the Isolated Atoms, also in Connection with the Critical Quantities of Mercury"*. II. (Conclusion). By Dr. J. J. VAN LAAR. (Communicated by Prof. H. A. LORENTZ).

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### § 9. General Relation for the Degree of Dissociation x of the Double Molecules.

If $Z$ is the thermodynamic potential of the mixture of double and single molecules, then it may assumed to be known that[1])

$$Z = n_1 C_1 + n_2 C_2 - \int p\,dv + pv + RT\,(n_1 \log n_1 + n_2 \log n_2),$$

when $n_1$ and $n_2$ represent the number of molecules resp. of the single and the double molecules, and $C_1$ and $C_2$ are given by

$$C_1 = -k_1 T (\log T - 1) + (e_1)_0 - T (s_1)_0 \Big\}$$
$$C_2 = -k_2 T (\log T - 1) + (e_2)_0 - T (s_2)_0 \Big\} .$$

In this $k_1$ and $k_2$ are the capacities of heat at infinitely large constant volume, $(e_1)_0$ and $(e_2)_0$ the constants of energy, $(s_1)_0$ and $(s_2)_0$ the constants of entropy of the components.

With equilibrium between the two components we have:

$$\mu_1 - {}^1/_2\,\mu_2 = 0, \quad \dots \dots \dots \quad (a)$$

when $\mu_1$ and $\mu_2$ represent the two *molecular* potentials (viz. $\mu_1 = \dfrac{\partial Z}{\partial n_1}$ and $\mu_2 = \dfrac{\partial Z}{\partial n_2}$) of the components. [$\mu_1$ refers, therefore, in mercury to 200,6 Gr., $\mu_2$ on the other hand to $2 \times 200,6$ Gr. mercury]. Now

$$\mu_1 = C_1 - \frac{\partial \omega}{\partial n_1} + RT\,(1 + \log(n_1 + n_2)) + RT \log c_1 \Bigg|$$
$$\mu_2 = C_2 - \frac{\partial \omega}{\partial n_2} + RT\,(1 + \log(n_1 + n_2)) + RT \log c_2 \Bigg| ,$$

as e.g. $\dfrac{\partial}{\partial n}(n_1 \log n_1 + n_2 \log n_2) = 1 + \log(n_1 + n_2) + \log \dfrac{n_1}{n_1 + n_2} = 1 +$

[1]) Cf. among others Arch. TEYLER (2) **11**, 3ième Partie, p. 1—97 (1908).

$+ \log(n_1 + n_2) + \log c_1$, while $\omega$ has been written for $\int p\,dv - pv$. Hence $(a)$ becomes:

$$(C_1 - {}^1/_2\,C_2) - \left(\frac{\partial \omega}{\partial n_1} - \frac{1}{2}\frac{\partial \omega}{\partial n_2}\right) + \tfrac{1}{2}RT\,(1 + \log(n_1 + n_2)) + \tfrac{1}{2}RT \log \frac{c_1{}^2}{c_2} = 0.$$

Further evidently $n_1 = {}^1/_2 \times 2x = x$, $n_2 = {}^1/_2\,(1-x)$, because from 1 single molecule $= {}^1/_2$ double molecule arise ${}^1/_2\,(1-x)$ double molecules and ${}^1/_2 \times 2x$ single molecules.

Now $\dfrac{\partial \omega}{\partial x} = \dfrac{\partial \omega}{\partial n_1}\dfrac{dn_1}{dx} + \dfrac{\partial \omega}{\partial n_2}\dfrac{dn_2}{dx} = \dfrac{\partial \omega}{\partial n_1} - \dfrac{1}{2}\dfrac{\partial \omega}{\partial n_2}$, so that we get:

$$(C_1 - {}^1/_2\,C_2) - \frac{\partial \omega}{\partial x} + \tfrac{1}{2} RT\,(1 + \log \tfrac{1}{2}\,(1 + x)) + \tfrac{1}{2} RT \log \frac{c_1{}^2}{c_2} = 0,$$

i.e.

$$\frac{1}{2} \log \frac{c_1{}^2}{c_2} = \frac{\tfrac{1}{2}C_2 - C_1}{RT} + \frac{\dfrac{\partial \omega}{\partial x}}{RT} - \tfrac{1}{2}\,(1 + \log \tfrac{1}{2}\,(1 + x)) \quad \dots \quad (b)$$

From $p = \dfrac{{}^1/_2\,(1 + x)\,RT}{v - b} - \dfrac{a}{v^2}$ follows for $\omega = \int p\,dv - pv$ [in which in $\int p\,dv$ $x$ must be kept constant, because in the original equation for $Z$ (which holds for *any* mixture, whether in equilibrium or not) the later possible state of equilibrium of the components, given by $(a)$, must not be taken into account, so that $n_1$ and $n_2$, hence $x$ remain constant]:

$$\omega = \tfrac{1}{2}\,(1 + x)\,RT\left[\log(v - b) + \int_{(x=konst.)}\frac{db}{v - b}\right] + \frac{a}{v} - pv.$$

In general $b$ is still a function of $v$, hence in $\int p\,dv$ the part $\int \dfrac{dv}{v - b}$ will be represented by $\int \dfrac{d(v - b)}{v - b} + \int \dfrac{db}{v - b} = \log(v - b) + \int \dfrac{db}{v - b}$.

[We may point out that in the assumed equation of state the quantities $v$, $a$, and $b$ of the mixture refer to simple molecular quantities (e.g. 200,6 Gr. mercury). For with $v' = nv$, $b' = nb$, $a' = n^2 a$, in which $n$ is the degree of association $2:(1 + x)$, the original equation $p = \dfrac{RT}{v' - b'} - \dfrac{a'}{v'^2}$ (cf. the first part of this paper) passes into the given equation. If e.g. ${}^1/_2\,(2x)$ simple and ${}^1/_2\,(1-x)$ double molecules arise from 1 single $= {}^1/_2$ double molecule, then

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$b = x b_1 + \frac{1}{2}(1-x) b_2$, — when $b_1$ represents the co-volume of 1 single molecule and $b_2$ that of 1 double molecule — which quantity refers, therefore, to the original single-molecular quantity. But $b'$ refers to the molecular quantity, which on an average yields 1 molecule after the association, and which is $2 : (1 + x)$ times greater than the single-molecular quantity. [i.e. at $x = 0$ (exclusively double molecules) twice greater; at $x = 1$ (exclusively single molecules) once greater; etc.]. For from the original single molecule there have been formed $\frac{1}{2}(1 + x)$ new molecules, so that every new molecule corresponds averagely to $2 : (1 + x)$ original single molecules].

We can now compute $\dfrac{\partial \omega}{\partial x}$. As $b$ is a function of $v$ (through $b_1$ and $b_2$) and of $x$, and also $v$ a function of $x$ on account of the equation of state $v = f(p, T, x, a, b)$, in which also $a$ and $b$ are functions of $x$, we have:

$$\frac{d}{dx}\Big(log(v - b) + \theta\Big) = \frac{1}{v-b}\left[\frac{dv}{dx} - \Big(\frac{\partial b}{\partial v}\Big)_x \frac{dv}{dx} - \Big(\frac{\partial b}{\partial x}\Big)_v\right] + \left[\frac{1}{v-b}\Big(\frac{\partial b}{\partial v}\Big)_x \frac{dv}{dx} + \Big(\frac{\partial \theta}{\partial x}\Big)_v\right],$$

when $\theta$ is written for $\displaystyle\int_{x=const.} \frac{db}{v-b} = \int_{x=const.} \frac{\frac{db}{dv}}{v-b} dv$, and because evidently

$\Big(\dfrac{\partial \theta}{\partial v}\Big)_v = \dfrac{1}{v-b}\Big(\dfrac{\partial b}{\partial v}\Big)_x$. Hence

$$\frac{d}{dx}\Big(log(v - b) + \theta\Big) = \frac{1}{v-b}\frac{dv}{dx} - \frac{1}{v-b}\Big(\frac{\partial b}{\partial x}\Big)_v + \Big(\frac{\partial \theta}{\partial x}\Big)_v.$$

For the further calculation of $\Big(\dfrac{\partial \theta}{\partial x}\Big)_v$ the quantity $\theta$ must be known, i.e. $b$ in function of $v$. When we assume for this the approximate relation derived by me before [1]:

$$\frac{v-b}{v-b_0} = \beta \frac{b}{b_0},$$

in which $\beta$ is a coefficient that depends on the nature of the substance, then $\Big(\dfrac{\partial b}{\partial v}\Big)_x = \dfrac{(1-\beta) b_0^2}{N^2}$ and $v - b = \dfrac{\beta v (v - b_0)}{N}$ easily follows from $b = \dfrac{b_0 v}{\beta v + (1-\beta) b_0}$. In consequence of this $\theta$ becomes:

$$\theta = \int_{x=const} \frac{(1-\beta) b_0^2}{\beta v (v-b_0)(\beta v + (1-\beta) b_0)} dv = \int \left[\frac{\beta}{\beta v + (1-\beta) b_0} - \frac{1/\beta}{v} + \frac{1/\beta - 1}{v - b_0}\right] dv,$$

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[1] See Recueil des Trav. Chim. N⁰. 3 and 5 of 1920.

i.e.

$$\theta = log(\beta v + (1-\beta) b_0) - \frac{1}{\beta} log\, v + \frac{1-\beta}{\beta} log(v - b_0),$$

which properly becomes $= 0$ for $\beta = 1$ (ideal substances, where $b$ is independent of $v$).

For this may also be written, because (see above) $\beta v + (1-\beta) b_0 = \dfrac{b_0 v}{b}$:

$$\theta = log \frac{b_0 v}{b} - \frac{1}{\beta} log\, v + \frac{1-\beta}{\beta} log(v - b_0) = -\frac{1-\beta}{\beta} log \frac{v}{v-b_0} - log \frac{b}{b_0}.$$

Now $v = \dfrac{(1-\beta) b}{1 - \beta\, b/b_0}$, hence $v - b_0 = \dfrac{b - b_0}{1 - \beta\, b/b_0}$, and $\theta$ becomes:

$$\theta = -\frac{1-\beta}{\beta} log \frac{(1-\beta) b}{b - b_0} - log \frac{b}{b_0} = \frac{1-\beta}{\beta} log(b - b_0) - \frac{1}{\beta} log\, b + log\, b_0 - \frac{1-\beta}{\beta} log(1-\beta). [1]$$

Thus we find for $\Big(\dfrac{\partial \theta}{\partial x}\Big)_v$:

$$\Big(\frac{\partial \theta}{\partial x}\Big)_v = \frac{1-\beta}{\beta} \frac{1}{b - b_0}\left(\Big(\frac{\partial b}{\partial x}\Big)_v - \Big(\frac{\partial b_0}{\partial x}\Big)_v\right) - \frac{1}{\beta}\frac{1}{b}\Big(\frac{\partial b}{\partial x}\Big)_v + \frac{1}{b_0}\Big(\frac{\partial b_0}{\partial x}\Big)_v,$$

or also:

$$\Big(\frac{\partial \theta}{\partial x}\Big)_v = \frac{b_0/\beta - b}{b(b - b_0)}\Big(\frac{\partial b}{\partial x}\Big)_v - \frac{b_0/\beta - b}{b_0(b - b_0)}\Big(\frac{\partial b_0}{\partial x}\Big)_v.$$

Now $v - b = b(b - b_0) : (b_0/\beta - b)$ (see the note), hence finally:

$$\Big(\frac{\partial \theta}{\partial x}\Big)_v = \frac{1}{v-b}\Big(\frac{\partial b}{\partial x}\Big)_v - \frac{b}{b_0}\frac{1}{v-b}\Big(\frac{\partial b_0}{\partial x}\Big)_v.$$

For $\dfrac{d}{dx}(log(v - b) + \theta)$ may therefore simply be written

$\dfrac{1}{v-b}\dfrac{dv}{dx} - \dfrac{b}{b_0}\dfrac{1}{v-b}\Big(\dfrac{\partial b_0}{\partial x}\Big)_v$, i.e. $\dfrac{1}{v-b}\dfrac{dv}{dx} - \dfrac{b}{b_0}\dfrac{\triangle b_0}{v-b}$. For as $b_0 = x(b_1)_0 + \frac{1}{2}(1-x)(b_2)_0$, we have $\Big(\dfrac{\partial b_0}{\partial x}\Big)_v = (b_1)_0 - \frac{1}{2}(b_2)_0$, which quantity we shall represent by $\triangle b_0$. This is accordingly the increase of volume, when $\frac{1}{2}$ double molecule passes into 1 single molecule. From the above given expression

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[1] In $\theta = \displaystyle\int \frac{db}{v-b}$ we might at once have substituted $v - b = b\,\dfrac{\beta(b/b_0 - 1)}{1 - \beta\, b/b_0}$ (derived from the above given expression for $v$) for $v - b$, and

$\theta = \displaystyle\int \frac{b_0 - \beta b}{\beta b (b - b_0)} db = \int \left(\frac{1/\beta - 1}{b - b_0} - \frac{1/\beta}{b}\right) db = \left(\frac{1}{\beta} - 1\right) log(b - b_0) - \frac{1}{\beta} log\, b$

might have been written, but then the constant term (i.e. constant with regard to $v$) $log\, b_0$, essential for the differentiation with respect to $x$, would have been wanting, and $\theta$ would not have become $= 0$ for $\beta = 1$ (the integral is indefinite).

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for $\omega$ we now find for $\dfrac{d\omega}{dx}$:

$$\frac{d\omega}{dx} = \tfrac{1}{2} RT \left[ log\,(v-b+\theta) \right] + \tfrac{1}{2}(1+x) RT \left[ \frac{1}{v-b}\frac{dv}{dx} - \frac{b}{b_0}\frac{\Delta b_0}{v-b} \right] -$$
$$- \frac{a}{v^2}\frac{dv}{dx} + \frac{1}{v}\frac{da}{dx} - p\frac{dv}{dx}.$$

In this all the terms with $\dfrac{dv}{dx}$ are eliminated in consequence of the equation of state, and we keep:

$$\frac{1}{RT}\frac{d\omega}{dx} = \tfrac{1}{2}\left[ log\,(v-b)+\theta \right] - \tfrac{1}{2}(1+x)\frac{b}{b_0}\frac{\Delta b_0}{v-b} + \frac{1}{RTv}\frac{da}{dx}.$$

With regard to the quantity $a$, the following equation may be given:

$$Va = xVa_1 + {}^1\!/_2(1-x)Va_2 = {}^1\!/_2 Va_2 + x(Va_1 - {}^1\!/_2 Va_2) = {}^1\!/_2 Va_2 + x\Delta Va,$$

when $Va_1$ refers to one single molecule and $Va_2$ to one double molecule, and $\Delta Va$ represents the *increase* of the attraction, when ${}^1\!/_2$ double molecule passes into 1 single molecule (atom). As for mercury ${}^1\!/_2\;Va_2$ is about $= 10 \cdot 10^{-2}$ and $Va_1$ about $= 40 \cdot 10^{-2}$, $\Delta Va$ has there the exceedingly high value $30 \cdot 10^{-2}$, i.e. $\Delta Va$ three times the value of $Va_2$.

Hence from $a = (Va)^2$ follows ${}^{da}\!/_{dx} = 2Va \cdot \Delta Va$, and thus the equation (b) becomes finally:

$$\tfrac{1}{2} log\frac{x^2}{1-x^2} = C + \tfrac{1}{2}\left[ log\frac{v-b}{{}^1\!/_2(1+x)} + \theta \right] - \tfrac{1}{2}(1+x)\frac{b}{b_0}\frac{\Delta b_0}{v-b} + \frac{2Va \cdot \Delta Va}{RTv}, \quad (c)$$

when we combine $\dfrac{{}^1\!/_2\,C_2 - C_1}{RT} - \tfrac{1}{2} - log\,2$ to one constant (temperature function) $C_1$, and write for $c_1$ and $c_2$ resp. $c_1 = x : {}^1\!/_2(1+x)$ and $c_2 = {}^1\!/_2(1-x) : {}^1\!/_2(1+x)$.

It is now this last equation that serves as basis for the determination of the degree of dissociation $x$ of the double molecules, i.e. for the determination of the quantity $\dfrac{dx}{dv}$, which will occur in the expressions for $\dfrac{dp}{dv}$ and $\dfrac{d^2p}{dv^2}$. In the equation mentioned the quantity $\Delta b_0$ will probably be always exceedingly small, and may be neglected in most cases, whereas on the contrary in this special case, where the dissociation of the double molecules $Hg_2$ leads to *isolated atoms* $Hg$, $\Delta Va$ will possess a very large value, which quite governs the modification of the critical quantities.

## § 10. Determination of $\left(\dfrac{dx}{dv}\right)_t$.

Let us now differentiate the relation (c), i.e. $x = f(v,T)$ at $T$ constant with respect to $v$, again taking into account that $b = f(v,x)$ and $a = f(x)$. We then get:

$$\tfrac{1}{2}\left( \frac{2}{x} + \frac{2x}{1-x^2} \right)\frac{dx}{dv} = \tfrac{1}{2}\left[ \frac{1}{v-b}\left\{ 1 - \left(\frac{\partial b}{\partial v}\right)_x - \left(\frac{\partial b}{\partial x}\right)_v\frac{dx}{dv} \right\} + \right.$$
$$\left. + \left\{ \left(\frac{\partial\theta}{\partial v}\right)_x + \left(\frac{\partial\theta}{\partial x}\right)_v\frac{dx}{dv} \right\} \right] - \tfrac{1}{2}\frac{1}{1+x}\frac{dx}{dv} -$$
$$- \tfrac{1}{2}\left[ \frac{\Delta b_0}{\beta(v-b_0)}\frac{dx}{dv} + \frac{(1+x)\Delta b_0}{\beta}\frac{d}{dv}\left(\frac{1}{v-b_0}\right) \right] - \frac{2Va \cdot \Delta Va}{RTv^2} + \frac{2(\Delta Va)^2}{RTv}\frac{dx}{dv},$$

because $\dfrac{1}{\beta(v-b_0)}$ can also be written for $\dfrac{b}{b_0}\dfrac{1}{v-b}$ (see § 9). As further

$$\left(\frac{\partial\theta}{\partial v}\right)_x = \frac{1}{v-b}\left(\frac{\partial b}{\partial v}\right)_x \text{ and } \left(\frac{\partial\theta}{\partial x}\right)_v = \frac{1}{v-b}\left(\frac{\partial b}{\partial x}\right)_v - \frac{b_0}{\beta(v-b_0)} \text{ (see § 9),}$$

we get:

$$\left( \frac{1}{x(1-x^2)} + \frac{1}{2}\frac{1}{1+x} \right)\frac{dx}{dv} = \tfrac{1}{2}\left[ \frac{1}{v-b} - \frac{\Delta b_0}{\beta(v-b_0)}\frac{dx}{dv} \right] -$$
$$- \tfrac{1}{2}\left[ \frac{\Delta b_0}{\beta(v-b_0)}\frac{dx}{dv} + \frac{(1+x)\Delta b_0}{\beta}\frac{1-\Delta b_0\frac{dx}{dv}}{(v-b_0)^2} \right] - \frac{2Va \cdot \Delta Va}{RTv^2} + \frac{2(\Delta Va)^2}{RTv}\frac{dx}{dv},$$

or also

$$\left[ \frac{1 + {}^1\!/_2 x(1-x)}{x(1-x^2)} + \frac{\Delta b_0}{\beta(v-b_0)} + \frac{(1+x)(\Delta b_0)^2}{\beta(v-b_0)^2} - \frac{2(\Delta Va)^2}{RTv} \right]\frac{dx}{dv} = $$
$$= \frac{1}{2}\frac{1}{v-b} + \frac{1}{2}\frac{(1+x)\Delta b_0}{\beta(v-b_0)^2} - \frac{2Va \cdot \Delta Va}{RTv^2} \Biggr\}.$$

When to obviate unnecessary complications in what follows, we disregard all the terms with $\Delta b_0$ — which may the sooner be done, as at the *limiting volume* $v_0 = b_0$ the volume of ${}^1\!/_2$ double molecule will probably be equal to that of 1 single molecule, and as besides $\Delta Va$ is very large with regard to $\Delta b_0$ — we thus get:

$$\left(\frac{dx}{dv}\right)_t = \frac{\dfrac{1}{2}\dfrac{1}{v-b} - \dfrac{2Va \cdot \Delta Va}{RTv^2}}{\dfrac{1 + {}^1\!/_2 x(1-x)}{x(1-x^2)} - \dfrac{2(\Delta Va)^2}{RTv}},$$

i.e.

$$\left(\frac{dx}{dv}\right)_t = \frac{1}{v-b}\;\frac{{}^{1}/_{2}\,x\,(1-x)\left(1-\dfrac{v-b}{v}\dfrac{4\sqrt{a}\cdot\Delta\sqrt{a}}{RTv}\right)}{(1-{}^{1}/_{2}\,x)-2x\,(1-x)\,(\Delta\sqrt{a})^2:RTv}=$$

$$=\frac{1}{v-b}\;\frac{x\,(1-x)\left(RTv-4\dfrac{v-b}{v}\sqrt{a}\cdot\Delta\sqrt{a}\right)}{(2-x)\,RTv-4x\,(1-x)\,(\Delta\sqrt{a})^2},$$

because $1+{}^{1}/_{2}\,x\,(1-x):(1+x)$ is $=1-{}^{1}/_{2}\,x$. If we put for brevity:

$$\frac{v-b}{v}\sqrt{a}=a\quad\text{and}\quad\Delta\sqrt{a}=\Delta,$$

we have finally:

$$\left(\frac{dx}{dv}\right)_t=\frac{1}{v-b}\;\frac{x\,(1-x)\,(RTv-4a\,\Delta)}{(2-x)\,RTv-4x\,(1-x)\,\Delta^2}\quad\ldots\quad(1)$$

When $\Delta=0$, or may be neglected, as in all cases of dissociation which do *not* eventuate in isolated atoms, then $\left(\dfrac{dx}{dv}\right)_t=\dfrac{1}{v-b}\dfrac{x(1-x)}{2-x}$, the already known expression, which is always positive, and which becomes $=0$ for $x=0$ and $x=1$.

But if $\Delta$ is large, as with $Hg_2\to 2\,Hg$, then in consequence of $RTv-4a\Delta=RTv-4\dfrac{v-b}{v}\sqrt{a}\cdot\Delta\sqrt{a}=v\left[RT-4\dfrac{a}{v}\dfrac{v-b}{v}\dfrac{\Delta\sqrt{a}}{\sqrt{a}}\right]$

the quantity $dx/dv$ can become *negative* at lower temperatures or comparatively small values of $v$. In mercury, where $\sqrt{a}={}^{1}/_{2}\sqrt{a_2}+$ $+\,x\,.\,\Delta\sqrt{a}$ is $=(10+30x)\,.\,10^{-2}$, $\Delta\sqrt{a}:\sqrt{a}$ will approach $30:10=3$ with small values of $x$, so that then the transition from positive to negative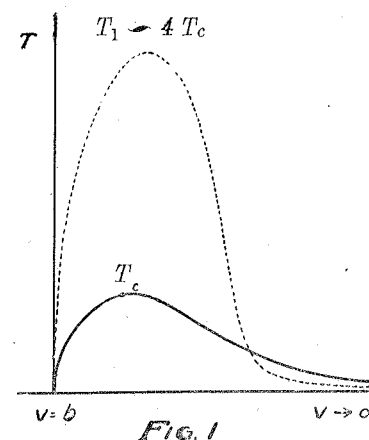 is reached, when $RT=12\dfrac{a}{v}\dfrac{v-b}{v}$. If $v=v_c$, then with $v_c=1,8\,b_c$, and $a$ about $={}^{3}/_{4}\,a_c$, $b={}^{3}/_{4}\,b_c$, this temperature will be given by $RT=12\times\dfrac{0,75}{1,8}\dfrac{a_c}{b_c}\dfrac{1,8-0,75}{1,8}=\dfrac{35}{12}\dfrac{a_c}{b_c}$. And as in mercury $RT_c$ is $\dfrac{8}{27}\dfrac{a_c}{b_c}\times 2\times\text{(about }1,25)=\dfrac{20}{27}\dfrac{a_c}{b_c}$ (compare the first part in these Proc.), $T$ becomes about $={}^{63}/_{16}\,T_c$, i.e.

$$T\sim 4\,T_c\,\text{(at }v=v_c),$$

so that with a volume $=v_c$ the quantity $dx/dv$ becomes positive again only above about $6700°$ abs.

**Fig. 1.**

Hence $dx/dv$ is always *negative* at the *critical temperature itself*, when $\Delta\sqrt{a}$ has such a high value as in mercury and similar substances. Then the degree of dissociation of the double molecules $Hg_2$ *decreases* when the volume becomes greater, instead of increasing — as it generally does.

As $a\,(v-b):v^2$ ($a$ and $b$ assumed constant) has its maximum value at $v=2b$, the transition temperature for values of $v$ both about $<2b$ and $>2b$ will be lower than that $(T_1)$ at $v=2b$, which latter will be only little higher than that at $v=v_c$ (about $4\,T_c$) [1]). See fig. 1.

The decrease of $x$ with increasing volume is of course accounted for in this way, that on increase of the degree of dissociation $x$ with increasing volume also $a$ becomes greater. But this causes the volume to decrease again, in which the decrease in the end exceeds the original increase.

At high temperature the pressure will be comparatively great, so that then, in consequence of an increase of $a$, $p+{}^{a}/_{v^2}$ will be increased little; $v-b$, hence also $v$, will then be lowered comparatively little. For this reason $dx/dv$ will always be positive at high

[1]) The righthand branch of the transition curve (dotted in the figure) will get more to the left, and $T_1$ possibly *slightly* lower than would follow from the above calculation, because then $x$ can no more be assumed near 0. The intersection with the vapour branch of the saturation curve takes place at $T=$ about $0,8\,T_c$. For from $pv={}^{1}/_{2}(1+x)\,RT$ and $p=p_c\,e^{-4,14(1/m-1)}$, where $4,14$ is the vapour pressure factor $f=1,8\times 2,303$ and $m=T:T_c$, follows $p_c\,v\,e^{-etc.}={}^{1}/_{2}(1+x)\,mRT_c$. When $x$ is put approximately $={}^{1}/_{2}$, then $n\,e^{-etc.}$ becomes $={}^{3}/_{4}\,m\,s$. (with $v=nv_c$ and $RT_c:p_cv_c=s$). Now in mercury $s=2,62$ (see the cited first part), so that finally $n=1,965\,m\,e^{4,14(1/m-1)}$ (saturation curve). This must now be combined with $RT=4\dfrac{a}{v}\dfrac{v-b}{v}\dfrac{\Delta\sqrt{a}}{\sqrt{a}}$. In this $\Delta\sqrt{a}=30\,.\,10^{-2}$, while $\sqrt{a}$ becomes $=25,10^{-2}$ with $x={}^{1}/_{2}$. When at the point of intersection $a$ is put about $=1{}^{1}/_{4}\,a_c$, $b=1{}^{1}/_{4}\,b_c$, then $mRT_c=6\dfrac{a_c}{nv_c}\dfrac{nv_c-1{}^{1}/_{4}\,b_c}{nv_c}$, i.e. with $v_c=1,8\,b_c$ and $RT_c=\dfrac{20}{27}\dfrac{a_c}{b_c}$ (see above) $m=2,5\dfrac{1,8n-1{}^{1}/_{4}}{n^2}$ (transition curve). Both equations are satisfied by $m=0,778$, $n=4,99$ (point of intersection), so that this will lie at about $T=0,8\,T_c$, where $v=5v_c$.

temperatures (higher than the critical transition temperature $T_1 = 4T_c$ in $Hg$). The same thing is also the case with great values of $v$, for then $a/v^2$ has only slight influence by the side of $p$.

As regards the values of $v$ near $b$, here too $dx/dv$ will always be positive, because $v$ cannot become smaller than $b$, and $x$ not smaller than 0. In consequence of the increase of $a$ the volume will indeed become somewhat smaller; but this decrease can only be exceedingly small, as $v$ is already almost $= b$.

*Remark.* In the equation $(c)$ the constant $C$ will contain the term $(1/2 (e_2)_0 - (e_1)_0) : RT = -Q_0 : RT$ (on account of $(1/2 C_2 - C_1) : RT$), in which $Q_0$ represents the — always positive — heat of dissociation (see § 9), while $\theta$ contains the term $(1/\beta - 1) \log (v - b)$ (for $v - b = (v - b_0) \times \beta^{b/b_0}$); hence $x : \sqrt{1 - x^2}$ will have the form $k \times (v - b)^{1/2\beta} \times e^{\left(-Q_0 + \frac{2\sqrt{a} \cdot \Delta\sqrt{a}}{v}\right) : RT}$, in which $k$ will contain exponentially neither $v - b$ nor $T$. If, therefore, the term with $\Delta\sqrt{a}$ is smaller than $Q_0$, then $x$ will approach 0 exponentially at $T = 0$, $v = b$. (If the term with $\Delta\sqrt{a}$ should be larger than $Q_0$, $1 - x$ approaches 0 exponentially). Hence according to (1) the differential quotient $dx/dv$ will approach exponentially to 0 at any rate at $T = 0$, $v = b$, as it contains the factor $x (1 - x) : (v - b)$. If, however, $T$ is $> 0$, everything depends at $v = b$ on the exponent of $v - b$, which will evidently be $1/2\beta - 1$. In "ideal" substances, where $\beta = 1$, this exponent is negative, hence $dx/dv$ approaches to $\infty$. But for "ordinary" substances, in which $1/\beta$ ranges between a little more than 2 and a little more than 4 (according as, in view of the factor $1 : a$ occurring in $\beta$, the temperature is higher or lower), the exponent in question will be positive, and $dx/dv$ will thus approach 0.

## § 11. The Differential Quotient $\left(\dfrac{dp}{dv}\right)_t$ and the Value of $RT_c$.

From the equation of state $p = \dfrac{1/2 (1 + x) RT}{v - b} - \dfrac{a}{v^2}$ follows:

$$\left(\frac{dp}{dv}\right)_t = \frac{1/2 RT}{v - b}\left(\frac{dx}{dv}\right)_t - \frac{1/2 (1 + x) RT}{(v - b)^2}\left(1 - \left(\frac{\partial b}{\partial v}\right)_x - \left(\frac{\partial b}{\partial x}\right)_v\left(\frac{dx}{dv}\right)_t\right) + $$
$$+ \frac{2a}{v^3} - \frac{2\sqrt{a} \cdot \Delta\sqrt{a}}{v^2}\left(\frac{dx}{dv}\right)_t.$$

Putting again $\left(\dfrac{\partial b}{\partial x}\right)_v = \Delta b = 0$, just as before $\Delta b_0$, and writing

$b'$ for $\left(\dfrac{\partial b}{\partial v}\right)_x$, we get:

$$\left(\frac{dp}{dv}\right)_t = \frac{1}{2}\left(\frac{dx}{dv}\right)_t\left[\frac{RT}{v - b} - \frac{4\sqrt{a} \cdot \Delta\sqrt{a}}{v^2}\right] - \frac{1/2 (1 + x) RT}{(v - b)^2}(1 - b') + \frac{2a}{v^3}.$$

Now substituting for $dx/dv$ its value from (1), we find:

$$\left(\frac{dp}{dv}\right)_t = \frac{1}{2}\frac{x (1 - x)}{v - b}\frac{RTv - 4a\Delta}{(2 - x) RTv - 4x (1 - x)\Delta^2}\left[\frac{RT}{v - b} - \frac{4a\Delta}{v (v - b)}\right] - $$
$$- \frac{1/2 (1 + x) RT}{(v - b)^2}(1 - b') + \frac{2a}{v^3},$$

writing simply $a\, v/v - b$ for $\sqrt{a}$ (see § 10) and $\Delta$ for $\Delta\sqrt{a}$; hence also:

$$\left(\frac{dp}{dv}\right)_t = \frac{1}{2v (v - b)^2}\left[\frac{x (1 - x) (RTv - 4a\Delta)^2}{(2 - x) RTv - 4x (1 - x)\Delta^2} - (1 + x) RTv (1 - b') + 4a^2\right].$$

This must now be $= 0$ at the critical point; thus we have:

$$x (1 - x) (RTv - 4a\Delta)^2 = [(2 - x) RTv - 4x (1 - x)\Delta^2][(1 + x) RTv) 1 - b') - 4a^2],$$

i.e. after some reduction and division of the two members by $RTv$:

$$x (1 - x) RTv - 8 x (1 - x) a\Delta = (2 - x) (1 + x) RTv (1 - b') - 4 (2 - x) a^2 - $$
$$- 4 x (1 - x^2) (1 - b')\Delta^2,$$

and from this:

$$\frac{1}{4} RT_c v_c = \frac{(2 - x) a^2 - 2 x (1 - x) a\Delta + x (1 - x^2) (1 - b')\Delta^2}{(2 - x) (1 + x) (1 - b') - x (1 - x)}, \quad (2)$$

for which we may also write:

$$\frac{1}{4} RT_c v_c = a\Delta + \frac{(a - (1 + x) (1 - b')\Delta) ((2 - x) a - x (1 - x)\Delta)}{(2 - x) (1 + x) (1 - b') - x (1 - x)}. \quad (2a)$$

This is, therefore, already the expression for $RT_c$, expressed in $v_c$, $b_c$, etc. As a check may serve that at $\Delta = 0$ this passes into

$$RT_c = \frac{4 (2 - x) a^2}{Nv_c} = \frac{4 (2 - x) a_c}{N}\frac{(v_c - b_c)^2}{v_c^3},$$

our former expression (Arch. Teyler loc. cit.), derived for the case that there does not take place any change in the molecular attraction in consequence of the dissociation of the double molecules.

If also $x = 1$ (all the molecules single), then becomes

$$RT_c = \frac{2a_c}{1 - b'_c}\frac{(v_c - b_c)^2}{v_c^3} = \frac{2}{1 - b'_c}\frac{(r - 1)^2}{r^3}\frac{a_c}{b_c},$$

as we also found before. (Cf. among others These Proc. Vol. XVI, p. 45, and Ibid., p. 810). In this the value of $r = v_c : b_c$ can of course not be determined until we have also put $\left(\dfrac{d^2 p}{dv^2}\right)_t = 0$.

In ideal substances $b'_c = 0$, $r = 3$, hence $RT_c = \dfrac{8}{27}\dfrac{a_c}{b_c}$. In ordinary

substances, where $b'_c$ approaches $^1/_8$ and $r$ approaches 2, $RT_c$ becomes $= \frac{8}{28} \frac{a_c}{b_c}$; both known expressions.

We will now first substitute the found value of $RT_c$ in (1), in order to determine the value of $dx/dv$ at the critical point. If we write for brevity:

$$\alpha - (1+x)(1-b')\Delta = A ; \quad (2-x)\alpha - x(1-x)\Delta = B$$
$$(2-x)(1+x)(1-b') - x(1-x) = 2 - (2-x)(1+x)b' = N$$

we get, after substitution of

$$\tfrac{1}{4} RT_c v_c = \alpha\Delta + \frac{AB}{N} \quad . \quad . \quad . \quad . \quad . \quad (2b)$$

in

$$\left(\frac{dx}{dv}\right)_t = \frac{x(1-x)}{v-b} \frac{^1/_4 RTv - \alpha\Delta}{(2-x)\,^1/_4 RTv - x(1-x)\Delta^2},$$

the equation

$$\left(\frac{dx}{dv}\right)_t = \frac{x(1-x)}{v-b} \frac{AB:N}{(2-x)\alpha\Delta + (2-x)AB:N - x(1-x)\Delta^2}.$$

In this $(2-x)\alpha\Delta - x(1-x)\Delta^2 = B\Delta$, hence also

$$\left(\frac{dx}{dv}\right)_t = \frac{x(1-x)}{v-b} \frac{A}{N\Delta + (2-x)A} = \frac{x(1-x)}{v-b} \frac{A}{B},$$

because $N\Delta + (2-x)A$ is evidently $= B$. Hence we have now for $\left(\frac{dx}{dv}\right)_t$ at the critical point the exceedingly simple expression

$$\left(\frac{dx}{dv}\right)_c = \frac{x(1-x)}{v_c-b_c} \frac{A}{B} = \frac{x(1-x)}{v_c-b_c} \frac{\alpha - (1+x)(1-b')\Delta}{(2-x)\alpha - x(1-x)\Delta}, \quad . \quad . \quad (3)$$

in which $x$, $b'$, $\alpha$, and $\Delta$ all refer to $T_c$.

It is self-evident that it is unnecessary to derive an expression for $p_c$, as it follows immediately from the equation of state after substitution of the obtained value of $RT_c$. (Compare the first paper).

## § 12. The Second Differential Quotient $\left(\frac{d^2p}{dv^2}\right)_t$ and the Value of $r = v_c : b_c$.

As we observed already above, we cannot determine the final expression for $RT_c$, until also $v_c$ has been expressed in $b_c$. But for this the knowledge of the second differential quotient is required, which must again be put $= 0$ at the critical point.

As $\left(\frac{dp}{dv}\right)_t = 0$ is identical with the expression (2) or (2b) derived from it, $\left(\frac{d^2p}{dv^2}\right)_t = 0$ is identical with $\frac{d}{dv}\left[^1/_4 RTv - \left(\alpha\Delta + \frac{AB}{N}\right)\right] = 0$. When we take (2) instead of (2b),

$$^1/_4 RTv\,N = (2-x)\alpha^2 - 2x(1-x)\alpha\Delta + x(1-x^2)(1-b')\Delta^2$$

should be differentiated with respect to $v$ ($T$ constant); which yields, when again, as in § 11, $\left(\frac{\partial b}{\partial x}\right)_v = \Delta b$ is put $= 0$, so that $b$ is only a function of $v$:

$$\tfrac{1}{4} RT(N + N'v) = 2(2-x)\alpha\alpha' - \alpha^2\left(\frac{dx}{dv}\right)_t - 2x(1-x)\alpha'\Delta + 2(2x-1)\alpha\Delta\left(\frac{dx}{dv}\right)_t$$
$$- x(1-x^2)b''\Delta^2 - (3x^2-1)(1-b')\Delta^2\left(\frac{dx}{dv}\right)_t.$$

After multiplication by $v$ and substitution for $^1/_4 RTv$ of its value (2b), we get:

$$\left(\alpha\Delta + \frac{AB}{N}\right)\left(N + x(1-x)(2x-1)\frac{v}{v-b}b'\frac{A}{B} - (2-x)(1+x)b''v\right) =$$
$$= 2\alpha'vB - v\left(\frac{dx}{dv}\right)_t\left[\alpha^2 - 2(2x-1)\alpha\Delta + (3x^2-1)(1-b')\Delta^2\right] - x(1-x^2)b''v\Delta^2.$$

For from $N = 2 - (2-x)(1+x)b'$ follows $N' = -(2-x)(1+x)b'' + (2x-1)b'\left(\frac{dx}{dv}\right)_t$, hence $N'v$ becomes with $\left(\frac{dx}{dv}\right)_t = \frac{x(1-x)}{v-b}\frac{A}{B}$, which is written down above. Further $(2-x)\alpha - x(1-x)\Delta$ has been replaced by $B$.

For $\alpha' = \left(\frac{d\alpha}{dv}\right)_t = \frac{d}{dv}\left(\frac{v-b}{v}\sqrt{a}\right)_t$ we find $\left(\frac{1-b'}{v} - \frac{v-b}{v^2}\right)\sqrt{a} + \frac{v-b}{v}\Delta\sqrt{a}\left(\frac{dx}{dv}\right)_t$, hence

$$\alpha'v = \alpha\left(\frac{v}{v-b}(1-b') - 1\right) + x(1-x)\frac{A}{B}\Delta = \alpha\frac{v}{v-b}(1-b') - \frac{1}{B}\left(\alpha B - x(1-x)A\Delta\right),$$

so that we find:

$$\left(\alpha\Delta + \frac{AB}{N}\right)\left(N + x(1-x)(2x-1)\frac{v}{v-b}b'\frac{A}{B}\right) -$$
$$- \frac{(1+x)b''v}{N}\left[2-x)(N\alpha\Delta + AB) - x(1-x)N\Delta^2\right] =$$

$$= 2B \left[ \alpha \frac{v}{v-b}(1-b') - \frac{\alpha B - x(1-x) A \Delta}{B} \right] -$$

$$- x(1-x) \frac{v}{v-b} \frac{A}{B} \left[ \alpha^2 - 2(2x-1)\alpha\Delta + (3x^2-1)(1-b')\Delta^2 \right].$$

When now for brevity $C$ is written for

$$N\alpha\Delta + AB = (2-x)\alpha^2 - 2x(1-x)\alpha\Delta + x(1-x^2)(1-b')\Delta^2$$

(according to (2) and (2b)), then

$$C + x(1-x)(2x-1)\frac{v}{v-b} b' \frac{AC}{NB} - (1+x)\frac{B^2}{N} b''v =$$

$$= 2B\alpha \frac{v}{v-b}(1-b') - 2C - x(1-x)\frac{v}{v-b}\frac{A}{B}[\alpha^2 - \text{etc.}],$$

because $\alpha B - x(1-x) A\Delta$ is $= C$ and $(2-x)C - x(1-x)N\Delta^2 = B^2$.

Hence we have also:

$$3C - (1+x)\frac{B^2}{N} b''v = 2\alpha B \frac{v}{v-b}(1-b') - x(1-x)\frac{A}{B}\frac{v}{v-b}\left[ (2x-1)b'\frac{C}{N} + (\alpha^2 - \text{etc.}) \right].$$

For $(2x-1)b'C + N(\alpha^2 - \text{etc.})$ may be written $B^2(1-b') - A^2(x^2-4x-2)$, hence we have:

$$3C - \frac{(1+x)B^2}{N} b''v = 2\alpha B \frac{v}{v-b}(1-b') - x(1-x)\frac{A}{B}\frac{v}{v-b}\frac{B^2(1-b')-A^2(x^2-4x+2)}{N} \quad (a)$$

Before proceeding, we shall apply a control-calculation to this equation. When $\Delta$ is $= 0$, then $A$ becomes $= \alpha$, $B = (2-x)\alpha$, $C = (2-x)\alpha^2$, so that then $(a)$ passes into

$$3(2-x)\alpha^2 - \frac{(1+x)(2-x)^2\alpha^2}{N} b''v = 2(2-x)\alpha^2 \frac{v}{v-b}(1-b') -$$

$$- \frac{x(1-x)}{2-x}\frac{v}{v-b}\frac{(2-x)^2\alpha^2(1-b') - \alpha^2(x^2-4x+2)}{N},$$

i.e. after division by $(2-x)\alpha^2$:

$$3 - \frac{(1+x)(2-x)}{N} b''v = 2\frac{v}{v-b}(1-b') - x(1-x)\frac{v}{v-b}\frac{(1-b') - (x^2-4x+2):(2-x)^2}{N},$$

in which $N = (2-x)(1+x)(1-b') - x(1+x) = 2 - (2-x)(1+x)b'$. This gives:

$$3 - \frac{b''v}{1-b'} \frac{1}{1 - \dfrac{x(1-x)}{(2-x)(1+x)(1-b')}} = \frac{v}{v-b}\left[ 2(1-b') - \frac{x(1-x)(1-b')}{N} + \right.$$

$$\left. + \frac{x(1-x)((2-x)^2-2)}{(2-x)^2 N} \right],$$

or

---

$$3 - \frac{b''v}{1-b'} \frac{1}{1-\tau} = \frac{v}{v-b}\left[ 2(1-b') - \frac{x(1-x)}{(2-x)^2} \frac{2-(2-x)^2 b'}{2-(2-x)(1+x)b'} \right].$$

In ideal substances, where $b' = 0$, $b'' = 0$, the equation would become:

$$3 = \frac{v}{v-b}\left[ 2 - \frac{x(1-x)}{(2-x)^2} \right] = \frac{v}{v-b}\frac{8-9x+3x^2}{(2-x)^2},$$

identical with what we have already derived. (Arch. TEYLER and these Proc., loc. cit.).

If $x = 0$ or $1$, we get:

$$3 - \frac{b''v}{1-b'} = 2\frac{v}{v-b}(1-b'),$$

and this too is a known result (These Proc., loc. cit.), which with $b' = 0$, $b'' = 0$ reduces to $3 = 2\frac{v}{v-b}$, i.e. $v_c = 3b_c$.

We shall now reduce the above equation $(a)$ still somewhat. When we divide by $(2-x)\alpha^2$, we get the following form (see below for the meaning of $\tau$):

$$3\left[ 1 - \frac{2x(1-x)}{2-x}\frac{\Delta}{\alpha} + \frac{x(1-x^2)(1-b')}{2-x}\frac{\Delta^2}{\alpha^2} \right] - \frac{(1+x)(2-x)\left(1 - \dfrac{x(1-x)}{2-x}\dfrac{\Delta}{\alpha}\right)^2}{(2-x)(1+x)(1-b')(1-\tau)} b''v =$$

$$= \frac{v}{v-b}(1-b')\left[ 2\left(1 - \frac{x(1-x)}{2-x}\frac{\Delta}{\alpha}\right) - \frac{x(1-x)}{2-x}\frac{1-(1+x)(1-b')\dfrac{\Delta}{\alpha}}{1-\dfrac{x(1-x)}{2-x}\dfrac{\Delta}{\alpha}} \times \right.$$

$$\left. \times \frac{(2-x)\left(1 - \dfrac{x(1-x)}{2-x}\dfrac{\Delta}{\alpha}\right)^2 - \dfrac{x^2-4x+2}{(2-x)(1-b')}\left(1-(1+x)(1-b')\dfrac{\Delta}{\alpha}\right)^2}{(2-x)(1+x)(1-b')(1-\tau)} \right],$$

in which $\dfrac{\Delta}{\alpha} = \dfrac{v}{v-b}\dfrac{\Delta\sqrt{a}}{\sqrt{a}}$. When we now put:

$$(1+x)(1-b')\frac{\Delta}{\alpha} = \varrho \quad ; \quad \frac{x(1-x)}{2-x}\frac{\Delta}{\alpha} = \sigma \quad ; \quad \frac{x(1-x)}{(2-x)(1+x)(1-b')} = \tau,$$

so that $\sigma = \tau\varrho$, the above becomes:

$$3(1 - 2\sigma + \varrho\sigma) - \frac{(1-\sigma)^2}{1-\tau}\frac{b''v}{1-b'} =$$

$$= \frac{v-b}{v}(1-b')\left[ 2(1-\sigma) - x(1-x)\frac{1-\varrho}{1-\sigma}\frac{(1-\sigma)^2 - \dfrac{x^2-4x+2}{(2-x)^2(1-b')}(1-\varrho)^2}{(2-x)(1+x)(1-b')(1-\tau)} \right],$$

or

$$3\left(1 + \tau\varrho\,(\varrho-2)\right) - \dfrac{(1-\sigma)^2}{1-\tau}\dfrac{b''v}{1-b'} =$$

$$= \dfrac{v}{v-b}(1-b')\left[2(1-\sigma) - \dfrac{\tau}{1-\tau}\dfrac{1-\varrho}{1-\sigma}\left\{(1-\sigma)^2 - \dfrac{x^2-4x+2}{(2-x)^2(1-b')}(1-\varrho)^2\right\}\right].$$

When further $\dfrac{\Delta\sqrt{a}}{\sqrt{a}} = \varphi$ is put, then $\dfrac{\Delta}{\alpha} = \varphi\dfrac{v}{v-b}$, hence $\dfrac{v}{v-b} \times$

$\times(1-b') = \dfrac{\Delta}{\alpha}\dfrac{1-b'}{\varphi} = \dfrac{\varrho}{\varphi(1+x)}$; so that with $-\dfrac{b''v}{1-b'}=\beta$ and

$\dfrac{x^2-4x+2}{(2-x)^2(1-b')} = \dfrac{1}{1-b'}\left(1-\dfrac{2}{(2-x)^2}\right) = \omega$ we get:

$$3(1 + \tau\varrho\,(\varrho-2)) + \dfrac{(1-\tau\varrho)^2}{1-\tau}\beta =$$

$$= \dfrac{\varrho}{\varphi(1+x)}\left[2(1-\tau\varrho) + \dfrac{\tau}{1-\tau}\dfrac{\varrho-1}{1-\tau\varrho}\left\{(1-\tau\varrho)^2 - \omega(\varrho-1)^2\right\}\right], \quad . \ (4)$$

when $-(\varrho-1)$ is substituted for $1-\varrho$, because $\varrho$ is always $> 1$. In this latter equation $\varrho = \varphi(1+x)(1-b')\times\dfrac{v_c}{v_c-b_c}$, being in direct connection with $r = v_c : b_c$, the principal unknown quantity; i.e. it expresses $\varrho$ (hence $r = v_c : b_c$) in $b', b''$ (or $\beta$), $x$ [1]) and the parameter $\varphi = \dfrac{\Delta\sqrt{a}}{\sqrt{a}}$, being in connection with, $\dfrac{\Delta\sqrt{a}}{1/_2\sqrt{a_2}}$, as $\sqrt{a_c} = 1/_2\sqrt{a_2} + x\Delta\sqrt{a}$. For mercury $\varphi$ is therefore $= \dfrac{3}{1+3x}$, because then $\Delta\sqrt{a}: 1/_2\sqrt{a_2} = 30:10 = 3$.

With small values of $x$ $\tau$ is very slight; then $\varphi$ is in the neighbourhood of 3, and $\omega$ in that of $1:2(1-b')$.

When we now express also the values of $RT_c$ and $\left(\dfrac{dx}{dv}\right)_{tc}$, found in § 11, in the auxiliary unknowns assumed just now, we may write for (2) in the first place:

$$RT_c = \dfrac{4}{v_c}\dfrac{(2-x)\,\alpha^2\,(1+\tau\varrho\,(\varrho-2))}{(2-x)(1+x)(1-b')\,1-\tau} = \dfrac{2}{1+x}\dfrac{2(v_c-b_c)^2 a_c}{v_c^2(1-b')}\dfrac{1+\tau\varrho\,(\varrho-2)}{1-\tau},$$

i.e.

$$RT_c = \dfrac{2}{1+x}\cdot\dfrac{2(r-1)^2}{(1-b')r^3}\dfrac{a_c}{b_c}\times\dfrac{1+\tau\varrho\,(\varrho-2)}{1-\tau}, \quad . \ . \ . \ . \ (5)$$

in which $\sqrt{a_c} = 1/_2\sqrt{a_2} + x\Delta\sqrt{a} = 1/_2\sqrt{a_2}(1+3x)$, whilst $r = v_c : b_c$ is determined by (4).

And in the second place we may write for (3):

1) The value of $x$ at the critical point will be determined by $(c)$, and depends besides on $T_c$ and $v_c$ also on the constants of energy and entropy (contained in $C$).

$$\left(\dfrac{dx}{dv}\right)_t = \dfrac{1}{v_c-b_c}\dfrac{x(1-x)}{2-x}\dfrac{1-\varrho}{1-\tau\varrho}, \quad . \ . \ . \ . \ . \ (6)$$

in which $\varrho = \psi(1+x)(1-b')\dfrac{v_c}{v_c-b_c} = \dfrac{3(1+x)}{1+3x}(1-b')\dfrac{r}{r-1}$ (see above). In mercury, where $\varphi_0 = 3$, $1-\varrho$ will, therefore, always be negative at $T_c$, hence also $dx/dv$.

## § 13. Calculation of some Numerical Values.

The value of $x$ being always very small at $T_c$, we way write approximately for (4), when $1-\tau = 1$ and $1+x = 1$ is put:

$$3(1+\tau\varrho\,(\varrho-2)) + \beta(1-\tau\varrho)^2 = \dfrac{\varrho}{\varphi}\left[2(1-\tau\varrho) + \tau\dfrac{\varrho-1}{1-\tau\varrho}\left\{(1-\tau\varrho)^2 - \omega(\varrho-1)^2\right\}\right],$$

and from this follows for $\tau\left(=\dfrac{x}{2(1-b')}, \text{when } x \text{ is small (see above)}\right)$:

$$\tau = \dfrac{\dfrac{2\varrho}{\varphi}(1-\tau\varrho) - (3+\beta(1-\tau\varrho)^2)}{3\varrho(\varrho-2) - \dfrac{1-\tau\varrho}{\varphi}\varrho(\varrho-1) + \dfrac{\omega}{1-\tau\varrho}\dfrac{\varrho(\varrho-1)^3}{\varphi}} =$$

$$= \dfrac{2\left[(1-\tau\varrho) - \dfrac{3+\beta(1-\tau\varrho)^2}{2}\dfrac{\varphi}{\varrho}\right]}{3\varphi(\varrho-2) - (1-\tau\varrho)(\varrho-1) + \dfrac{\omega}{1-\tau\varrho}(\varrho-1)^3}.$$

With very small values of $x$ also $1-\tau\varrho$ can be put $=1$, and we have approximately:

$$\tau = \dfrac{2\left[1 - \dfrac{3+\beta}{2(1-b')}\dfrac{r-1}{r}\right]}{3\varphi(\varrho-2) - (\varrho-1) + \omega(\varrho-1)^3}.$$

With small $x$ we way write $1:2(1-b')$ for $\omega$. Now $\varrho$ is large (6 or 7), and it can easily be calculated that in the denominator the two first terms may be neglected by the side of $\omega(\varrho-1)^3$, provided the latter is provided with a factor about 1,35. When we also write $\delta$ for $1 - \dfrac{3+\beta}{2(1-b')}\dfrac{r-1}{r}\left[\delta \text{ becomes } 0 \text{ at } x=0\ (\tau=0) \text{ and } \dfrac{r}{r-1} \text{ is then } = \dfrac{3+\beta}{2(1-b')}\right]$, we get:

$$\tau = \frac{2\delta}{1,35 \times \dfrac{1}{2(1-b')}(\varrho-1)^3}, \quad \text{hence } \tau(\varrho-1)^2 = 3(1-b')\,\delta.$$

Now $1 + \tau(\varrho-1)^2$ may be written for the factor $(1 + \tau\varrho(\varrho-2))$ : $(1-\tau)$ in (5) for small values of $\tau$, which in view of the above approximated relation becomes $1 + \dfrac{3(1-b')\delta}{\varrho-1}$.

Now $\varrho = 3(1-b')\dfrac{r}{r-1}$ for small values of $x$. This being about 6, $2,5(1-b')\dfrac{r}{r-1}$ may be put for $\varrho-1$, so that we get approximately $1 + \dfrac{6}{5}\dfrac{r-1}{r}\delta$ for the factor in question. Hence the factor $\theta$ in

$$R\,T_c = \frac{2}{1+x}\frac{8}{27}\frac{a_c}{b_c} \times \theta,$$

referred to in the first part of this paper, will evidently according to (5), when for $\delta$ its value is substituted, amount to:

$$\theta = \frac{2(r-1)^2}{(1-b')r^3} \times \frac{27}{8}\left[1 + \frac{6}{5}\frac{r-1}{r}\left\{1 - \frac{3+\beta}{2(1-b')}\frac{r-1}{r}\right\}\right],$$

holding for very small values for $x$. Only a small value of $r$, e.g. $r=1,5$, satisfies this. If $\beta$ has then become $=0$, and $b' = \frac{1}{2}$, $\theta$ becomes

$$\theta = 1\left[1 + \frac{2}{5}(1-1)\right] = 1,$$

while with $r = 1,5$ (see the first part of this Paper in these Proceedings, § 8, p. 278) $\theta$ should be exactly $=1$. Possibly $x$ is not small enough to justify the above approximations and the neglect of certain values, and then it is possible that $r > 1,5$ drops out. But the calculations get very intricate then.

At any rate the formulae (4), (5), and (6) contain the full solution of the problem put by us.

*La Tour près Vevey*, spring 1920.

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**Chemistry**. — *"Catalysis"* VIII. By Nil Ratan Dhar (with A. K. Datta and D. N. Bhattacharya). (Communicated by Prof. Ernst Cohen).

*a. Reaction between silver nitrate and ferrous-ammonium sulphate.*

I tried to determine the kinetics of the reaction between ferrous ammonium sulphate and silver nitrate. The reaction seems to be very rapid.

When $N/_{50}$ silver nitrate and $N/_{50}$ ferrous ammonium sulphate are mixed at 25°, a bimolecular velocity coefficient of 0.0007 is obtained, but unfortunately this coefficient falls off as the chemical reaction proceeds. Since the metallic silver formed reacts on the ferric salt produced and we get an equilibrium of this nature

$$2\,Ag + Fe_2(SO_4)_3 \rightleftarrows Ag_2SO_4 + 2\,FeSO_4$$
$$Ag + Fe(NO_3)_3 \rightleftarrows AgNO_3 + Fe(NO_3)_2$$
$$\text{or } \frac{(Fe^{++})(Ag^+)}{Fe^{+++}} \text{ at equilibrium } = 0.128$$

(cf. Noyes en Braun, Jour. Amer. Chem. Soc. 1912, **34**, 1016) the reaction between ferrous ammonium sulphate and silver nitrate is rapid even at 0° and has a small value for its temperature coefficient.

The reaction is markedly accelerated by acids; nitric, sulphuric, citric, tartaric, and acetic acids have been tried; the greater the concentration of hydrogen ions, the greater is the velocity. This catalytic activity may be utilised in determining the concentration of hydrogen ions.

Magnetic force has practically no effect on this reaction. It is extremely sensitive to the influence of dirt etc.

Potassium nitrate appreciably retards the reaction, so do manganese salts very markedly.

Carbonic acid markedly accelerates the reaction. Boric acid is practically without any influence. So is phenol, which is probably slightly retarding in its effect. Glucose markedly accelerates the reaction. This is a case of induced reaction. A mixture of excess of silver nitrate and very little of ferrous ammonium sulphate was prepared and divided into equal parts, to one of which glucose was

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