Physics. — *On the Heats, resp. Pressures of Evaporation, Sublimation and Melting, also in the Neighbourhood of the Absolute Zero; in Connection with* Nernst's *So-Called Heat-Theorem. (On the Equation of State of Solid Substances,* IV. *(Conclusion)).* By Dr. J. J. van Laar. (Communicated by Prof. H. A. Lorentz).

I. Introduction.

In the first of three papers [1]) I drew up an equation of state for *solid* substances, which, as regards form, corresponds to that of Van der Waals for liquids and gases. I showed that not only the values of the coefficients of expansion and compressibility, calculated from this equation of state, are in very good harmony with the values found experimentally, but also the coefficients of the pressure and the temperature of this latter coefficient.

In the second paper I derived the relation which, according to a known thermodynamic formula, must exist at high and low temperatures between the second member of the equation of state (the temperature part) and the temperature part of the expression for the *Energy*.

Finally in the third paper the expressions for Energy and Entropy were more closely considered, also at very low temperatures; and the known expression for the Entropy constant in the RT-region was derived from the value of the so-called elementary volume, in connection with the zero-point energy.

As was already announced on p. 698 of the third paper, it remains reserved for this fourth (concluding) paper to draw up the different equations of the pressure in connection with the different heats of trans-formation in case of coexistence of liquids resp. solid substances with their vapour, of liquids with solid substances, and of solid substances inter se.

Let us first state that I think I have proved in the third of the papers cited, that the so-called *"energy-degeneration"* at *very low* temperatures, in consequence of which RT becomes $A'T^4$, resp. AT^4 both in the equation of state and in the equation of energy, is found only with *solid* substances, in which the molecules (atoms) move round fixed positions of equilibrium; but that liquids and gases (unless at exceedingly high pressures) remain in the RT-region down to the lowest temperatures, i.e. do *not* degenerate. For gases this is clear, because there at very low

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[1]) These Proc. **29**, 95—112, 497—514 and 683—698 (1926).

temperatures the quantity θ (the so-called "characteristic" temperature of DEBYE) would approach 0 (cf. p. 684—685 loc. cit.) in consequence of the exceedingly great volume, that is if there could be question of degeneration in gases. And for liquids (with the exception of Helium), which can only exist at higher temperatures (above the melting point), this is, after all, a matter of course.

All the same — even at high temperatures — the assistance of the energy-degeneration has been very often called in (especially in Germany) to account for deviations in liquids, which could of course *not* be explained by the aid of the equation of state of v. D. WAALS *with a and b constant*, but which already found a ready explanation by the assumption of $b = f(v)$.

With regard to what has been adduced above, we may point out that PALACIOS MARTINEZ and K. ONNES (Comm. **164**, 1923) have shown already before for gaseous H_2 and *He*, that even at $20°,5$ abs. there is no question as yet of any quantum effect. Besides it was very recently proved by me in two papers [1]), that also *liquid Helium does not* degenerate down to the very lowest temperatures, and that *all* the abnormal phenomena appearing there — e. g. maximum density at $2°,3$ abs., minimum density at $0°.5$ abs., maximum internal heat of evaporation at $3°,4$ abs., minimum ibid. at $1°,5$ abs., etc. — can be explained in a natural way by the assumption that a and b are also functions of the temperature. This latter is, of course, likewise the case for other sub-stances, but there the two decreases with T *counteract* each other in the equation of state, whereas in Helium b also decreases, but a *increases* with T, on account of the exceedingly low temperatures below the critical temperature ($5°,2$ abs.). (c.f. p. 1305 loc. cit., fig. 3).

The formulae for a and b, viz.

$$10^6\, a = 39{,}515 + 11{,}178\, T - 1{,}1177\, T^2 \text{ (valid to slightly past } T_k)$$
$$10^6\, b = 1223{,}4 - 118{,}\overline{45}\, T + 10{,}356\, T^2 \text{ (valid to } \pm 2°,3 \text{ abs.)}$$

have been derived from known *experimental* data, whereas our considera-tions concerning λ and L are further based — besides on this material — on the *experimental* vapour-pressure observations, which go as far down as $1°.3$ abs. Hence the *minimum* of λ at $1°,5$ has been experimentally established, though the direct confirmation through more accurate measurements of the heat of evaporation L has at present not yet been extended so far (loc. cit. p. 1333—1334). And as a minimum at $1°,5$ abs. is certain ($\pm 16{,}5$ gr. cal., cf. p. 1331 loc. cit.), it is clear that λ and L will approach at $T = 0$ to a slightly greater **finite** limiting value ($= 17{,}5$ gr. cal.).

This is in contradiction with the opinion of some recent writers, who on the ground of an *erroneous* interpretation of the so-called NERNST-Theorem (which is only valid in the case of coexistence of two

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[1]) These Proc. **29**, 1303—1316, 1317—1334 (1926).

solid phases, and even then only in the neighbourhood of $T = 0$, see § VI) have come to the conclusion that at $T = 0$ the quantities λ and L would approach 0 even with the equilibria liquid-vapour (in *He*) and solid-vapour! [1])

II. Equations of state, and expressions for E and S.

We will recapitulate here some formulae, of which repeatedly use will be made in the future. (see in particular the third of the papers cited of 1926, presented to the Academy).

a. Liquids and gases for all temperatures (i f n o t a t e x t r e m e l y h i g h p r e s s u r e s, see § IV).

$$\left. \begin{array}{l} p + \dfrac{a}{v^2} = \dfrac{RT}{v-b} \\[2ex] E = kT + \left(\dfrac{a_{00}}{v_{00}} - \dfrac{a}{v} \right) \\[2ex] S = k \, log \, T + R \, log \, (v-b) + S_0 \end{array} \right\}.$$

For the sake of simplicity it has been assumed here, that a and b are no functions of T, for else a term with $\dfrac{db}{dt}$ would have to be added in E, and $a - T \dfrac{da}{dt}$ would have to be substituted for a. Besides b has been supposed to be no function of v either, for else a somewhat more complicated expression would have come in the place of $log\,(v-b)$ in S. But for our purpose it is perfectly unnecessary to introduce these complications, as we wish to develop only general points of view, which are quite independent of the said complications, which would needlessly render the formulae unmanageable and difficult to survey — only for the sake of a quantitative accuracy unnecessary here.

In the term a_{00}/v_{00} the limiting volume at $T = 0$, $p = \infty$ is represented by v_{00}. As at high pressures the quantity a may possibly be dependent on v, and at all events dependent on T, we have written a_{00} at $T = 0$, $p = \infty$, and we shall write a_0 at $T = 0$, $p = 0$, to which the volume v_0 corresponds.

For the so-called *Entropy constant* S_0 the following expression is found:
$$S_0 = - k \, log \, \theta - R \, log \, \omega + k,$$

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[1]) See among others an article by DE KOLOSSOWSKY of Leningrad in the J. de Ch. ph. of Oct. 25, 1926, (**23**, N⁰. 8), p. 728—732. The writer makes there, nota bene, use of a perfectly wrong formula for $\dfrac{dL}{dT} - \dfrac{L}{T}$. Compare also my article to refute this in the J. de Ch. ph. of Febr. 25, 1927 (**24**, N⁰. 2), p. 115—119, and an article by VERSCHAFFELT (Ibid. March 25, 1926 (**23**, N⁰. 3), p. 238—241) refuting an earlier paper of DE KOLOSSOWSKY (Ibid. **22**, 77—79, 1925). To this we may add a still fooler article in the Zeitschr. f. Physik, **43**, 509 (Heft 7).

through which the expression for S becomes *homogeneous*, viz.

$$S = k \, log \, \frac{T}{\theta} + R \, log \, \frac{v-b}{\omega} + k.$$

In this θ is the so-called „*characteristic*" temperature in the *solid* state at $v = v_0$ $(p = 0)$, and ω the so-called "*elementary volume*", i.e. the joint volume within the paths which the molecule centres describe round the positions of equilibrium at $T = 0$ and $p = 0$ in consequence of the still remaining "zero-point energy". This in consequence of the alternate action of the mutual attractions and repulsions of molecule nuclei and electrons, which still continues to exist also at $T = 0$ (zero-point paths). For mon-atomic substances (see my derivation in the third of the papers cited, p. 696) ω is represented by (k' is $R : N$):

$$\omega = \frac{9}{16} \frac{N}{\sqrt{\pi}} \frac{h^3}{(k' \, \theta)^{3/2} \, (2\pi m)^{3/2}}.$$

The quantity k in the expressions for S and S_0 is everywhere the specific heat at infinitely large constant volume. Its value for mon-atomic substances is $= {}^3/_2 R = 3$ gr. cal.

b. Solid substances at higher temperatures (if not at extremely high pressures).

$$\left. \begin{array}{l} p + \dfrac{a}{v^2} - \beta = \dfrac{RT}{v-b} \\[2ex] E = kT + \left(\dfrac{a_{00}}{v_{00}} - \dfrac{a}{v} \right) + P \\[2ex] S = k \, log \, T + R \, log \, (v-b) + S_0 \end{array} \right\}.$$

The same remark as above concerning the simplifications with respect to a and b.

In the equation of state (see the first of the papers cited) a term $-\beta$ has now been introduced, which relates to the (static) repulsive virial. I gave it the form $\beta = \dfrac{\lambda/v}{v-b}$, but this special form is of no consequence for what follows [1]). The quantity P in the expression for E is evidently

$$= \int_v^\infty \beta \, dv.$$

The quantity S_0 has the value indicated above; only the double value $3R = 6$ gr. cal. (for mon-atomic substances) must now be put for k, just as in kT and $k \, log \, T$ in E and S, whereas ω has the same value for all the states of aggregation.

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[1]) GRÜNEISEN and others assumed the form $\lambda/_{vn}$.

c. Solid substances at very low temperatures.

$$p + \frac{a}{v^2} - \beta = \frac{A'T^4}{v-b}$$

$$E = AT^4 + \left(\frac{a_{00}}{v_{00}} - \frac{a}{v} \right) + P + E_0$$

$$S = \frac{4}{3} AT^3$$

The quantity E_0 is the so-called „*zero-point energy*" (see above). Further A' in the equation of state is related to A in the equation of the Energy (compare for this the second of the papers cited). Both are functions of v. The variability of S with the volume, which at higher temperatures was chiefly embodied in the term $R \log (v-b)$, has now got into the coefficient A.

III. Equilibrium liquid-vapour.

(Above the melting-point; only in Helium down to $T=0$).

If in what follows we always denote the solid state by the index 1, the liquid by 2, and the vapour by 3, the following equation follows immediately from the equalization of the thermodynamic potentials $Z = = E + pV - TS$ of liquid and vapour:

$$(E_3 - E_2) + p(v_3-v_2) = T(S_3-S_2), \quad \text{i.e.} \quad L = T(S_3-S_2),$$

when $L = (E_3-E_2) + p(v_3-v_2)$ represents the *total* heat of evaporation. Hence we have according to **a.** of § II, because the limiting values a_{00}/v_{00} for the smallest volume v_{00} possible are of course identical for liquid and vapour at $T=0$, $p=\infty$:

$$L = (k_3 - k_2) T + \left(\frac{a_2}{v_2} - \frac{a_3}{v_3} \right) + p(v_3-v_2).$$

But also $k_2 = k_3$, because both refer to $v=\infty$. Further at comparatively low temperatures (i.e. far enough from the critical temperature, e.g. below the boiling-point) the liquid volume v_2 may be neglected by the side of the vapour volume v_3 (and therefore $1/v_3$ by the side of $1/v_2$), so that, as $pv_3 = RT$ may then be put, finally simply

$$L = \frac{a_2}{v_2} + RT \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

is found. In this a_2/v_2 is the *internal* heat of evaporation and RT the external work.

From $L = T(S_2-S_1)$ follows:

$$L = RT \log \frac{v_3-b_3}{v_2-b_2} = RT \log \frac{p + a_2/v_2^2}{p + a_3/v_3^2},$$

as k_2 is again $= k_3$ in $(k_3 - k_2) \log T$, and also $(S_0)_2$ will be $= (S_0)_3$, the fraction after the *log*-sign having been transformed by means of the equation of state. At comparatively low temperatures (see above) p is, however, neglected by the side of $a_2/_{v_2{}^2}$, but for vapour exactly inversely $a_3/_{v_3{}^2}$ with respect to p (in consequence of the great value of v_3), so that we get:

$$L = RT \log \frac{a_2/_{v_2{}^2}}{p}. \quad \ldots \ldots \ldots \quad (2)$$

The equation (1) serves to determine L; equation (2) for the calculation of p.

It follows immediately from (1), that at $T = 0$ [this is realizable in Helium; in all other substances only through extrapolation below the melting-point] L approaches the **finite** value $a_0/_{v_0}$[1]), in which a_0 and v_0 refer to $T = 0$ and the corresponding vapour pressure $p = 0$.

From the equating of (1) and (2) follows after division by RT:

$$\log p = - \frac{a_2/_{v_2} + RT}{RT} + \log \frac{a_2}{v_2{}^2} = - \frac{L}{RT} + \log \frac{a_2}{v_2{}^2}, \quad . \quad . \quad (3)$$

that is to say at "comparatively" low temperatures, where the above mentioned simplifications are valid. We see that the extrapolated vapour pressure exponentially approaches 0 at $T = 0$, this also being the case with $dp/_{dt}$. The latter follows, indeed, also from $\dfrac{dp}{dt} = \dfrac{L}{T(v_3 - v_2)} = \dfrac{L}{T v_3}$, in which v_3 (exponentially) approaches more strongly to ∞ than T to 0.

When (3) is written in the form

$$\log p = - \frac{L_0}{RT} + C + DT + \ldots = - \frac{a_0/_{v_0}}{RT} + \log \frac{a_0}{v_0{}^2} - a_0 T \ldots \quad (3 \, bis)$$

by the expansion of $a_2/_{v_2}$ and $\log a_2/_{v_2{}^2}$ into a series with respect to T^2[2]), $L_0 = a_0/_{v_0}$ can be easily determined from vapour pressure observations, and therefore, if v_0 is known at $T = 0$, $p = 0$ by extrapolation, also

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[1]) We saw already in § I that DE KOLOSSOWSKY lately came to the amazing discovery, that also at this equilibrium L would have to approach 0! In the liquid also the constant of attraction a would then have to approach 0, which is of course, nonsense. We might communicate more discoveries of this kind; some Italian authors have in view no less than the substitution of an entirely "new" theory of Thermodynamics for the earlier "antiquated" one. Also these authors arrive at the most startling, and (it need hardly be said) the most absurd results!

[2]) When a and b are assumed to be constant, one finds easily by the aid of the equation of state $\dfrac{a}{v} = \dfrac{a_0}{v_0} - RT - x_0 RT^2 \ldots$, in which x_0 is the coefficient of expansion at $T = 0$, i.e. $\dfrac{1}{v_0} \left(\dfrac{dv}{dt} \right)_0 = \dfrac{Rv_0}{a}$. Further $\log \dfrac{a}{v^2}$ is then $= \log \dfrac{a_0}{v_0{}^2} - 2x_0 T \ldots$

a_0 is known, i.e. the *extrapolated* limiting value of a_2 at very low temperatures. In this way the quantity a has been calculated by me in many cases (also for melted metals and salts, where a varies very little with the temperature).

If $b = f(v)$ had been taken into consideration, a term with $log\ T$ would have been added in the second member in (3), and also the vapour pressure constant $log\ {}^{a_0}/_{v_0{}^2}$ would have become somewhat more complicated, especially when also a and b are considered as functions of T. But in any case these constants C at the equilibrium liquid-vapour have nothing whatever to do with the "chemical" constants, introduced by NERNST, which are in relation with the constants of entropy [1]. In the case $b = f(v)$ the coefficient of $log\ T$ will always be **negative**, and depend in a simple way on the degree of variability of b with v. (Compare also my "Zustandsgl.",

p. 265—278). As $\dfrac{dL}{dt}$ is $= (c_p)_3 - (c_p)_2{}^2$), i.e. $L = L_0 + [(c_p)_3 - (c_p)_2]_0\ T\ldots$,

it follows from $\dfrac{dp}{dt} = \dfrac{L}{Tv_3}$ or $\dfrac{1}{p}\dfrac{dp}{dt} = \dfrac{L}{RT^2}$, that $log\ p$ will be $= -\dfrac{L_0}{RT} +$

$+ \dfrac{[(c_p)_3 - (c_p)_2]_0}{R}\ log\ T +$ etc. Now (when a and b are no functions of T)

$(c_v)_3$ is always $= (c_v)_2$; but when $b = f(v)$, $(c_p)_3$ in the vapour will always be considerably smaller than $(c_p)_2$ in the liquid, so that the coefficient of $log\ T$ $[(c_p)_3 - (c_p)_2$ at $T = 0$ (extrapolated) differs but little from this quantity at higher temperatures] is always *negative*. Hence never $= + 1.75$, as NERNST c.s. on the ground of a certain Theorem of Heat, which is absolutely misapplied here, would try to make us believe — even at 4000 to 5000°!

IV. Equilibrium solid-vapour.

a. At higher temperatures.

As long as no degeneration of the energy is perceptible in the solid phase, and we are, therefore, still in the RT-region, there is no essential difference with the equilibrium liquid-vapour. The diffe rence is only, that in the expression (1) for L (the total *sublimation heat*) a term $- P_1$ of the (static) repulsive forces is added, according to **b.** of § II, and k_3 (vapour) $= {}^3/_2\ R$ for mon-atomic gases will now not be $= k_1$ (solid) $= 3\ R$. We thus obtain:

$$L = (k_3 - k_1)\ T + \left(\frac{a_1}{v_1} - P_1\right) + RT, \quad \ldots \quad (1^a)$$

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[1] The vapour-pressure constants $C = log\ {}^{a_0}/_{v_0{}^2}$ at a and b constant are evidently in relation to the logarithms of the *critical pressures* $\left(p_k = \dfrac{1}{27}\ \lambda\ \dfrac{a_k}{b_k^2}\right)$.

[2] This formula, too, is only valid at "comparatively" low temperatures. Cf. Zustandsgl. p. 121—123, and the Article in the J. Chim. phys. against DE KOLOSSOWSKY cited in § I.

(2) becoming:

$$L = T\left[(k_3 - k_1)\ log\ T + R\ log\ \frac{a_1/v_1{}^2 - \beta_1}{p} + (S_0)_3 - (S_0)_1 \right],$$

which with $(S_0)_3 - (S_0)_1 = -(k_3 - k_1)\ log\ \theta + (k_3 - k_1)$ according to § II passes into

$$L = T\left[(k_3 - k_1)\left(1 + log\ \frac{T}{\theta} \right) + R\ log\ \frac{a_1/v_1{}^2 - \beta_1}{p} \right], \quad . \quad . \quad (2^a)$$

in which $a_1/v_1{}^2 - \beta_1$ will now approach 0 at $T = 0$ ($p = 0$). For with $\beta = \dfrac{\lambda/v}{v - b}$ the equation of state, neglecting p, becomes $\dfrac{a}{v^2} = \dfrac{\lambda/v + RT}{v - b}$;

so that (*extrapolated*) $\dfrac{a}{v^2}$ becomes $= \dfrac{\lambda/v}{v - b} = \beta$ at $T = 0$, i.e. $a/v^2 - \beta = 0$.

And since λ/v remains finite at $T = 0$, $p = 0$, this must also necessarily be the case with $v - b$. (Not before $p = \infty$ will v become $= b$). As the extrapolated value of $a_1/v_1{}^2 - \beta_1$ will approach 0 at $T = 0$, $p = 0$, this expression must be replaced by $RT : (v - b)$ in (2^a), in consequence of which we get:

$$log\ p = -\frac{L}{RT} + \frac{k_3 - k_1}{R}\left(1 + log\ \frac{T}{\theta} \right) + log\ T + log\ \frac{R}{v - b}, \quad . \quad (3^a)$$

in which L is given by (1^a), and $k_3 - k_1$ will be *negative*. Again both p and dp/dt (extrapolated) will approach 0 at $T = 0$, as $L_0 = a_0/v_0 - P_0$ remains *finite*.

Let us write (3^a) in the form

$$log\ p = -\frac{a_1/v_1 - P_1}{RT} + \frac{k_3 - k_1 + R}{R}\ log\ T - \frac{k_3 - k_1 + R}{R} +$$
$$+ \frac{k_3 - k_1}{R}\ (1 - log\ \theta) + log\ \frac{R}{v - b},$$

as $(k_3 - k_1)\ T + RT$ of L, divided by RT, yields the constant term $-(k_3 - k_1 + R) : R$. Hence we get:

$$log\ p = -\frac{a_1/v_1 - P_1}{RT} + \frac{k_3 - k_1 + R}{R}\ log\ T + \left[log\ \frac{R}{v - b} - \left(1 + \frac{k_3 - k_1}{R}\ log\ \theta \right) \right],$$

in which $a_1/v_1 - P_1$, expanded into a series with regard to T, will yield no term with T, so that — divided by RT — no further constant term is to be expected [1]). Accordingly again no "chemical" constants occurs in

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[1]) For from $\dfrac{a}{v^2} = \dfrac{\lambda/v + RT}{v - b}$ follows $-\dfrac{2a}{v^3}\dfrac{dv}{dt} = -\dfrac{\lambda/v + RT}{(v - b)^2}\dfrac{dv}{dt} - \dfrac{\lambda/v^2}{v - b}\dfrac{dv}{dt} + \dfrac{R}{v - b}$,

i.e. $\dfrac{dv}{dt}\left[-\dfrac{2a}{v^3} + \dfrac{a}{v^2}\dfrac{1}{v - b} + \dfrac{\lambda/v^2}{v - b} \right] = \dfrac{R}{v - b}$, when $\dfrac{a}{v^2}\ (v - b)$ is put for $\lambda/v + RT$. Hence

we get $\dfrac{dv}{dt}\dfrac{a}{v^2}\left[-2\dfrac{v - b}{v} + 1 + \dfrac{\lambda}{a} \right] = R$. Now according to the equation of state

the vapour-pressure constant C, no more than in the case liquid-vapour.

If now $a_1/v_1 - P_1 = (a_0/v_0 - P_0) + \alpha T^2$ (see Note 1) is written, and further $log \dfrac{R}{v-b} = log \dfrac{R}{v_0-b_0} + \gamma T$, in which according to the subjoined Note $v_0 - b_0$ is $= v_0 \times \dfrac{\lambda}{a_0}$, so that $log \dfrac{R}{v_0-b_0}$ becomes $= log \left(\dfrac{R}{v_0} \dfrac{a_0}{\lambda} \right)$, we get finally:

$$log\, p = -\frac{a_0/v_0 - P_0}{RT} + \frac{k_3 - k_1 + R}{R} log\, T + \left[log \left(\frac{R}{v_0} \frac{a_0}{\lambda} \right) - \left(1 + \frac{k_3 - k_1}{R} log\, \theta \right) \right] + DT + \text{etc.} \Bigg\} \, , \quad (3^a \ bis)$$

so that the extrapolated limiting value $L_0 = a_0/v_0 - P_0$ can be calculated from vapour pressure observations. At present a_0 can only be determined, if P_0 should be known.

The coefficient of $log\, T$ agrees with $dL/dt = k_3 - k_1 + R$ according to (1^a); which also ensues from $dL/dt = (c_P)_3 - (c_P)_1 = (k_3 + R) - k_1$, so that also on integration of $\dfrac{d\, log\, p}{dt} = \dfrac{L}{RT^2}$ a term $\dfrac{k_3 - k_1 + R}{R} log\, T$ duly occurs.

If b is still dependent on v (in solid substances in a much smaller degree than in liquids), some supplementary terms must be added. But in any case the coefficient of $log\, T$ will be *negative* again (in monatomic substances $= \frac{5}{2} R - 3 R = - \frac{1}{2} R$, or greater negative, when $b = f(v)$ is assumed); but never $+ 1,75$. For it is entirely disregarded by NERNST and many others, that the expansions into series, holding at *very low* temperatures in the T^4-region, are *not* valid at *higher* temperatures in the RT-region, and vice versa. In the intermediate region, where neither of the expansions into series are valid, only the complete DEBYE-formula for E and S can be used. The impermissible application of expansions into series, holding only at *very low* temperatures, also at much higher temperatures; and besides the assumption of Energy-degradation also for liquids and gases, have been the two greatest errors of the adherents of the Theorem of Heat.

Besides, it was a serious error of NERNST's to think that *merely* by

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evidently $\dfrac{v_0 - b_0}{v_0}$ is $= \dfrac{\lambda}{a}$ at $T = 0$, so that $\left(\dfrac{dv}{dt} \right)_0 = \dfrac{Rv_0^2}{a} \dfrac{1}{1 - \lambda/a} = \dfrac{Rv_0^2}{a} \dfrac{v_0}{b_0}$. And as

$\dfrac{1}{v} = \dfrac{1}{v_0} - \dfrac{1}{v_0^2} \left(\dfrac{dv}{dt} \right)_0 T \ldots, \dfrac{a}{v}$ becomes $= \dfrac{a}{v_0} - \dfrac{v_0}{b_0} RT$. Further $P = P_0 + \left(\dfrac{dP}{dv} \dfrac{dv}{dt} \right)_0 T \ldots,$

which with $P = \displaystyle\int_v^\infty \dfrac{\lambda/v}{v-b} \, dv$, hence $\left(\dfrac{dP}{dv} \right)_0 = - \dfrac{\lambda/v_0}{v_0 - b_0} = - \dfrac{a}{v_0^2}$, becomes $P = P_0 - \dfrac{v_0}{b_0} RT$.

For $\dfrac{a}{v} - P$ we find, therefore, $\dfrac{a_0}{v_0} - P_0 +$ terms with T^2 etc., but not with T.

the application of his Theorem of Heat it would be possible to get to know something concerning the vapour pressure constants, i.e. of the integration constant of the equation $\dfrac{d\,log\,p}{d\,t} = \dfrac{L}{RT^2}$. He overlooked, that the *direct* calculation of *log p* from the equating of the thermodynamic potentials, which leads to (3) and (3ᵃ), immediately yields the vapour pressure constant; i.e. it yields the *true* value of this constant [1]), and not the *wrong* value in consequence of the application of a theorem, which is *not valid* at higher temperatures!

b. At very low temperatures (d o e s n o t o c c u r i n H e l i u m).

As soon as there is question of degeneration in the solid phase, the matter is entirely different. According to **c.** of § II the following equation will be found for L — that is to say when the T^4-region is entered:

$$L = \left[k_3\,T + \left(\frac{a_{00}}{v_{00}} - \frac{a_3}{v_3} \right) \right] - \left[A_1 T^4 + \left(\frac{a_{00}}{v_{00}} - \frac{a_1}{v_1} \right) + P_1 + E_0 \right] + p\,(v_3 - v_1),$$

in which the first part refers to the vapour. When $A_1 T^4$ is neglected with respect to $k_3 T$, a_3/v_3 by the side of a_1/v_1, v_1 by the side of v_3, while $pv_3 = RT$ is put, we find:

$$L = \left(\frac{a_1}{v_1} - P_1 - E_0 \right) + (k_3 + R)\,T \quad \cdots \quad (1^b)$$

The heat of sublimation continues, therefore, to be finite unto $T = 0$, as then evidently $L_0 = a_0/v_0 - P_0 - E_0$.

From $L = T(S_3 - S_1)$ follows:

$$L = T \left[\{ k_3\,log\,T + R\,log\,(v_3 - b_3) + (S_0)_3 \} - {}^4/_3\,A_1 T^3 \right],$$

i.e. when the term with T^3 is neglected, and with $v_3 - b_3 = v_3 = RT:p$:

$$L = T \left[(k_3 + R)\,log\,T - R\,log\,p + R\,log\,R + (S_0)_3 \right]. \quad \cdots \quad (2^b)$$

And from (1ᵇ) and (2ᵇ) follows for p:

$$log\,p = -\frac{L}{RT} + \frac{k_3 + R}{R}\,log\,T + \left(log\,R + \frac{(S_0)_3}{R} \right), \quad \cdots \quad (3^b)$$

which, at $T = 0$, again gives $p = 0$, $dp/dt = 0$.

The form of the vapour pressure formula has remained the same, but *not until now* has the coefficient of *log T* become *positive*, viz. $c_p : R$ in the vapour; i.e. $^5/_2$ in monatomic vapours, $^7/_2$ in diatomic vapours, etc. — but all the same *never* $+ 1.75$, as NERNST c.s. always give.

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[1]) When in 1906 NERNST published his first communication in reference to this, I immediately brought forward my objections to his views. The paper had, already, been printed and corrected, when the Editor of the Z. Elektrochem., ABEGG, requested me kindly but urgently, to withdraw my paper, because NERNST had "energetically" protested against its insertion. The corrected Revision of the paper, written Nov. 10 (eingegangen Nov. 22) 1906, has lain in a drawer of my writing-desh for 20 years now.

If for L its value according to (1^b) is written, bearing in mind that $a_1/v_1 - P_1 - E_0$ again does not yield a term with T [1]), we get the following equation, taking into consideration that $S_0 = -k \log \theta - R \log \omega + k$ (cf. **a.** of § II):

$$\log p = -\frac{a_0/v_0 - P_0 - E_0}{RT} + \frac{k_3 + R}{R} \log T + \left[-\frac{k_3 + R}{R} + \log R - \right.$$
$$\left. - \frac{k_3}{R} \log \theta - \log \omega + \frac{k_3}{R} \right] + DT^4 \ldots,$$

i.e.

$$\left. \begin{aligned} \log p = -\frac{a_0/v_0 - P_0 - E_0}{RT} + \frac{k_3 + R}{R} \log T + \left[\log \frac{R}{\omega} - \right. \\ \left. - \left(1 + \frac{k_3}{R} \log \theta \right) \right] + DT^4 + \text{etc.} \end{aligned} \right\}, \quad (3^b \ bis)$$

so that only now the vapour pressure constant C is in connection with the so-called *"chemical"* constant through $(S_0)_3$ or ω. From vapour-pressure observations (if possible, see below) $(S_0)_3$ might be determined.

As according to § 2 $\log \omega = \log \omega_0 - \frac{3}{2} \log \theta - {}^3/_2 \log m$ may be written for $\log \omega$, in which, therefore, ω_0 has the same value for all substances, we may write for C in *monatomic* substances $C = \log \frac{R}{\omega_0} + \frac{3}{2} \log \theta + \frac{3}{2} \log m - 1 - \frac{3}{2} \log \theta$, $\frac{k_3}{R}$ then being $= {}^3/_2$.

Accordingly we get in this case:

$$C = \left(\log \frac{R}{\omega_0} - 1 \right) + \frac{3}{2} \log m = C_0 + \frac{3}{2} \log m,$$

in which m is the atomic weight of the (monatomic) substance. (In multi-atomic substances likewise C' will be $= C_0' + {}^3/_2 \log m$, but then C_0' is not $= C_0$ in monatomic substances, and besides C_0' will depend on θ, which quantity will be different in every substance). [2])

If in solid substances at such low temperatures as those at which ($3^b \ bis$) is valid, vapour-pressure observations are possible (the vapour pressures will mostly be so low then, that they are inaccessible to direct measurement; at any rate so far they have not yet been measured

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[1]) Even no terms with T^2 and T^3, because $\frac{dv}{dt}$ is now of the order of T^3, hence $1/v - 1/v_0$ and $P - P_0$ of the order of T^4. (See also the Note in **a.**).

[2]) With regard to the homogenity of the different formulae it may be pointed out, that e.g. in ($3^b \ bis$) ω is a volume, hence it has the dimensions $R\theta : \pi$. $Log(R : \omega)$ is therefore of the dimensions $\log \pi - \log \theta$, so that we may write $\log \frac{p}{\pi} = -\frac{a_0/v_0 \ \text{etc.}}{RT} + \frac{k_3 + R}{R} \log \frac{T}{\theta} - 1$, which is perfectly homogeneous.

in any substance), the limiting value $L_0 = a_0/v_0 - P_0 - E_0$ could be calculated. And since from vapour-pressure observations at higher temperatures (see under **a.**) the extrapolated value of $a_0/v_0 - P_0$ can be determined, E_0 could in this way be found experimentally.

V. Equilibrium solid-liquid.

a. At higher temperatures.

This occurs with all substances, from the triple point to not too high pressures; and also in *Helium* as continuation of the low-temperature curve.

For the *melting-heat* $Q = (E_2 - E_1) + p(v_2 - v_1)$ the following equation is found:

$$Q = (k_2 - k_1) T + \left(\frac{a_1}{v_1} - \frac{a_2}{v_2} - P_1\right) + p(v_2 - v_1), \quad . \quad . \quad \textbf{(4ª)}$$

in which $k_2 - k_1$ is negative. $Q = T(S_2 - \dot{S_1})$ gives further:

$$Q = T\left[(k_2 - k_1) \log T + R \log \frac{v_2 - b_2}{v_1 - b_1} + (S_0)_2 - (S_0)_1\right].$$

But $(S_0)_2 - (S_0)_1 = (k_2 - k_1)(1 - \log \theta)$, hence we get:

$$Q = T\left[(k_2 - k_1)\left(1 + \log \frac{T}{\theta}\right) + R \log \frac{v_2 - b_2}{v_1 - b_1}\right] \quad . \quad . \quad \textbf{(5ª)}$$

As in liquids $v_2 - b_2 = RT : (p + a_2/v_2^2)$ is always greater than $v_1 - b_1 = RT : (p + a_1/v_1^2 - \beta)$ in the solid phase, because a_1 is much greater than a_2, v_1 and v_2 differing only comparatively little, so that even $a_1/v_1^2 - \beta$ will be $> a_2/v_2^2$ also if v_2 should be $< v_1$; and as T soon approaches to a limiting value above or below the triple point (according as v_2 is $> v_1$ or $< v_1$), the second term of (5ª) can be slightly greater than the first (negative), and Q can be small positive. Experimentally comparatively small positive values are actually always found, much smaller than the much greater heats of evaporation and sublimation.

It also follows from (4ª) that, as also $a_1/v_1 - P_1$ will always be $> a_2/v_2$, Q can become small positive. The negative term $(k_2 - k_1) T$ has little influence on this, no more than $p(v_2 - v_1)$ for the case that v_2 should be $< v_1$, at least at not too high values of the pressure.

But at very high pressures the matter is different. Then in consequence of the characteristic temperature θ becoming higher and higher (see the third of the paper cited, p. 683; the expression for θ has, in the denominator, the root from the coefficient of compressibility, which will approach 0), T/θ becomes smaller and smaller, and as the expansions into series for E and S used, holding for comparatively great values of $T : \theta$, are no longer valid, and we then enter the T^4-region, other expressions will have to be substituted for (4ª) and (5ª). With very great values of

p it is then, however, not immediately to be seen from the modified equation (4ª), whether Q can still remain positive with $v_2 < v_1$. But it appears with the greatest clearness from $Q = T(S_2 - S_1) = T({}^4/_3 A_2 T^3 - {}^4/_3 A_1 T^3) = {}^4/_3 (A_2 - A_1) T^4$, in which A_2 and A_1 are both very small (these quantities have θ_2^3 resp. θ_1^3 in the denominator), while A_2 in the liquid (where the high-pressure degradation is not so far advanced as in the solid phase) will always be $> A_1$, that Q always remains small positive; and not before $p = \infty$, when A_2 would become $= A_1$, does it approach 0.

It follows then further from the relation of CLAPEYRON $\dfrac{dp}{dt} = \dfrac{Q}{T(v_2 - v_1)}$, that with $v_2 > v_1$ (the most frequently occurring case) $\dfrac{dp}{dt}$ will always be positive, and will approach to $+\infty$ at $p = \infty$. For Q then approaches $(a_2 - a_1)\dfrac{T^4}{\theta^3}$, $v_2 - v_1$ approaching to $(\gamma_2 \sigma_2 - \gamma_1 \sigma_1)\dfrac{T^4}{\theta^3}$, in which σ_2 and σ_1 represent the coefficients of compressibility. For

$$\left(\frac{dv}{dt}\right)_p = \left(\frac{dp}{dt}\right)_v \times -\left(\frac{dv}{dp}\right)_t = \gamma \frac{T^3}{\theta^3}\,\sigma,$$

because A' in the equation of state $\left(\text{as regards }\left(\dfrac{dp}{dt}\right)_v\right)$ has likewise θ^3 in the denominator, so that $v = v_0 + \gamma\dfrac{T^4}{\theta^3}\,\sigma$. Hence CLAPEYRON's equation becomes:

$$\frac{dp}{dt} = \frac{a_2 - a_1}{\gamma_2\,\sigma_2 - \gamma_1\,\sigma_1} \times \frac{1}{T}.$$

in which T remains finite, σ_2 and σ_1 both verging on 0, so that dp/dt will approach ∞, because a and γ are of the same order of magnitude according to (24) of the second of the papers cited (p. 511). Q and $\triangle v$ then approach both 0 at $p = \infty$, but $\triangle v$ (on account of σ) much more strongly than Q. In the case $v_2 > v_1$ the melting-point line has, therefore, a vertical asymptote at a finite value of T above the triple point.
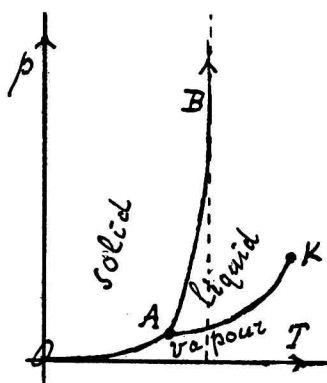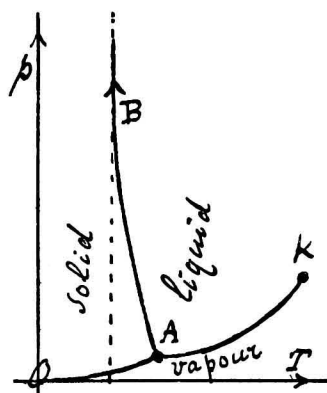
Fig. 1 $(v_2 > v_1)$ Fig. 2 $(v_2 < v_1)$

If $v_2 > v_1$ (retrogressive melting-point line), $\frac{dp}{dt}$ will approach $-\infty$, and there will be a vertical asymptote at a temperature below A.

The case might, however, also present itself, that in the latter case the melting-point line is so strongly retrogressive, or that the triple point is situated so low, that it enters the T^4-region already at comparatively low, i. e. not too high pressures. Hence not because in $T : \theta$ the quantity θ approaches ∞ at very high pressures at a temperature that remains finite, but because T itself will approach 0 with θ remaining finite. But this case will presently be considered more closely under **b.**

From (4^a) follows for p (Q is given by (5^a)):

$$p = \frac{Q - \left(\frac{a_1}{v_1} - \frac{a_1}{v_2} - P_1\right) + (k_1 - k_2)\,T}{v_2 - v_1}, \quad \ldots \quad (6^a)$$

which will be of the form $p = -c + \gamma T$ (6^a bis) with $v_2 > v_1$, and of the form $p = c - \gamma T$ with $v_2 < v_1$, i. e. at not too high pressures.

b. At very low temperatures (occurs with $v_2 > v_1$ only for Helium). Though we have already devoted a special article to this case [1]), we will briefly return to this subject in connection with what we have said above. We now find for Q:

$$Q = \left[k_2 T + \left(\frac{a_{00}}{v_{00}} - \frac{a_2}{v_2}\right)\right] - \left[A_1 T^4 + \left(\frac{a_{00}}{v_{00}} - \frac{a_1}{v_1}\right) + P_1 + E_0\right] + p(v_2 - v_1),$$

i. e. with neglect of $A_1 T^4$ with respect $k_2 T$:

$$Q = k_2 T + \left(\frac{a_1}{v_1} - \frac{a_2}{v_2} - P_1 - E_0\right) + p\,(v_2 - v_1) \quad \ldots \quad (4^b)$$

It also follows from $Q = T(S_2 - S_1)$, that

$$Q = T\left[(k_2 \log T + R \log (v_2 - b_2) + (S_0)_2) - \frac{4}{3} A_1 T^3\right],$$

or with $v_2 - b_2 = RT : (p + a_2/v_2^2) = RT : a_2/v_2^2$ (because here the comparatively low values of p can be neglected with regard to a_2/v_2^2) and with omission of the term with T^4:

$$Q + T\left[(k_2 + R) \log T - R \log a_2/v_2^2 + R \log R + (S_0)_2\right] \quad \ldots \quad (5^b)$$

From this follows that at $T = 0$ Q will approach to $(k_2 + R)T \log T$, i. e. to -0. At temperatures somewhat above $0°$ abs. the *negative* value of Q will however (in consequence of $\log T$) soon pass through zero, after which it will become and remain *positive*.

Hence it follows from $\frac{dp}{dt} = \frac{Q}{T(v_2 - v_1)}$, that at $T = 0$ $\frac{dp}{dt}$ will approach

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[1]) These Proc. **30**, 244—248 (1927).

$\dfrac{(k_2 + R)\,\log T}{v_2 - v_1}$, i. e. to $-\infty$ at $v_2 > v_1$ (Helium; see Fig. 3), and to $+\infty$ at $v_2 < v_1$ (retrogressive melting-point lines at low temperatures; see above the conclusion of **a.** and Fig. 4). The further course will now be at once evident from the two subjoined figures and from (5^b). The position of the minimum, resp. maximum, at M will in both cases be given by $Q = 0$, i. e. $(k_2 + R)\,\log T_m = R\,\log a_2/v_2^2 - R\,\log R - (S_0)_2$.
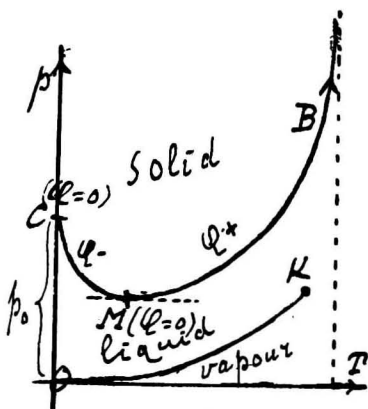

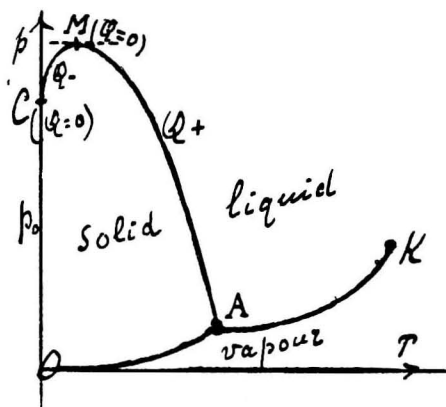Fig. 3 (Helium) $(v_2 > v_1)$ Fig. 4 $(v_2 < v_1)$

From (4^b) follows for p:

$$p = \frac{Q - k_2 T - \left(\dfrac{a_1}{v_1} - \dfrac{a_2}{v_2} - P_1 - E_0 \right)}{v_2 - v_1} - \frac{Q - k_2 T + C}{v_2 - v_1}, \quad . \quad (6^b)$$

as $a_1/v_1 - a_2/v_2 - P_1 - E_0$ will be negative owing to E_0. And as at very low temperatures $Q - T[k_2 + R)\,\log T - C']$ according to (5^b), p assumes $(v_2 > v_1)$ the form

$$p = a\,T\,\log T - \beta T + \gamma \,. \quad . \quad . \quad . \quad . \quad (6^b \ bis)$$

The latest very interesting observations bij KEESOM[1]) extend only to 1°.2 abs., so that the minimum at about 1°,14 abs. and the subsequent increase of pressure at still lower temperatures (portion MC in Fig. 3) have not yet been confirmed experimentally. But the observations, and the Fig. on p. 1142, lead us to expect a minimum somewhat below 1°,19 with pretty great certainty.

The following values namely have been found.

															(boiling p.)	(crit.)	
T	= 0	0.5	0.7	0.8	0.9	1	**1,19**	1.42	1.60	1.83	2.04	2.40	2.72	3.12	3.61	4.21	5.19 —
$p^{atm.}$	= —	—	—	—	—	—	**25.3**	26.5	27.4	29.8	35.7	48.6	62.8	81.5	108.8	140.5	— —
p (calc.)	54.1	31.0	27.8	26.7	25.7	25.5	**25.3** (min.)	26.1	27.4	29.8	35.7	49.6	63.1	81.5	106.5	140,5	205 —

[1]) These Proc. **29**, 1136—1145 (1926).

For the *higher* temperatures from $2°$ abs. the "calculated" values of p have been determined according to the formule $p = -c + \gamma T$ (see (6^a *bis*)) above at **a.**), to which still a term with T^2 has been added, viz.

$$p^{atm.} = -16.4 + 14.54\ T + 5.40\ T^2 \text{ (Helium, } 2° \text{ abs. and higher, provided}$$
$$\text{the pressures be not too high).}$$

This formula is in good agreement, but would give entirely wrong results below $2°$ abs. (gives much too low values for p then), because then we gradually get into the T^4-region of the solid state. Then the formula $p = aT\ log\ T - \beta T + \gamma$ must be used, i.e. in our case:

$$p^{atm.} = 58.4\ T\ log\ ^{10}T - 28.6\ T + 54.1 \text{ (Helium, below } 2° \text{ abs.),}$$

which formula would yield $p = 54.1$ atm. at $T = 0$ ($dp/dt = -\infty$) and presents a minimum at $T = 1°.14$, as follows from

$$dp/dt = 58.4\ (0.4343 + log^{10}\ T) - 28.6 = 58.4\ log^{10}\ T - 3.24,$$

which is zero at $log\ ^{10}T = 0.0554$, $\underline{T_{min.} = 1.136}$, giving $p_{min.} = \underline{25.26}$ atm. $= 25.3$ atm.

Experiment will be able to establish an appreciable rise of the pressure not before about $T = 0°.8$ abs., which will probably increase to more than 50 atm. at $T = 0$ [1]).

Remark I. If — what we consider improbable on the ground of several facts (cf. Chapter I) — *liquid* Helium were degenerated between $1°.19$ and $1°.83$, dp/dt would have to decrease in direct ratio to T^3 on decrease of temperature. Now the quantities dp/dt between $1°.19$ and $1°.42$, $1°.42$ and $1°.60$, etc. are proportional as $\dfrac{0.8}{0.23} : \dfrac{1.3}{0.18} : \dfrac{2.4}{0.23}$, i.e. as $3.2 : 7.2 : 10.5$ or as $1 : 2.25 : 3.3$, whereas the third powers of the middle temperatures $1°.305$, $1°.51$, $1°.715$ are in the ratio of $2.22 : 3.44 : 5.04$ or as $1 : 1.55 : 2.3$. Hence the decrease follows in reality another law, in casu the $T\ log\ T$-law, which is valid when the liquid Helium does *not* degenerate.

Remark II. According to (5^b) at $T = 0$ also $Q = 0$, and according to (6^b) p_0 becomes $= -\dfrac{(a_1/v_1 - a_2/v_2) - (P_1 + E_0)}{v_2 - v_1}$. Now both in the case of $v_2 > v_1$

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[1]) *Note added in the English text.* In a recent Article (These Proc. **30** (1927)) KEESOM has doubt of the existence of a minimum in the neighbourhood of $1°$ abs. (or a little lower, for it is very good possible that at that temperature we are still not entirely entered in the T^4-region), and believes that $\dfrac{dp}{dt}$ will approach to 0 at $T = 0$. But I think, one cannot conclude this with some certainty from his Figure on the page 1142 l.c. All things are still possible, and a decision will be reserved to further experiments.

I still remark, that KEESOM has calculated the coefficients of my formula (6^b bis) from experimental data at $1°.2$, $1°.8$ and $2°.4$ abs. and has — of course — found no agreement (see the Fig. **2** in his recent Article). For this formula is only valid at *very low* temperatures; for Helium certainly not higher than $1°.8$, so that his coefficients are entirely wrong and must be substituted by those, given above.

and of $v_2 < v_1$ p_0 is positive. In the first case the numerator must be negative, in the second case, however, positive. This can only be accounted for, when we assume that — a_1 being greater than a_2 — in the first case (Helium) $a_1/v_1 - a_2/v_2$ yet remains smaller than $P_1 + E_0$; whereas in the second case $P_1 + E_0 < a_1/v_1 - a_2/v_2$.

VI. Equilibrium between two solid phases.

Here for the first time — in consequence of the degeneration as regards the thermic energy of *both* the phases at very low temperatures — we meet with something, that can be brought in connection with a "Theorem of Heat". But we prefer, also here, to speak of the T^4-law of DEBYE, according to which Q/T becomes $= 0$ at $T = 0$, and accordingly the line of equilibrium will present a *horizontal* tangent at C.
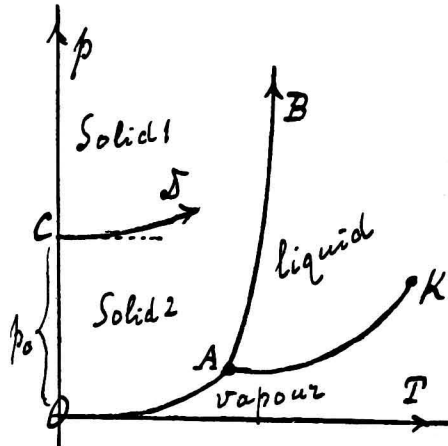

Fig. 5

a. At higher temperatures (e.g. at D).
We then find for Q at the transition $1 \rightarrow 2$:

$$Q = (k_2 - k_1) T + \left[\left(\frac{a_1}{v_1} - \frac{a_2}{v_2} \right) - (P_1 - P_2) \right] + p (v_2 - v_1), \quad . \quad (7^a)$$

and also

$$Q = T \left[(k_2 - k_1) \log T + R \log \frac{v_2 - b_2}{v_1 - b_1} \right] + (S_0)_2 - (S_0)_1, \quad . \quad (8^a)$$

the course of p along the transformation line according to (7^a) being determined by

$$p = \frac{Q - (k_2 - k_1) T - [(a_1/v_1 - a_2/v_2) - (P_1 - P_2)]}{v_2 - v_1}, \quad . \quad . \quad (9^a)$$

in which Q is given by (8^a). From $\dfrac{dp}{dt} = \dfrac{Q}{T(v_2 - v_1)}$ follows, that p is ascending or descending according as Q and $\triangle v$ have equal or opposite signs. We shall, however, see presently that only the first case will occur.

b. At very low temperatures (e.g. in the neighbourhood of C).
In this case we have:

$$Q = (A_2 - A_1)T^4 + \left[\left(\frac{a_1}{v_1} - \frac{a_2}{v_2} \right) - (P_1 - P_2) - \left\{ (E_0)_1 - (E_0)_2 \right\} \right] + p(v_2 - v_1), \quad (7^b)$$

and also

$$Q = \text{\textonequarter} (A_2 - A_1) T^4, \quad . \quad . \quad . \quad . \quad . \quad (8^b)$$

so that now Q will approach 0 proportionally to T^4, hence $Q/T \therefore T^3$, in consequence of which in this special case (equilibrium between two *solid* phases) $\frac{dp}{dt}$ will approach 0, since $v_2 - v_1$ remains finite to the end. There is, therefore, a horizontal tangent at C.

We find for p:

$$p = \frac{\text{\textonethird}(A_2 - A_1) T^4 - [\ ]}{v_2 - v_1}. \quad . \quad . \quad . \quad . \quad . \quad (9^b)$$

According to the formula of CLAPEYRON the pressure will again be ascending or descending, according as Q (i.e. $A_2 - A_1$) and $v_2 - v_1$ have the same or opposite signs. Now $A = {}^3/_5 R \pi^4 : \theta^3$, in which θ (cf. equation (24) in the second of the papers cited) is proportional to $v^{-5/2}$. In consequence of this A will be $\therefore v^{5/2}$, and thus $A_2 - A_1$ and $v_2 - v_1$ will always possess the same sign, so that the line of transformation will always be an *ascending* one. (See Fig. 5).

As at $T = 0$ in Fig. 5 we have assumed p_0 positive, necessarily again according to (9^b) $(a_1/_{v_1} - a_2/_{v_2}) - (P_1 - P_2) - ((E_0)_1 - (E_0)_2)$ and $v_2 - v_1$ will have to possess opposite signs. In Fig. 5 v_2 (under lower pressure) is probably $> v_1$, hence $(a_1/_{v_1} - a_2/_{v_2}) -$ etc. negative (see also the conclusion of § V under **b.**).

And now all possible cases of lines of equilibrium between gaseous, liquid and solid phases have been treated. The NERNST-theorem is nowhere to be found, except at the equilibrium between two *solid* phases, and then only at very low temperatures. The transference of the formulae holding at these temperatures to higher temperatures, as e.g. NERNST does in the case of the two sulphur modifications at $\pm 100°$ C. ($273°$ abs.), is absolutely impermissible, for these formulae are no longer valid then. Nor is it permissible to write $+ 1,75 \, log \, T$ at higher temperatures in the vapour-pressure formulae, the coefficient for *log T* always being evidently *negative* then! (See § III and IV). Even at very low temperatures the coefficient mentioned is only positive at the equilibrium solid-vapour, and even then never $+ 1,75$, but at least $+ 2,5$ (in monatomic substances).

Tavel sur Clarens (Suisse), Febr.-March 1927.