TABLE V.

v	p (15°.7) 1864	p (15°.7) 1893	Δp
39820	26 29	26 36	0 27
31790	32 85	32 96	0 33
26440	39.43	39 58	0 37
22610	46.00	46.22	0 48
19760	52.57	52 84	0.51
17550	59 14	59 45	0.53
15790	65.71	66.04	0 50
14340	72 28	72 69	0 56
13140	78 85	79 33	0 61
12140	85 42	85.88	0.53

sures, whereas the determination of the pressure in 1864 with an open manometer 65 meters high has been very difficult. 3$^{\text{nd}}$ Comparison of the accurate hydrogen isotherm of SCHALKWIJK (Diss. 1902) with the values extrapolated from AMAGAT's determinations gives differences of about 0,1 %.

Chemistry. — "*On the shape of meltingpoint-curves for binary mixtures, when the latent heat required for the mixing is very small or* $=0$ *in the two phases.*" (3$^{\text{rd}}$ communication). By J. J. VAN LAAR. Communicated by Prof. H. W. BAKHUIS ROOZEBOOM.

I. By the side of the *ideal* case, that the latent *heat of mixing* in the *liquid* phase $=0$, whereas it is ∞ in the *solid* phase ($\alpha=0$, $\alpha'=\infty$) — so that the *solid* phase consists only of one component — there is another case, also *ideal,* viz. that the latent heat of mixing $=0$ in *both* phases, or may be neglected. ($\alpha=0, \alpha'=0$). The solid phase consists then of the two components in a proportion which is comparable to that in the liquid phase.

The former ideal case is that of the processes of solidification, in which *no* solid solutions (or mixed crystals) are found, the latter may be appropriately called the ideal case of the *mixed crystals.*

To consider such ideal cases has always this use — apart from the simplifications in the considerations and calculations — that these cases may be adopted as the *normal* ones, from which all the other cases are to be considered as deviations in greater or smaller degree.

In our case the consideration of the limiting case $\alpha = 0$, $\alpha' = 0$ offers another advantage, viz. that much of what will be deduced in what follows, may be transferred with some restrictions to the *boilingpoint-lines* for *ideal* liquid and gaseous phases. For the thermodynamic relations of equilibrium agree perfectly, when the distinguishing feature between the two kinds of equilibrium, viz. the degree of the mutual influence of the two components in each of the phases has vanished. The difference consists only in this, that for the processes of melting the pure latent heat of melting may be assumed to be independent of the temperature, whereas for the processes of boiling the latent heat of evaporation will decrease with increasing temperature. Only in those cases, therefore, in which the boiling points of the two components do not differ much, the following considerations may be transferred to boilingpoint-curves of liquids, where α may be put $= 0$. When the difference between the boiling points is larger, this cannot be done any more.

II. The fundamental equations (2) of my *first* paper[1]) become $\left(\beta = \dfrac{\alpha}{q_1} = 0,\ \beta' = \dfrac{\alpha'}{q_1} = 0\right)$ simply:

$$T = \frac{T_1}{1 + \dfrac{RT_1}{q_1} \log \dfrac{1-x'}{1-x}} = \frac{T_2}{1 + \dfrac{RT_2}{q_2} \log \dfrac{x'}{x}} \quad . \quad . \quad . \quad . \quad (1)$$

It is now possible to eliminate x', and to express x explicitly in T, and in the same way to express the quantity x' explicitly in T after eliminating x.

In the first place we find:

$$\frac{1-x'}{1-x} = e^{\frac{q_1}{R}\left(\frac{1}{T}-\frac{1}{T_1}\right)} \quad ; \quad \frac{x'}{x} = e^{-\frac{q_2}{R}\left(\frac{1}{T_2}-\frac{1}{T}\right)}, \quad . \quad . \quad . \quad . \quad (2)$$

so that, when for shortness we put:

$$\frac{q_1}{R}\left(\frac{1}{T} - \frac{1}{T_1}\right) = \lambda_1 \quad ; \quad \frac{q_2}{R}\left(\frac{1}{T_2} - \frac{1}{T}\right) = \lambda_2, \quad . \quad . \quad (3)$$

we get, in consequence of $(1-x') + x' = 1$, the relation:

$$(1-x)\, e^{\lambda_1} + x e^{-\lambda_2} = 1.$$

1) These Proc. VI, June 27, 1903, p. 151.

In the same way

$$(1-x')\,e^{-\lambda_1}+x'e^{\lambda_2}=1.$$

From this we solve:

$$x=\frac{e^{\lambda_1}-1}{e^{\lambda_1}-e^{-\lambda_2}}\quad,\qquad x'=\frac{e^{-\lambda_1}-1}{e^{-\lambda_1}-e^{\lambda_2}},$$

or, in a form convenient for the calculation:

$$x'=\frac{e^{\lambda_1}-1}{e^{\lambda_1+\lambda_2}-1}\quad;\quad x=x'\,e^{\lambda_2}\,.\quad.\quad.\quad.\quad.\quad.\quad.\qquad(4)$$

From these equations, and also from equation (4) of the first communication (in which $w_1=q_1$ and $w_2=q_2$) we find easily:

$$\frac{dT}{dx}=-\frac{RT^2}{(1-x')q_1+x'q_2}\cdot\frac{x-x'}{x(1-x)}\;;\;\frac{dT}{dx'}=-\frac{RT^2}{(1-x)q_1+x\,q_2}\cdot\frac{x-x'}{x'(1-x')}.$$

For the *initial course* of the meltingpoint-curve follows from this ($T=T_1$)

$$\left(\frac{dT}{dx}\right)_0=-\frac{RT_1^{\,2}}{q_1}\left(1-\left(\frac{x'}{x}\right)_0\right)\;;\;\left(\frac{dT}{dx'}\right)_0=-\frac{RT_1^{\,2}}{q_1}\left(\left(\frac{x}{x'}\right)_0-1\right),$$

or, in connection with (2):

$$\left(\frac{dT}{dx}\right)_0=-\frac{RT_1^{\,2}}{q_1}\left(1-e^{-\theta_2}\right)\;;\;\left(\frac{dT}{dx'}\right)_0=-\frac{RT_1^{\,2}}{q_1}\left(e^{\theta_2}-1\right),\quad.\quad.\qquad(5)$$

when we put

$$\frac{q_2}{R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right)=\theta_2\quad.\quad.\quad.\quad.\quad.\quad.\quad.\quad.\qquad(6)$$

The *final course* (for the lowest temperature T_2) is found by changing the letters, so, by putting further $1-x=y$ and $1-x'=y'$.

$$\left(\frac{dT}{dy}\right)_0=-\frac{RT_2^{\,2}}{q_2}\left(1-\left(\frac{y'}{y}\right)_0\right)\;;\;\left(\frac{dT}{dy'}\right)_0=-\frac{RT_2^{\,2}}{q_2}\left(\left(\frac{y}{y'}\right)_0-1\right),$$

i.e. taking (2) into account:

$$\left(\frac{dT}{dy}\right)_0=\frac{RT_2^{\,2}}{q_2}\left(e^{\theta_1}-1\right)\;;\;\left(\frac{dT}{dy'}\right)_0=\frac{RT_2^{\,2}}{q_2}\left(1-e^{-\theta_1}\right),\;.\;.\;.\;.\qquad(5a)$$

when putting:

$$\frac{q_1}{R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right)=\theta_1\;.\quad.\quad.\quad.\quad.\quad.\quad.\quad.\qquad(6a)$$

θ_1 and θ_2 being both *positive* quantities (T_2 is always smaller than T_1), e^{θ_1} and e^{θ_2} will always be >1, $e^{-\theta_1}$ and $e^{-\theta_2}$ always <1. From this follows, that the quantities $\left(\frac{dT}{dx}\right)_0$ and $\left(\frac{dT}{dx'}\right)_0$ will always be *negative*, the quantities $\left(\frac{dT}{dy}\right)_0$ and $\left(\frac{dT}{dy'}\right)_0$ always *positive*. For the latent heat of mixing q_1 and q_2 can never become negative.

So in the ideal case $\alpha = 0$, $\alpha' = 0$ the meltingpoint-curve always begins to *descend* at the *highest* temperature, and to *ascend* at the *lowest* temperature, so that in this case a minimum is excluded. This appears also from the fact that the condition for a minimum is $\beta' > \frac{T_1 - T_2}{T_1}$ (loc. cit. p. 168), so that for $\beta' = 0$ this can never occur, and the meltingpoint-curve will therefore gradually descend from T_1 to T_2.

That a maximum cannot occur in *any* case for *normal* components, whatever value α or α' may have, — provided α' be larger than α — has been proved already in my first communication (loc. cit. p. 156).

The equations (5) and (5*a*) give rise to the following discussion.

In the limiting case $\underline{q_1 = 0}$ (q_2 finite) we have $\left(\frac{dT}{dx}\right)_0 = -\infty$, $\left(\frac{dT}{dx'}\right)_0 = -\infty$, $\left(\frac{dT}{dy}\right)_0 = 0$, $\left(\frac{dT}{dy'}\right)_0 = 0$, so that the two meltingpoint-curves will approach to the type A (fig.1).

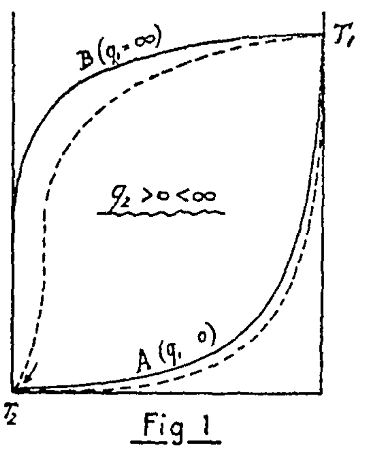

Fig 1

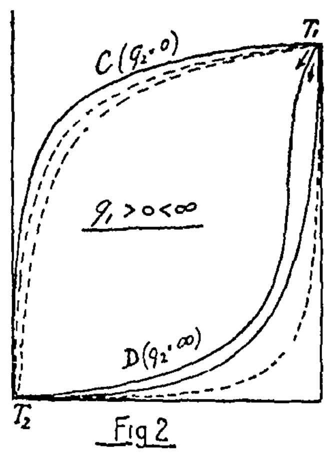

Fig 2

For $\underline{q_1 = \infty}$, $\left(\frac{dT}{dx}\right)_0$ and $\left(\frac{dT}{dx'}\right)_0$ will approach to 0, $\left(\frac{dT}{dy}\right)_0$ to ∞ (on account of the term e^{θ_1}), but $\left(\frac{dT}{dy'}\right)_0$ to a *limit*, viz. $\frac{RT_2^2}{q_2}$, as $e^{-\theta_1}$ converges to 0 This gives the limiting-type B (fig.1).

When $\underline{q_2 = 0}$ (q_1 finite), we have $\left(\frac{dT}{dx}\right)_0$ and $\left(\frac{dT}{dx'}\right)_0 = 0$; $\left(\frac{dT}{dy}\right)_0$

and $\left(\frac{dT}{dy'}\right)_0 = \infty$. The meltingpoint-curves approach to the type C (fig.2).

If, however, $q_2 = \infty$, then $\left(\frac{dT}{dx}\right)_0 = -\frac{RT_1^{\,2}}{q_1}$, $\left(\frac{dT}{dx'}\right)_0 = -\infty$, and $\left(\frac{dT}{dy}\right)_0$ and $\left(\frac{dT}{dy'}\right)_0$ approach both to 0. Now $\left(\frac{dT}{dx}\right)_0$ approaches to a limit, as $e^{-\theta_2}$ converges to 0. This gives rise to the limiting-type D (fig.2).

We shall see presently, that according to q_1 being greater or smaller, the final course for $T = f(x')$ in the case C, and the initial course for $T = f(x)$ in the case D may vary as to their curvature.

All the other cases lie between these extremes, but we shall see that there can yet be a great difference in course as to *concavity* and *convexity*. In order to form an opinion on this, however, we must write down the *second* differential-quotients.

III. We found for them in our *second* communication [1]) for $T = T_1$, when α and $\alpha' = 0$:

$$\left.\begin{aligned}\left(\frac{d^2T}{dx^2}\right)_0 &= \frac{1}{q_1}\left(\frac{dT}{dx}\right)_0\left[(q_1 - 4T_1) - \left(\frac{x'}{x}\right)_0\left\{(q_1 - 4T_1) - 2\,(q_1 - q_2)\right\}\right] \\ \left(\frac{d^2T}{dx'^2}\right)_0 &= \frac{1}{q_1}\left(\frac{dT}{dx'}\right)_0\left[(q_1 + 4T_1) - \left(\frac{x}{x'}\right)_0\left\{(q_1 + 4T_1) - 2\,(q_1 - q_2)\right\}\right]\end{aligned}\right\}, \quad (7)$$

in which $\left(\frac{x'}{x}\right)_0$ is $e^{-\theta_2}$ according to (2) and (6). For the corresponding expressions for T_2 we find by the same changes as for $\frac{dT}{dx}$ (see above):

$$\left.\begin{aligned}\left(\frac{d^2T}{dy^2}\right)_0 &= \frac{1}{q_2}\left(\frac{dT}{dy}\right)_0\left[(q_2 - 4T_2) - \left(\frac{y'}{y}\right)_0\left\{(q_2 - 4T_2) + 2\,(q_1 - q_2)\right\}\right] \\ \left(\frac{d^2T}{dy'^2}\right)_0 &= \frac{1}{q_2}\left(\frac{dT}{dy'}\right)_0\left[(q_2 + 4T_2) - \left(\frac{y}{y'}\right)_0\left\{(q_2 + 4T_2) + 2\,(q_1 - q_2)\right\}\right]\end{aligned}\right\}, \quad (7a)$$

in which $\left(\frac{y'}{y}\right)_0 = e^{\theta_1}$ according to (2) and (6a).

That these equations can give rise to a *point of inflection* in the meltingpoint-curve, so even at $\alpha' = 0$, I have already proved in my second communication (loc. cit. p. 256—257).

1) These Proc. VI, Oct. 31, 1903, p. 256.

For a *concave beginning* (i. e. turned towards the X-axis) $\frac{d^2T}{dx^2}$ is always negative $\left(\text{for } \frac{dT}{dx} \text{ becomes larger negative}\right)$. Hence $\frac{d^2T}{dx^2} : \frac{dT}{dx}$ *positive*. On the other hand this quotient will be *negative* for a *convex beginning*. In the same way for $T = f(x')$.

With a *concave end* $\frac{d^2T}{dy^2}$ will again be negative $\left(\frac{dT}{dy} \text{ becomes smaller positive}\right)$, so $\frac{d^2T}{dy^2} : \frac{dT}{dy}$ *negative*. For a *convex end* this quantity will be *positive*. We have therefore the following transition conditions.

$$\left.\begin{array}{llll}
\text{I} & \text{For } T=f(x) \begin{array}{c}\text{concave}\\ \text{convex}\end{array}\Big\} & \text{beginning} & 2(q_1-q_2)+(q_1-4T_1)(e^{\theta_2}-1) \gtrless 0 \\[2ex]
\text{II} & \text{For } T=f(x) \begin{array}{c}\text{concave}\\ \text{convex}\end{array}\Big\} & \text{end} & -2(q_1-q_2)-(q_2-4T_2)(1-e^{-\theta_1}) \lessgtr 0 \\[2ex]
\text{III} & \text{For } T=f(x') \begin{array}{c}\text{concave}\\ \text{convex}\end{array}\Big\} & \text{beginning} & 2(q_1-q_2)-(q_1+4T_1)(1-e^{-\theta_2}) \gtrless 0 \\[2ex]
\text{IV} & \text{For } T=f(x') \begin{array}{c}\text{concave}\\ \text{convex}\end{array}\Big\} & \text{end} & -2(q_1-q_2)+(q_2+4T_2)(e^{\theta_1}-1) \lessgtr 0
\end{array}\right\},$$

or in another form ·

$$\left.\begin{array}{ll|ll}
\text{I} & q_1 \gtrless 4T_1 + \dfrac{2(q_2-4T_1)}{1+e^{\theta_2}} & \text{III} & q_1 \gtrless -4T_1 + \dfrac{2(q_2+4T_1)}{1+e^{-\theta_2}} \\[3ex]
\text{II} & q_2 \lessgtr 4T_2 + \dfrac{2(q_1-4T_2)}{1+e^{-\theta_1}} & \text{IV} & q_2 \lessgtr -4T_2 + \dfrac{2(q_1+4T_2)}{1+e^{\theta_1}}
\end{array}\right\} \quad . \quad (8)$$

The different regions with their limits, which occur in these conditions, are represented in fig. 3 (Plate). The figure holds for $T_2 = {}^1/_2\, T_1$, the values of q_1 and q_2 are expressed in multiples of T_1.

Let us subject the limiting-curves to a closer examination (see fig. 3).

a. Curve I, viz.

$$q_1 = 4T_1 + \frac{2(q_2-4T_1)}{1+e^{\theta_2}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8^I)$$

According to (8) all the curves $T = f(x)$ with a *concave beginning* will lie *above* this curve, with a *convex* beginning *below* it. For q_1 must then be respectively larger or smaller than the values given by the second member.

The curve will also yield $q_1 = 0$ for $q_2 = 0$, for which $e^{\theta_2} = 1$. The *initial direction* is given by $q_1 = q_2$ (45°). Further for $q_2 = 4T_1$ is evidently also $q_1 = 4T_1$, and for $q_2 = \infty$, e^{θ_2} becoming $= \infty$, q_1 will again be $4T_1$. The curve I will therefore run pretty rapidly *asymtotically* to the straight line $q_1 = 4T_1$ for higher values of q_2, and will show a *maximum* somewhere past $q_2 = 4T_1$. (M_1 in fig. 3). This maximum is represented by $\left(\frac{dq_1}{dq_2} = 0\right)$:

$$(1 + e^{\theta_2}) - (q_2 - 4T_1)\frac{1}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)e^{\theta_2} = 0,$$

as $\theta_2 = \frac{q_2}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$, according to (6). We have then:

$$(1 + e^{-\theta_2}) - \frac{\theta_2}{q_2}(q_2 - 4T_1) = 0,$$

or

$$\theta_2 - e^{-\theta_2} = 1 + 4T_1\frac{\theta_2}{q_2},$$

or ($R = 2$)

$$\theta_2 - e^{-\theta_2} = 2\frac{T_1}{T_2} - 1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8a)$$

From this we may find θ_2 by approximation, so also q_2, and q_1 is found from (8^l). As $q_2 - 4T_1 = \frac{q_2}{\theta_2}(1 + e^{-\theta_2})$, we have:

$$q_1 = 4T_1 + 2\frac{q_2}{\theta_2}e^{-\theta_2} = 4T_1 + 2\frac{q_2}{\theta_2}\left(\theta_2 - 1 - 4T_1\frac{\theta_2}{q_2}\right),$$

hence

$$q_1 = 2q_2 - 4T_1 - 2\frac{q_2}{\theta_2},$$

or

$$q_1 = 2q_2 - 4\frac{T_1^2}{T_1 - T_2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8b)$$

Now fig.3 holds for $T_1 = {}^1/_2\, T_2$, so (8a) becomes:

$$\theta_2 - e^{-\theta_2} = 3,$$

yielding $\theta_2 = 3{,}05$. Consequently $q_2 = 2\,\theta_2 T_1 = 6{,}10\ T_1$. Further according to (8b) $q_1 = 2q_2 - 8T_1 = 4{,}20\ T_1$.

Of the curve I (comp. 8^l) I have determined the following points with $T_1 = {}^1/_2 T_2$, so that $\theta_2 = \frac{q_2}{2T_1}$.

$q_2 = 1\ T_1$	$e^{\theta_2} = 1,65$	$q_1 = 1,73\ T_1$	$q_2 = 7\ T_1$	$e^{\theta_2} = 33,1$	$q_1 = 4,17^5\ T_1$
2 ,,	2,72	2,92 ,,	8 ,,	54,6	$4,14^6$,,
3 ,,	4,48	3,63 ,,	10 ,,	148	4,08 ,,
5 ,,	12,2	4,15 ,,	15 ,,	1810	4,01 ,,
6 ,,	20,1	4,19 ,,	20 ,,	22000	4,00 ,,

Really the maximum lies just past $q_2 = 6T_1$. (We saw already above, that for $q_2 = 4T_1$ also $q_1 = 4T_1$).

b. The curve II, viz.

$$q_2 = 4T_2 + \frac{2\,(q_1 - 4T_2)}{1 + e^{-\theta_1}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8^{II})$$

This curve separates the curves $T = f(x)$ with *concave end* (*left* of this curve, because q_2 is then smaller than the second member) from that with a *convex* end (*right* of the curve, where q_2 is larger).

For $q_1 = 0$ also $q_2 = 0$, as $\theta_1 = 0$; (*initial direction* again $\underline{q_1 = q_2}$ (45°)); for $q_1 = 4T_2$ also $q_2 = 4T_2$, and for $q_1 = \infty$, q_2 will approach to $\underline{2\,q_1 - 4T_2}$, because $e^{-\theta_1}$ approaches to 0. The *limiting direction* of the curve II is therefore given by $q_2 = 2q_1$, or $\underline{q_1 = {}^1/_2\, q_2}$. (26°,5).

It will necessarily cut I. When $T_2 = {}^1/_2 T_1$, this point of intersection S_1 lies somewhat on the left of the maximum M_1. It is found by combining

$$q_1 = 4T_1 + \frac{2\,(q_2 - 4T_1)}{1 + e^{q_2/2T_1}} \quad \text{and} \quad q_2 = 2T_1 + \frac{2\,(q_1 - 2T_1)}{1 + e^{-q_1/2T_1}} \,.$$

By approximation we find $q_2 = \underline{5{,}90T_1}$, $q_1 = \underline{4{,}19T_1}$.

The further calculation leads to the following summary.

$q_1 = 1\ T_1$	$e^{-\theta_1} = 0,61$	$q_2 = 0,76\ T_1$	$q_1 = 8\ T_1$	$e^{-\theta_1} = 0,02$	$q_2 = 13,8\ T_1$
3 ,,	0,22	3,64 ,,	10 ,,	0,01	17,9 ,,
4 ,,	$0,13^5$	5,52 ,,	15 ,,	0,00	28,0 ,,
5 ,,	0,08	7,56 ,,	20 ,,	0,00	38,0 ,,
6 ,,	0,05	9,62 ,,			

For $q_1 = 2T_1$ ($= 4T_2$) also $q_2 = 2T_1$ (see above).

c. The curve III, i.e.

$$q_1 = -4T_1 + \frac{2\,(q_2 + 4T_1)}{1 + e^{-\theta_2}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (8^{III})$$

For values of q_1 larger than the second member the *beginning* of $T=f(x')$ is *concave*; these curves lie therefore *above* the curve. In the same way all the lines $T=f(x')$ with *convex* beginning lie below this curve.

Again $q_1=0$, when $q_2=0$ (*initial direction* $q_1=q_2$ (45°)). When q_2 approaches to ∞, q_1 approaches to $2\,q_2+4T_1$, so the *limiting direction* becomes $q_1=2\,q_2$ (63°,5). This curve lies entirely *outside* the two first, more to the left.

Some points of the curve III follow.

$q_2=1\,T_1$	$e^{-\theta_2}=0{,}61$	$q_1=2{,}20\,T_1$	$q_2=8\,T_1$	$e^{-\theta_2}=0{,}02$	$q_1=19{,}6\,T_1$
2 ,,	0,37	4,78 ,,	10 ,,	0,01	23,8 ,,
4 ,,	$0{,}13^5$	10,1 ,,	15 ,,	0,00	34,0 ,,
6 ,,	0,05	15,0 ,,	20 ,,	0,00	44,0 ,,

d. The curve IV, i. e.

$$q_2=-4T_2+\frac{2\,(q_1+4T_2)}{1+e^{\theta_1}} \quad . \quad . \quad . \quad . \quad . \quad (8^{IV})$$

If q_2 is smaller than the second member, the *end* of $T=f(x')$ will be *concave*; these lines lie accordingly *left* of the curve; on the *right* the lines $T=f(x')$ with *convex* end are found.

For $q_1=0$ again $q_2=0$ (*initial direction* $q_1=q_2$ (45°)). If $q_1=\infty$, q_2 evidently approaches *asymptotically* to $q_2=-4T_2$, just as the curve I approached asymptotically to $q_1=4T_1$, when $q_2=\infty$. The curve IV lies therefore only for a small part within the region of the positive q_2, and will therefore necessarily cut the q_1-axis somewhere in S_2, and yield a *maximum* value M_2 for q_2 before that time. This curve too lies therefore entirely outside the preceding curves, and again more to the left.

The q_1-axis is cut, when ($T_2={}^1/_2\,T_1$)

$$\frac{q_1+2T_1}{1+e^{q_1/2T_1}}=T_1,$$

or when

$$e^{q_1/2T_1}-2\,\frac{q_1}{2T_1}=1.$$

This is satisfied by

$$\frac{q_1}{2T_1}=1{,}25^7, \quad \text{or} \quad q_1=2{,}51T_1.$$

The maximum is found in exactly the same way as in I, and is determined by

$$\theta_1 - e^{-\theta_1} = 2\,\frac{T_2}{T_1} - 1, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8c)$$

to which belongs:

$$q_2 = 2q_1 - 4\,\frac{T_2^{\,2}}{T_1 - T_2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8d)$$

If $T_2 = {}^1/_2\, T_1$, then (8c) yields:

$$\theta_1 - e^{-\theta_1} = 0,$$

from which $\theta_1 = 0{,}567$, or $q_1 = 1{,}13\,T_1$. According to (8d) we have:

$$q_2 = 2q_1 - 2T_1 = 0{,}26\,T_1.$$

Further we have the following values for q_2 for increasing values of q_1.

$q_1 = 2\,T_1$	$e^{\theta_1} = 2{,}72$	$q_2 = 0{,}16\,T_1$	$q_1 = 10\,T_1$	$e^{\theta_1} = 148$	$q_2 = -1{,}84\,T_1$
4 ,,	7,39	$-0{,}57$,,	15 ,,	1810	$-1{,}98$,,
6 ,,	20,1	$-1{,}24$,,			

Already at $q_1 = 15\,T_1$ the limiting direction $q_2 = -4\,T_2$ (here $= -2\,T_1$) has been all but reached.

IV. So we have seen, that the four limiting curves (see fig.3), which divide the q_1, q_2-space into different fields, radiate from the origin ($q_1 = q_2 = 0$) in the space. All of them touch in the origin the straight line $q_1 = q_2$, the former two on the right, the latter two on the left. Only I is intersected by II; IV falls for the greater part outside the positive region, I and IV show maxima.

Below I and on the right of II lies the field A of the convex shaped meltingpoint-curves.

Between I and II on the left of the point of intersection S_1 lies a small region B_1, where the *end* of $T = f(x)$ has become concave; on its right is the region B_2, where the *beginning* of $T = f(x)$ has become concave.

Between II and III (on the left of S_1, between I and III) lies the field C, where $T = f(x)$ is concave throughout its course, $T = f(x')$ convex.

Between III and the q_1-axis (below S_2 between III and IV) lies the field D, where only the *end* of $T = f(x')$ is still convex.

Finally there is still a very small region between IV and the q_1-axis, where the meltingpoint curve — both $T = f(x)$ and $T = f(x')$ — is concave throughout its course.

If we assume a fixed value for q_2, e.g. $q_2 = 3\,T_1$, and vary q_1 from

0 *tot* ∞, *we pass successively through the four regions* A, B_1, C and D. For $q_2 = 10\ T_1$ e.g. we should pass through the region B_2 instead of through B_1.

If q_1 is assumed to be constant, e.g. $= 1\,T_1$, we pass successively through the fields A, B_1, C, D and E, when q_2 decreases from ∞ tot 0.

Fig.4 gives a representation of the first mentioned transition, viz. for $q_2 = 3\,T_1$.

Between the meltingpoint-curves, marked 2,4 and 2,8 (so holding for $q_1 = 2{,}4$ and $2{,}8\,T_1$), the transition from A to B_1 (hatched) is situated. Between 3,4 and 3,8 (see the hatched parts) is the transition from B_1 to C. Between 7 and 8 (in this case for $T = f(x')$) that from C to D. Further the cases $q_1 = 1$, $q_1 = 2$ (A), $q_1 = 5$ (C) and

$q_2 = 3\ T_1$

$q_1 =$	$1T_1$	$2T_1$	$2.4T_1$	$2.8T_1$	$3.4T_1$	$3.8T_1$	$5T_1$	$7T_1$	$8T_1$	$10T_1$
$T = 0.95\ T_1$	$x' = 0.00^{8}$	0.01^{6}	0.01^{9}	0.02^{2}	0.02^{6}	0.02^{9}	0.03^{8}	0.05^{1}	0.05^{7}	0.06^{9}
	$x = 0.03^{3}$	0.06^{6}	0.07^{9}	0.09^{1}	0.11	0.12	0.16	0.21	0.24	0.28
0.90 „	$x' = 0.01^{9}$	0.03^{6}	0.04^{3}	0.05^{2}	0.05^{8}	0.06^{6}	0.08^{0}	0.10	0.11	0.13
	$x = 0.07^{2}$	0.14	0.16	0.18^{5}	0.22	0.25	0.30	0.39	0.43	0.50
0.85 „	$x' = 0.03^{9}$	0.05^{2}	0.07^{2}	0.08^{2}	0.09^{6}	0.10	0.13	0.16	0.17	0.19
	$x = 0.11^{4}$	0.21	0.25	0.28	0.33	0.36	0.44	0.55	0.59	0.67
0.80 „	$x' = 0.05^{3}$	0.09^{5}	0.11	0.12	0.14	0.15	0.18	0 22	0.23	0.25^{5}
	$x = 0.16$	0.29	0.34	0.38	0.44	0.47	0 56	0.67	0.72	0.78^{5}
0.75 „	$x' = 0.08^{2}$	0.14	0.16	0.18	0.20	0.21^{5}	0.25	0.29	0.30	0.32
	$x = 0.22$	0 39	0.44	0.48	0.55	0.58	0.67	0.78	$0\ 81^{5}$	0.87
0.70 „	$x' = 0.12^{5}$	0.20	0.23	0.25	0.28	0.29	0.33	0.36	0.38	0 39
	$x = 0.29^{5}$	0.48	0.54	0.59	0.65	0.69	0.77	0.86	0.89	0.92^{8}
0.65 „	$x' = 0.19$	0.29	0.32	0.35	0.37	0.39	0.43	0.46	0.47	0.48
	$x = 0.38$	0.59	0.65	0.69	0.75	0.78	0.85	0.91^{8}	0.93^{8}	0.96^{4}
0.60 „	$x' = 0.30^{5}$	0.43	0.46	0.48	0.51	0.52^{5}	0.55^{6}	0.58	0.59	0 60
	$x = 0.50$	0.71	0.76	0.80	0.84	0.87	0.91^{5}	0.96^{0}	0.97^{1}	0.98^{6}
0.55 „	$x' = 0.52$	0.64	0.66^{6}	0.69^{5}	0.71	0.72	0.73^{5}	0.75	0.75^{6}	0.76
	$x = 0.68$	0.84	0.87	0.91^{3}	0.92^{7}	0.94^{0}	0.96^{5}	0.98^{6}	0.99^{1}	0.99^{7}

$q_1 = 10\,(D)$ have been traced. The curves 2,8 and 3,4 represent therefore the type B_1 with convex beginning and concave end for $T = f(x)$. The calculations (according to formulae (4)) are summarized in the annexed table, i.e. for $T_2 = \frac{1}{2}\,T_1$, to which fig.3 applies.

With this change of q_1 we do not enter the region E; therefore q_2 would have to be smaller than 0,26 T_1 (see above).

V. It remains to answer the question, to what modifications the fields and their limits drawn in fig. 3 are subjected, when T_2 is not $\frac{1}{2}\,T_1$, but e.g. 0,9 T_1 or 0,1 T_1.

The initial directions of the curves I to IV remain quite the same, also the final directions, but between them there are some modifications; specially the place of the points of intersection and of the maxima is changed.

a. If T_2 is no longer 0,5 T_1, but e.g. 0,9 T_1, so that T_2 and T_1 are *very near* to each other, we find for the maximum M_1 from (8*a*) and (8*b*):

$$\theta_2 - e^{-\theta_2} = 1^2/_9 \quad ; \quad q_1 = 2q_2 - 40\,T_1,$$

yielding $\theta_2 = 1{,}45^5$, hence, as $\theta_2 = \dfrac{q_2}{2}\left(\dfrac{1}{T_2} - \dfrac{1}{T_1}\right)$ is now $\dfrac{q_2}{18T_1}$ $q_2 = 26{,}2\;T_1$. For q_1 we find then $q_1 = 12{,}4\;T_1$.

The maximum has now got quite outside the limits of the values of q which occur practically, so that the curve I now gradually rises within these limits. (fig.5).

The point of intersection of I with II has not been displaced much. We find now for it $q_2 = 5{,}85\;T_1$, $q_1 = 5{,}55\;T_1$, so that the value of q_2 has remained nearly constant.

The consequence of the modified course of the curves I and II is, that the region B_1 has all but disappeared; on the left of S_1 I and II nearly coincide; the region B_2 has strongly diminished.

But also C and D have considerably diminished, so that the greater part of the space is left for A and E.

The considerable increase of the region E is due to the fact, that the point of intersection of the curve IV with the q_1-axis lies much higher than in fig. 3, and that the maximum has moved considerably to the right. In fact we find for the point of intersection mentioned:

$$\frac{q_1 + 3{,}6\,T_1}{1 + e^{q_1/18T_1}} = 1{,}8\;T_1\,, \quad \text{or} \quad e^{q_1/18T_1} - 10\,\frac{q_1}{18T_1} = 1,$$

from which $\dfrac{q_1}{18T_1} = 3{,}577$, so $q_1 = 64{,}4\;T_1$.

The maximum is given by (8*c*) and (8*d*), viz.

$$\theta_1 - e^{-\theta_1} = 0{,}8 \quad ; \quad q_2 = 2q_1 - 32{,}4\, T_1,$$

giving $\theta_1 = 1{,}125$, so $q_1 = \underline{20{,}3\, T_1}$, $q_2 = \underline{8{,}2\, T_1}$.

In the following table some more data are given, which have been used for the construction of fig.5.

Curve I	$q_2/T_1 =$	1	3	5	8	10	15	20	25	30	40	50	100	150
	$q_1/T_1 =$	1,09	3,09	4,86	7,13	8,37	10,7	11,9	12,3[8]	12,2[6]	11,0	9,39	4,74	4,07
Curve II	$q_1/T_1 =$	1	2	4	6	8	10	15	20	30	40	60	100	
	$q_2/T_1 =$	0,93	1,91	4,04	6,40	8,96	11,7	19,5	28,3	48,0	69,3	112[5]	196	
Curve III	$q_2/T_1 =$	1	2	4	6	8	10	15	20	30	40	60	100	
	$q_1/T_1 =$	1,14	2,33	4,88	7,65	10,6	13,8	22,5	32,1	53,2	75,4	120	203	
Curve IV	$q_1/T_1 =$	1	3	5	8	10	15	20	25	30	40	50	100	150
	$q_2/T_1 =$	0,87	2 45	3,81	5,46	6,32	7,67	8,09	7,82	7,08	4,93	2,68	-2,8	-3,53

b. Let us now take $T_2 = \underline{0{,}1\, T_1}$, so that the two temperatures of melting lie *very far* apart. This case (see fig.6) agrees more closely with that for which $T_2 = 0{,}5\, T_1$; only the maximum of the curve II has got nearer to $q_2 = 4\, T_1$, and the point of intersection of II with I has moved much farther to the right. This has made the field B_1 considerably larger than in the case $T_2/T_1 = 0{,}5$, which field had nearly vanished for $T_2/T_1 = 0{,}9$.

But nearly the whole of curve IV lies now outside the positive region, so that the appearance of bi-concave meltingpoint-curves is almost excluded.

The maximum of I is determined by

$$\theta_2 - e^{-\theta_2} = 19 \quad ; \quad q_1 = 2\, q_2 - 4^4/_9\, T_1,$$

yielding $\theta_2 = 19$. As $\theta_2 = \dfrac{q_2}{{}^2/_9 T_1}$, so $q_2 = \underline{4^2/_9\, T_1}$, q_1 being $\underline{4{,}0\, T_1}$.

For the point of intersection of II with I we find, as e^{θ_2} is very large and $e^{-\theta_1}$ very small,

$$q_1 = \underline{4{,}0\, T_1} \ , \ q_2 = 2\, q_1 - 4\, T_2 = 8{,}0\, T_1 - 0{,}4\, T_1 = \underline{7{,}6\, T_1}.$$

The curve IV cuts the q_1-axis, when

$$0{,}2\, T_1 = \frac{q_1 + 0{,}4\, T_1}{1 + e^{\frac{q_1}{{}^2/_9 T_1}}},$$

so when $$0{,}2\, e^{\frac{q_1}{{}^2/_9 T_1}} = \frac{q_1}{T_1} + 0{,}2\,,$$

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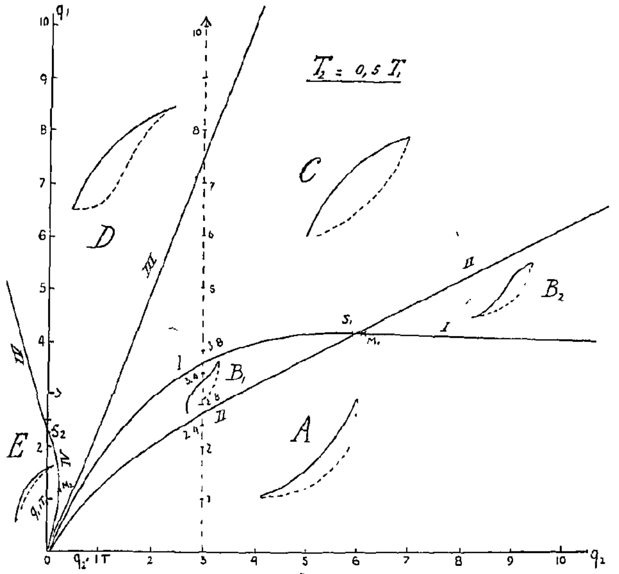

Fig 3

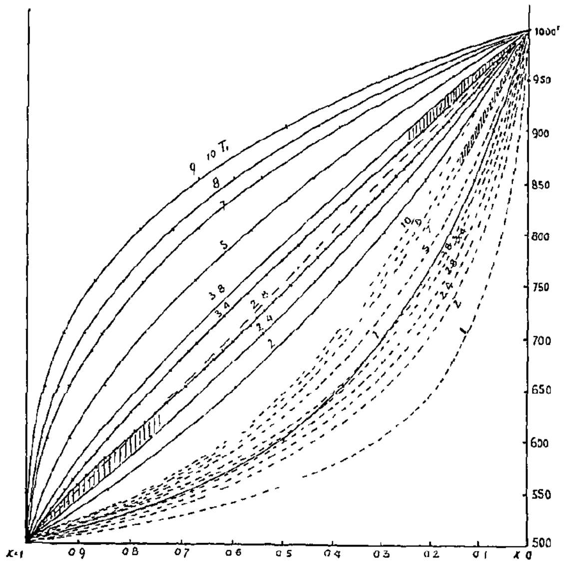

Fig 4

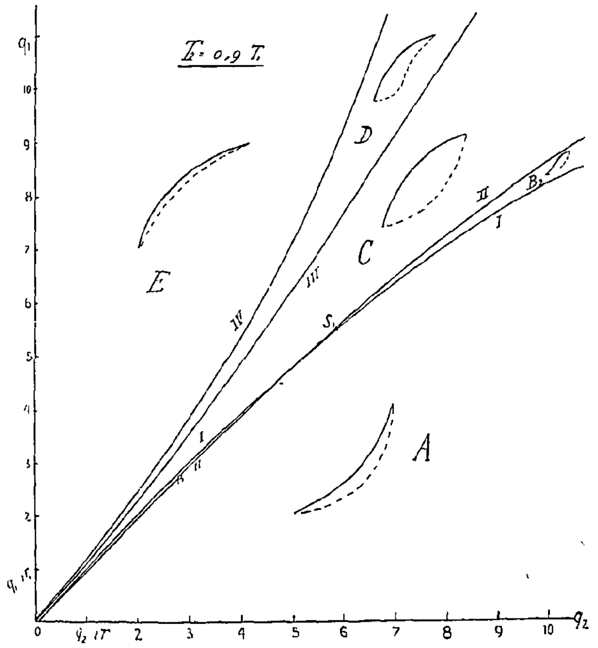

Fig 5

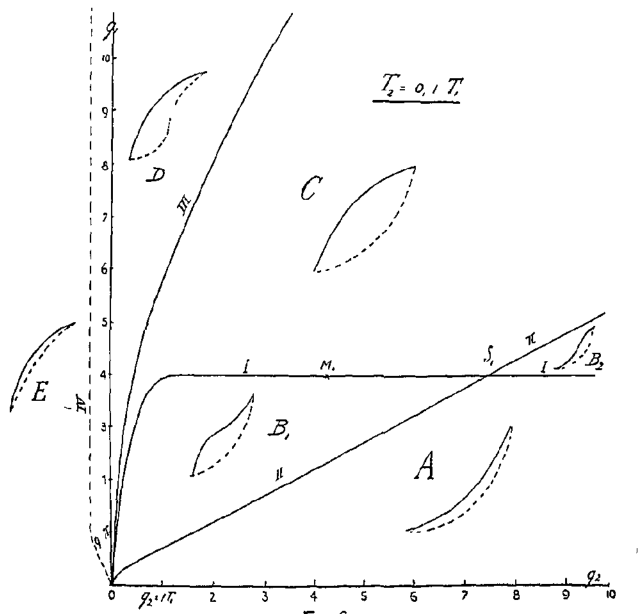

Fig 6.

or
$$e^{\frac{q_1}{2/_9 T_1}} - \frac{10}{9} \cdot \frac{q_1}{2/_9 T_1} = 1$$

This gives $\frac{q_1}{2/_9 T_1} = 0{,}203$, hence $q_1 = \underline{0{,}045 T_1}$.

The maximum is found from
$$\theta_1 - e^{-\theta_1} = -0{,}8 \ ; \ q_2 = 2\, q_1 - 0{,}0444\, T_1 .$$

This is satisfied by $\theta_1 = 0{,}1025$, hence $q_1 = \underline{0{,}0228\, T_1}$, $q_2 = \underline{0{,}0012\, T_1}$.

We can further calculate the following points of the four curves.

Curve I	$q_2/T_1 =$	$1/_9$	$2/_9$	$4/_9$	$6/_9$	$8/_9$	$10/_9$	$20/_9$		
	$q_1/T_1 =$	1,06	1,97	3,15	3,68	3,89	3,96	4,00		
Curve II	$q_1/T_1 =$	$1/_9$	$2/_9$	$4/_9$	$6/_9$	$8/_9$	$10/_9$	$20/_9$	3	4
	$q_2/T_1 =$	0,040	0,14	0,48	0,91	1,36	1,81	4,04	5,60	7,60
Curve III	$q_2/T_1 =$	$1/_9$	$2/_9$	$4/_9$	$6/_9$	$8/_9$	$10/_9$	$20/_9$	3	
	$q_1/T_1 =$	1,12	2,17	3,83	4,89	5,60	6,15	8,44	10,0	
Curve IV	$q_1/T_1 =$	$1/_9$	$2/_9$	$4/_9$	$6/_9$	$8/_9$	$10/_9$	$20/_9$		
	$q_2/T_1 =$	−0,014	−0,066	−0,20	−0,30	−0,35	−0,38	−0,40		

c. Hence when we draw near to the limiting case $T_2 = T_1$, all four curves will evidently approach to the straight line $\underline{q_1 = q_2}$, which cuts the angle of the coordinates in two equal parts. Fig.5 is to a certain extent already a representation of this case.

If, however, T_2 is very small, so that T_2/T_1 approaches to 0, then I passes evidently into the straight line $\underline{q_1 = 4T_1}$; II into $\underline{q_2 = 2q_1}$; III into $\underline{q_2 = 0}$, so into the q_1-axis; IV into $\underline{q_2 = -4T_2 = 0}$, so again into the q_1-axis. Of this fig.6 gives already an idea.

As to the two maxima and the two points of intersection, we have finally the following summary.

	M_1					M_2			
$T_2/T_1 = 0$	0,1	0,5	0,9	1	0	0,1	0,5	0,9	1
$q_2/T_1 = 4$	4,2	6,1	26,2	∞	0	0,0012	0,26	8,2	∞
$q_1/T_1 = 4$	4,0	4,2	12,4	∞	0	0,0228	1,13	20,3	∞

	S_1					S_2			
$T_2/T_1 = 0$	0,1	0,5	0,9	1	0	0,1	0,5	0,9	1
$q_2/T_1 = 8$	7,6	5,9	5,85	4	0	0	0	0	0
$q_1/T_1 = 4$	4,0	4,2	5,55	4	0	0,045	2,51	64,4	∞

And in this way I think that the ideal case $a = 0$, $a' = 0$ has been sufficiently elucidated.