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an amount of about $\frac{1}{100}$ atmosphere will keep such a phase in equilibrium, at least as far as the pressure is concerned. And a cause which accounts for a difference of pressure of about $\frac{1}{100}$ atmosphere accounts also for considerable differences in density as the critical isothermal runs nearly horizontally in the neighbourhood of the critical point.

A return to the time when we thought to explain a thing by speaking of solubility and insolubility, seems not to be desirable to me.

Chemistry. — *"On the possible forms of the meltingpoint-curve for binary mixtures of isomorphous substances."* By J. J. VAN LAAR. (Communicated by Prof. H. W. BAKHUIS ROOZEBOOM).

I. The occurrence of so called *"eutectic points"* in *meltingpoint-curves* does not seem to agree with the supposition of *perfect isomorphy* of the two solid components and of their mixtures. This fact has been repeatedly pointed out. It has been assumed that an interruption in the curve representing the solid mixtures (as in fig. 1 of the plate) can only occur for *isodimorphous* substances, and that the series of mixtures in the case of isomorphous substances was necessarily to be uninterrupted (as in fig. 2).

Lately STORTENBEKER [1]) expressed again the same idea and this induced me to subject the question to a closer investigation. In the following paper I hope to show that an interruption in the series of the mixtures can very well occur even for *perfectly isomorphous* substances. In order to do this we must keep in view that — especially in the *solid* condition — *unstable* phases may occur, and that in all occurring cases it is possible to trace the meltingpoint-curve *continuously through the eutectic point.* Only the stable conditions which generally lie above the eutectic point are liable to be realized, so the series of the mixtures is interrupted only *practically.*

Prof. BAKHUIS ROOZEBOOM has expressed the idea of prolonging the meltingpoint-curve beyond the eutectic point already before; the way however in which we must think this to be performed is indicated inaccurately in the figure of an earlier paper of STORTENBEKER [2]).

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[1]) Ueber Lücken in der Mischungsreihe bei isomorphen Substanzen, Zeitschrift für Ph. Ch. **43**, 629 (1903).

[2]) Ueber die Löslichkeit von hydratierten Mischkrystallen, Z. f. Ph. Ch. **17**, 645 (1895).

The following considerations are an abbreviated survey of a more elaborate paper which will be published elsewhere [1].

II. I have shown in a previous communication [2], that we may express the *molecular* thermodynamic potentials of the two components of a *liquid* mixture — if we assume the equation of state of VAN DER WAALS — as follows

$$\mu_1 = e_1 - c_1\, T - (k_1 + R)\, T \log T + \frac{a_1 x^2}{(1+rx)^2} + RT \log (1-x)$$

$$\mu_2 = e_2 - c_2\, T - (k_2 + R)\, T \log T + \frac{a_2(1-x)^2}{(1+rx)^2} + RT \log x$$

The different quantities occurring in these equations have the well known signification, indicated in the paper quoted above.

In order to simplify the calculation we shall always assume in the following, that $r\left(= \dfrac{-b_1 + b_2}{b_1} \right) = 0$, and therefore that the equations $a_1 = \dfrac{A}{b_1{}^3}$ and $a_2 = \dfrac{A}{b_2\,b_1{}^2}$ are identically satisfied, A representing $a_1\,b_2{}^2 - 2\,a_{12}\,b_1\,b_2 + a_2\,b_1{}^2$. This assumption comes to the same as the supposition that the molecular volumes of the two components differ only slightly, which supposition may be considered to be justified, as the terms $\dfrac{a_1 x^2}{(1+rx)^2}$ and $\dfrac{a_2(1-x)^2}{(1+rx)^2}$ represent the mutual influence of the two components in the mixture only *approximately*.

In the second place I shall assume that the above expressions also apply to the *solid* state, an assumption which we may expect to be satisfied in first approximation, as the case we are dealing with, namely that of *mixed crystals* or *solid solutions* [3], shows in many respects the greatest analogy with liquid solutions.

If we also suppose r in the solid phase to differ little from zero, and if we indicate all quantities in that phase with accents, then we may write:

For the *liquid* phase:

$$\mu_1 = e_1 - c_1\, T - (k_1 + R)\, T \log T + a\, x^2 + RT \log (1-x)$$

$$\mu_2 = e_2 - c_2\, T - (k_2 + R)\, T \log T + a\,(1-x)^2 + RT \log x$$

For the *solid* phase:

$$\mu'_1 = e'_1 - c'_1\, T - (k_1 + R)\, T \log T + a'\, x'^2 + RT \log (1-x')$$

$$\mu'_2 = e'_2 - c'_2\, T - (k_2 + R)\, T \log T + a'\,(1-x')^2 + RT \log x'$$

$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad (1)$$

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[1] In the *Archives Teyler*.

[2] These proceedings April 24, 1903.

[3] Mixed crystal will always be treated here as *solid solutions*, though in these latter years difficulties have sometimes arisen against this view. See i.a. STORTEN-BEKER, l.c., p. 633.

The components are in equilibrium in both phases if

$$\mu_1 = \mu'_1 \quad ; \quad \mu_2 = \mu'_2,$$

so that we get (the terms with $T \log T$ cancel each other):

$$e_1 - c_1 T + a\, x^2 + RT \log (1-x) = e'_1 - c'_1 T + a'\, x'^2 + RT \log (1-x') \Big\}$$

$$e_2 - c_2 T + a\, (1-x)^2 + RT \log x = e'_2 - c'_2 T + a'\, (1-x')^2 + RT \log x' \Big\}^,$$

or with

$$e_1 - e'_1 = q_1 \quad , \quad e_2 - e'_2 = q_2 \quad , \quad c_1 - c'_1 = \gamma_1 \quad , \quad c_2 - c'_2 = \gamma_2 :$$

$$RT \log \frac{1-x'}{1-x} = q_1 - \gamma_1 T + (a\, x^2 - a'\, x'^2) \Bigg\}$$

$$RT \log \frac{x'}{x} = q_2 - \gamma_2 T + [a(1-x)^2 - a'(1-x')^2] \Bigg\} .$$

If we pay attention to the circumstance that for $x=0$, $x'=0$ the quantity T must be equal to T_1, and in the same way $T=T_2$ for $x=1$, $x'=1$ (T_1 and T_2 are the meltingtemperatures of the pure components), then we may write·

$$\gamma_1 = \frac{q_1}{T_1} \quad , \quad \gamma_2 = \frac{q_2}{T_2} .$$

We have therefore

$$T \left(\frac{q_1}{T_1} + R \log \frac{1-x'}{1-x} \right) = q_1 + (a\, x^2 - a'\, x'^2) \Bigg\}$$

$$T \left(\frac{q_2}{T_2} + R \log \frac{x'}{x} \right) = q_2 + [a(1-x)^2 - a'(1-x')^2] \Bigg\}^,$$

or with

$$\alpha = q_1 \beta \quad , \quad \alpha' = q_1 \beta' :$$

$$T = T_1 \frac{1 + (\beta x^2 - \beta' x'^2)}{1 + \dfrac{RT}{q_1} \log \dfrac{1-x'}{1-x}} = T_2 \frac{1 + \dfrac{q_1}{q_2} [\beta(1-x)^2 - \beta'(1-x')^2]}{1 + \dfrac{RT_2}{q_2} \log \dfrac{x'}{x}} \cdot \cdot \cdot \text{(2)}$$

These are the two fundamental equations from which we may calculate the values of x' and T corresponding to each given value of x, and which represent a course of the meltingpoint-curve which is perfectly continuous, at least theoretically.

It is easy to see that in the case that no mixed crystals occur, x' is continuously equal to zero, and the equation is reduced to

$$T = T_1 \frac{1 + \beta x^2}{1 - \dfrac{RT_1}{q_1} \log (1-x)},$$

an equation which I have already deduced in a previous paper. But in the present paper we will assume that the mixing-proportion

in which one of the components occurs in the solid phase; though in the extreme case it can be exceedingly small (i. e. practically equal to zero), yet in general can never be rigorously equal to zero. In this way the *continuity* remains preserved, and we may give all possible values to the quantities β and β' — as to β' from 0 to ∞.

We shall observe here at once that the quantity which dominates the whole phenomenon is the quantity β' of the *solid* phase. When this quantity has a high value, the solid phase will contain only a very small trace of one of the two components, and only when the value of this quantity becomes comparable with the corresponding quantity β in the liquid phase, the case of fig. 2 can occur. It is therefore of the highest importance to know the exact signification of these quantities β and β', or rather of the quantities $\alpha = q_1 \beta$ and $\alpha' = q_1 \beta'$.

From the above deductions appears namely that the quantity αx^2 does not represent anything else but the absorbed *latent heat* required for the *mixing* per Gr. Mol. for the case that an infinitely small quantity of one of the components is mixed with the solution in which the mixing-proportion for this component is $1 - x$. In the same way the quantity $\alpha (1 - x)^2$ represents the latent heat for the other component in this solution. The quantity α itself is therefore the latent heat for the first component for $x = 1$; i.e. for the case that the first component is mixed with a solution which consists exclusively of the second component — or we may also say that α is the latent heat for the second component for $x = 0$; i. e. for the case that this component is mixed with a solution consisting exclusively of the first. The fact that these two quantities of latent heat are the same is a consequence of our supposition $b_1 = b_2$, from which follows that $\alpha_1 = \dfrac{A}{b_1{}^3}$ is equal to

$\alpha_2 = \dfrac{A}{b_2 b_1{}^2}$. In reality these two quantities will not always be equal.

That the signification we have ascribed to the quantities αx^2 and $\alpha (1 - x)^2$ is the true one, may be shown from the numerators of equation (2), which being respectively multiplied with q_1 and q_2, represent the *total* latent heats of liquefaction w_1 and w_2, namely

$$w_1 = q_1 (1 + \beta x^2 - \beta' x'^2) = q_1 + \alpha x^2 - \alpha' x'^2$$

$$\left.\begin{array}{c} w_2 = q_2 \left(1 + \dfrac{q_1}{q_2} [\beta (1-x)^2 - \beta' (1-x')^2]\right) = q_2 + \alpha (1-x)^2 - \alpha' (1-x')^2 \end{array}\right\} \cdot (3)$$

The total latent heat required for the liquefaction is therefore equal to the *pure* latent heat of liquefaction, *augmented* with the latent heat required for the mixing of the liquid phase, *diminished* with that required for the mixing of the solid phase.

A high value for α (or β) means therefore a high value of the latent heat of mixing, and when we shall presently see that a high value of β' leads to very small values of x' or of $1-x'$, this circumstance may be interpreted as follows:

If a large amount of energy is required in order to make one of the solid components enter into the solid solution (or the mixed crystal) then this solid solution will contain only a slight trace of one of these two components.

III. We now proceed to the discussion of the fundamental equations (2).

Let us in the first place determine the quantities $\dfrac{dT}{dx}$ and $\dfrac{dT}{dx'}$ by *totally* differentiating the conditions of equilibrium $-\mu'_1 + \mu_1 = 0$ and $-\mu'_2 + \mu_2 = 0$ according to T. After several transformations we get:

$$\frac{dT}{dx} = -T\frac{(x-x')\dfrac{\partial^2 \zeta}{\partial x^2}}{(1-x')w_1 + x'w_2} \quad ; \qquad \frac{dT}{dx'} = -T\frac{(x-x')\dfrac{\partial^2 \zeta'}{\partial x'^2}}{(1-x)w_1 + xw_2} \quad . \quad . \quad (4)$$

These well known equations have been deduced several times [1]), i. a. by Prof. van der Waals for the analogous equilibrium of liquid and gaseous phases.

From (4) we may deduce the quantity $\left(\dfrac{dT}{dx}\right)_0$, i. e. the *initial direction* of the meltingpoint-curve.

As $\dfrac{\partial \mu_1}{\partial x} = -\dfrac{RT}{1-x} + 2\alpha x$, we have

$$\frac{\partial^2 \zeta}{\partial x^2} = -\frac{1}{x}\frac{\partial \mu_1}{\partial x} = \frac{RT}{x(1-x)} - 2\alpha,$$

therefore, for $x = 0$, $T = T_1$

we have:
$$\left(\frac{\partial^2 \zeta}{\partial x^2}\right)_0 = \frac{RT_1}{x_0},$$

if we write x_0 for $x = 0$. For $x = 0$ we have also $x' = 0$. The denominator of $\dfrac{dT}{dx}$ appears therefore to be equal to $(w_1)_0 = q_1$, hence

$$\left(\frac{dT}{dx}\right)_0 = -T_1\frac{(x_0 - x'_0)\dfrac{RT_1}{x_0}}{q_1} = -\frac{RT_1^2}{q_1}\left(1 - \frac{x'_0}{x_0}\right),$$

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[1]) See i. a. my Lehrbuch der math. Chemie, p. 118 and 123—124. (Leipzig, J. A. Barth, 1901).

from which follows that — q_1 being supposed to be *positive* — the value of $\left(\dfrac{dT}{dx}\right)_0$ can only be positive if $\dfrac{x_0'}{x_0}$ should be greater than unity. Let us therefore determine the limiting value of $\dfrac{x_0'}{x_0}$. With $T = T_1$, $x = 0$, $x' = 0$ we may derive from the equations (2):

$$T = T_2 \frac{1 + \dfrac{q_1}{q_2}(\beta - \beta')}{1 + \dfrac{RT_2}{q_2} \log \dfrac{x_0'}{x_0}},$$

and we have :

$$\log \frac{x_0'}{x_0} = \frac{q_2}{R}\left(\frac{1 + \dfrac{q_1}{q_2}(\beta - \beta')}{T_1} - \frac{1}{T_2}\right).$$

Therefore the value of $\dfrac{x_0'}{x_0}$ remains smaller than unity, and the meltingpoint-curve continues to *descend*, as long as we have:

$$\beta - \beta' < \frac{q_2}{q_1}\left(\frac{T_1}{T_2} - 1\right) \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

In the following we will always assume $T_1 > T_2$ or $\dfrac{T_1}{T_2} - 1$ positive. The above condition will then the sooner be satisfied, according as β' in the solid phase has a *higher positive* value. Now probably β will nearly always have a very small positive value and β' a rather large positive value. The condition will therefore probably be nearly always satisfied. If we put $\beta = 0$, then we get simply .

$$- \alpha' = - q_1 \beta' < q_2\left(\frac{T_1}{T_2} - 1\right).$$

If β' (or α') is *positive*, i. e. if heat is *absorbed* in mixing the *solid* phase, then we shall *always* have $\dfrac{x_0'}{x_0} < 1$ and therefore the melting-point curve will *always descend* on the side of the *highest* temperature. An initially ascending part and in connection with this the occurrence of a maximum-meltingtemperature is therefore *almost totally excluded*. The *possibility* of a maximum exists only in the *exceptional and nearly inconceivable* case, that β' has a much smaller positive value than β, or even a negative value.

If we determine $\left(\dfrac{dT}{dx}\right)_{x=1}$ at the side of the *lowest* temperature quite in the same way, then we find, denoting $1 - x$ by y.

$$\left(\frac{dT}{dx}\right)_{x=1} = -\frac{RT_2^2}{q_2}\left(1 - \frac{y_0'}{y_0}\right),$$

where:

$$log\,\frac{y_0'}{y_0} = \frac{q_1}{R}\left(\frac{1+(\beta-\beta')}{T_2} - \frac{1}{T_1}\right).$$

The quantity $\frac{y_0'}{y_0}$ is therefore always smaller than unity if

$$\beta - \beta' < \frac{T_2}{T_1} - 1. \quad . \quad . \quad . \quad . \quad . \quad . \quad (5bis)$$

The second member being negative, this condition can only be satisfied if β' has a *high positive* value. Two cases may therefore occur, according to β' being larger or smaller. In the first case the initial part of the curve near T_2 descends again and a *minimum* will therefore occur (fig. 2). In the second case the curve ascends near T_2; it will therefore descend continuously from T_1 to T_2 without presenting a minimum.

For the case $T_1 = T_2$ the conditions (5) and (5ᵃ) pass into

$$\beta - \beta' < 0,$$

and a *minimum* will always in this case occur if $\beta' > \beta$, and probably this will always be the case.

The same considerations apply of course for $\left(\frac{dT}{dx'}\right)_0$.

In the above considerations we have tacitly assumed that *anomalous* components occur in neither of the phases; formation of *complex* molecules or *dissociation* are therefore always excluded in the cases which we consider. When one or both of the components of the solid phase for instance consist totally or partially of double molecules, then the occurrence of a *maximum* is not excluded at all.

We now proceed to the discussion of the equations (2) for different values of β', starting with very high values.

IV. In the following we shall always put $\beta = 0$ (in the liquid phase). This simplifies the calculations in a high degree and it does not alter the results qualitatively. The equations (2) then take the following form:

$$T = \frac{T_1(1-\beta'\,x'^2)}{1 + \frac{RT_1}{q_1}\,log\,\frac{1-x'}{1-x}} = \frac{T_2\left(1 - \frac{q_1}{q_2}\beta'(1-x')^2\right)}{1 + \frac{RT_2}{q_2}\,log\,\frac{x'}{x}}. \quad . \quad (6)$$

Let us further assume the following values, in order to be able to execute the calculations *numerically*:

$$T_1 = 1200 \qquad \qquad q_1 = 2400 \text{ Gr. cal.,}$$

$$T_2 = 500 \qquad \qquad q_2 = 2000 \quad \text{''}$$

Then we get $(R = 2)$:

$$T = \frac{1200\,(1 - \beta'\,x'^2)}{1 + log\,\dfrac{1-x'}{1-x}} = \frac{500\,(1 - 1{,}2\,\beta'\,(1-x')^2)}{1 + \dfrac{1}{2}\,log\,\dfrac{x'}{x}} \cdot \quad . \quad . \quad . \quad (6^a)$$

We will begin with assuming β' to be very large, e. g. $\underline{\beta' = 5}$. As we have $\alpha' = q_1\,\beta'$ this means that the latent heat of mixing for the first component when $x = 1$ (or of the second when $x = 0$) is five times as great as the latent heat of solidification of the first component. From the above equation:

$$T = \frac{1200\,(1 - 5x'^2)}{1 + log\,\dfrac{1-x'}{1-x}} = \frac{500\,(1 - 6(1-x')^2)}{1 + \dfrac{1}{2}\,log\,\dfrac{x'}{x}}$$

we may calculate the temperature T corresponding to an arbitrarily chosen value of x, the value of x' being exceedingly small. So we get for T:

$$T = \frac{1200}{1 - log(1-x)},$$

and for x':

$$1 + \frac{1}{2}\,log\,\frac{x'}{x} = -\,\frac{25}{12}\,(1 - log\,(1-x)).$$

The following table I (p. 159) gives a survey of the corresponding values of x, x' and T.

This represents the branch AA' of the meltingpoint-curves which starts from $1200°$ (see fig. 3). AB' is the curve $T = f(x')$.

If we put $1 - x = y$ and $1 - x' = y'$ then we have the equations

$$T = \frac{500\,(1 - 6y'^2)}{1 + \dfrac{1}{2}\,log\,\dfrac{1-y'}{1-y}} = \frac{1200\,(1 - 5(1-y')^2)}{1 + log\,\dfrac{y'}{y}},$$

from which we may calculate a new series of corresponding values of x, x' and T. So we get the branch BB' starting from $500°$ (BA' is again the curve $T = f(x')$). The value of y' being in this case very small, T may again be calculated from

$$T = \frac{500}{1 - 0{,}5\,log(1-y)},$$

and y' from

TABLE I.

x	T	$\frac{x'}{x}\times 10^4$	$x'\times 10^5$
0	1200	21	0
0.1	1086	14	14
0.2	981	8.3	17
0.3	884	4.8	14
0.4	794	2.6	10
0.5	709	1.2	6
0.6	626	0.46	3
0.7	545	0.14	1
0 8	460	0.026	0 2
0.9	363	0.0014	0.01
0.95	300	0,...	0,...
0 97	266	0,...	0,...
0.99	214	0,...	0,...
1	0	0	0

TABLE II.

y	T	$\frac{y'}{y}\times 10^6$	$y'\times 10^7$
0	500	25	0
0.1	475	15	15
0.2	450	8.6	17
0.3	424	4.5	14
0 4	398	2.0	8
0.5	371	0.89	4
0.6	343	0.31	2
0.7	312	0.078	0.5
0.8	277	0.11	0.09
0.9	232	0.00040	0.006
0.95	200	0,...	0,...
0.97	185	0,...	0,...
0.99	151	0,...	0,...
1	0	0	0

$$1 + log\,\frac{y'}{y} = -\,\frac{48}{5}\,(1-\,0{,}5\,log\,(1-y)).$$

The values calculated in this way are found in table II (see above).

The values found for y' are even smaller than those for the first branch. In both branches we clearly see the occurrence of a *maximum* in the curves $T = f(x')$, from which point the value x' (or y') does not increase any more, but falls again to zero.

The position of that maximum may be easily found from the general equation (4) for $\frac{dT}{dx'}$. The tangent running vertically, the denominator $(1-x)\,w_1 + x\,w_2 = 0$ must be zero and therefore we have, as we have assumed β to be equal to zero:

$$(1-x)\,q_1\,(1-\beta' x'^2) + x q_2\,(1-\frac{q_1}{q_2}\,\beta'\,(1-x')^2) = 0.$$

Neglecting x' we get:

$$(1-x)\,q_1 + x q_2\left(1-\frac{q_1}{q_2}\,\beta'\right) = 0,$$

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and therefore

$$x_m = \frac{q_1}{q_1 + q_2\left(\dfrac{q_1}{q_2}\beta' - 1\right)} = \frac{q_1}{q_1 - q_2 + q_1\beta'} \quad \dots \quad (7)$$

Introducing our values for q_1 and q_2 and $\beta' = 5$, we get $x_m = {}^6/_{31} = \underline{0,19}$.

With this value corresponds $T_m = \dfrac{1200}{1,211} = \underline{991°}$. Further we have

$\left(\dfrac{x'}{x}\right) = 0,00087$, and therefore $x'_m = \underline{0,00017}$, which agrees with the value found in the first table for the first branch.

For the second branch we have exactly in the same way:

$$y_m = \frac{q_2}{q_2 + q_1(\beta' - 1)} = \frac{q_2}{q_2 - q_1 + q_1\beta'} \quad \dots \quad (7bis)$$

With $\beta' = 5$ this yields $y_m = {}^5/_{29} = \underline{0,17}$.

T_m is there $\dfrac{500}{1,093} = \underline{457°}$, $\left(\dfrac{y'}{y}\right)_m = 0,000010$, and therefore $y'_m = \underline{0,0000017}$, which value again agrees with that found in the second table.

If x'_1 and x'_2 represent the proportions in which the second component occurs in the two solid phases which coexist in the *eutectic* point C with the liquid phase x, then the point C may be found by solving a double set of equations (6), namely those with x'_1 and those with x'_2. From these equations the quantities T, x, x'_1 and x'_2 may be solved.

If x'_1 and $1 - x'_2$ may be neglected, then we get simply:

$$T = \frac{T_1}{1 - \dfrac{RT_1}{q_1}\log(1-x)} = \frac{T_2}{1 - \dfrac{RT_2}{q_2}\log x}, \quad \dots \quad (8)$$

from which follows after introduction of our values for T_1, etc. $x = \underline{0,809}$, $T = \underline{452°}$.

The corresponding values of x' and y' (v'_1 and $1 - x'_2$) may be calculated as has been done above. (Compare also the tables for $x = 0,8$).

A closer consideration of the equations (6) shows (comp. fig. 3), that besides the branches mentioned above a third branch exists, which may to some extent be regarded as the connecting curve of the two former ones. This branch, however, lies wholly within the region of the *negative* absolute temperatures and has therefore only mathematical importance for the continuity of the meltingpoint-curve. The curve $T = f(x)$, namely $A'DB'$ forms the connection between

AA' and $B'B$. EDF is the corresponding curve $T=f(x')$, which touches $A'DB'$ in the common minimum D, where $x = x'$.

The point D is therefore determined by the equations

$$T = T_1 (1 - \beta' x^2) = T_2 \left(1 - \frac{q_1}{q_2} \beta' (1-x)^2\right), \quad \ldots \quad (9)$$

or with our values:

$$T = 1200 (1 - 5x^2) = 500 (1 - 6(1-x)^2),$$

which gives $x = x' = 0,494$, $T = -264°$.

The point E indicates another value of x', corresponding to the point A' of the curve $T = f(x)$, where $x = 1$, but now $T = -0°$. This point is obviously determined by the equation (comp. (6))

$$1 - \frac{q_1}{q_2} \beta' (1 - x')^2 = 0 \quad \text{(therefore } w_2 = 0\text{)}, \quad \ldots \quad (10)$$

which yields $x' = 0,592$.

The point F indicates a value of x' corresponding to the point B' of the curve $T = f(x)$, where $x = 0$, $T = -0°$. Now we have:

$$1 - \beta' x'^2 = 0 \quad \text{(therefore } w_1 = 0\text{)}, \quad \ldots \quad (10bis)$$

from which follows: $x' = 0,447$.

The curve $T = f(x)$ has therefore obtained a continuous course through the points A' and B', the curve $T = f(x')$ however changes abruptly at B' from B' to E, and at A' from A' to F; further its course is continuous from E through D to F.

The question might be put: in what case does the point E come in A' and the point F in B' and has the discontinuity in the curve $T = f(x')$ therefore reached its highest possible value? Obviously this is the case for $\beta' = \infty$. For then $w_2 = 0$ can vanish for $x' = 1$ and w_1 for $x' = 0$. In this case the lines $A'D$ and ED coincide over their whole length with the axis $x = 1$, and the lines $B'D$ and FD with the axis $x = 0$.

At all temperatures above the absolute zero the values of x' and y' vanish in this case continuously; this represents therefore the case, that the solid phase contains only *one* component.

The lines $A'DB$ and EDF lie, as we have seen, wholly in the region of negative absolute temperatures; besides this they lie with their whole course in the region of the *unstable* phases, as is shown by a closer examination of the relations

$$\frac{\partial^2 \zeta}{\partial x^2} = \frac{RT}{x(1-x)}; \quad \frac{\partial^2 \zeta'}{\partial x'^2} = \frac{RT}{x'(1-x')} - 2\alpha'.$$

V. The value of β', for which the point D, where $x = x'$, is found exactly at $T = 0$, may be calculated by solving the equations

$$0 = T_1\,(1-\beta' x^2) = T_2\,(1-\frac{q_1}{q_2}\beta'(1-x')^2),$$

which yield :

$$\beta' = \left(1 + \sqrt{\frac{q_2}{q_1}}\right)^2; \quad x' = \left(1 + \sqrt{\frac{q_2}{q_1}}\right)^{-1}, \quad \cdot \quad \cdot \quad \cdot \quad (11)$$

i. e. with our values of q_1 and q_2, $\beta' = 3{,}659$ and $x' = 0{,}523$.

The whole curve EDF or $T=f(x')$ of fig. 3 has here contracted to the single point D (see fig. 4), and the curve $A'DB'$ or $T = f(x)$ is degenerated into a *straight* line, *all* whose values coexist with that one value of x'.

This line $A'DB'$ and the point D still represent *unstable* phases.

If for this case we calculate the maxima for x' and y' of the two principle branches as we have done above, then we find:

$$x_m = 0{,}26, \quad T_m = 922°, \quad x'_m = 0{,}00088.$$

$$y_m = 0{,}24, \quad T_m = 439°, \quad y'_m = 0{,}000062.$$

The maximum value for x' appears to have increased to about 5 times the value it had with $\beta' = 5$, and that for y' to about 36 times its former value. The maximum value for y' now lies *below* the eutectic point. A simple calculation may show that in our case this already happens as soon as β' becomes smaller than 4,55. The maximum on the other side will require a much smaller value of β' before it descends below the eutectic point.

As soon as β' becomes smaller than $\left(1 + \sqrt{\frac{q_2}{q_1}}\right)^2$ or with our assumptions $< 3{,}66$, the curve $A'DB'$ begins to turn upwards and we get the course indicated in fig. 5 for e. g. $\beta' = 2{,}5$.

The line $A'DB'$ lies now wholly in the *stable* region for $T = f(x)$, $\dfrac{\partial^2 \zeta}{\partial x^2}$ being henceforth always positive. The line EDF on the other hand lies wholly in the *unstable* region for $T = f(x')$, as easily appears from the expression for $\dfrac{\partial^2 \zeta'}{\partial x'^2}$. This latter circumstance however is not permanently fulfilled; by continually diminishing β', a point of EDF may be reached for which $\dfrac{\partial^2 \zeta'}{\partial x'^2}$ is equal to zero and this is a condition for a further change of the shape of the melting-point curve. But this will be treated in another chapter.

The maximum values for x' and y' are now the following (namely for $\beta' = 2{,}5$) :

$$x_m = 0{,}375, \quad T_m = 816°, \quad x'_m = 0{,}0044.$$

$$y_m = 0{,}357, \quad T_m = 410°, \quad y'_m = 0{,}0016.$$

Gradually x' and y' assume practically measurable values.

We find from (9) for the maximum D:

$$x = x' = 0,571; \quad T = 223°.$$

We find for E, $x' = 0,423$; for F, $x' = 0,633$ (see (10) and (10bis)).

VI. We now proceed to the description of the further development of the parts of the meltingpoint-curve lying below C.

According as β' decreases, the curve $A'DB$ mounts higher and higher and finally it will touch the line BB', e.g. in P (Comp. fig. 6). But the values of x and T of both curves $T = f(x)$ coinciding in P, the values of x' also will necessarily coincide — or in other words the curves BA' and EDF will meet at the same time, namely in the point Q. In this point however $\dfrac{\partial^2 \zeta'}{\partial x'^2}$ must vanish, as P may be regarded as a *cusp* in the continuous curve $AA'DPB$. If therefore we trace in the figure the curve $\dfrac{\partial^2 \zeta'}{\partial x'^2} = 0$, — i.e. $T = a' \, x' \, (1 - x') = q_1 \, \beta' x' \, (1 - x')$, which will be a *parabolic* curve, whose axis of symmetry is the ordinate $x = \frac{1}{2}$, and whose summit lies lower according as β' decreases — then the curves BA' and EDF meet this curve at the same time in Q.

The direction of the two curves BA' and EDF will there *not* be horizontal, as appears immediately from the direction of the curve $\dfrac{\partial^2 \zeta'}{\partial' x^2} = 0$ in the point Q. Therefore not only the numerators in the expressions for $\dfrac{dT}{dx'}$ of those two curves must vanish in consequence of the factor $\dfrac{\partial^2 \zeta'}{\partial x'^2}$, but also the denominators $(1-x)w_1 + x w_2$. In other words: the two curves will meet each other at the place of their *maxima* for x' and $1 - x'$, exactly at a point where both curves had a vertical tangent a moment before. So the expressions for $\dfrac{dT}{dx'}$ are undetermined in Q and the real direction of the pieces BQ and $A'Q$, DQ and FQ must be determined in another way.

Fig. 7 represents the position of the different lines a moment later. β' is here somewhat smaller than in fig. 6. It may be clearly seen that the lower branches $B'P'B'$ and $A'Q'F$ have got detached; henceforth they are isolated and disappear more and more downwards according as β' decreases. They may be regarded as *rudiments* of the original meltingpoint-curve. The upper parts form henceforth the proper

meltingpoint-curve, namely $AA'DPB$, constituting the line $T = f(x)$, and $AB'EDQB$, constituting the corresponding line $T = f(x')$. The curves $T = f(x')$ now run horizontally in Q and Q', in consequence of the relation $\dfrac{\partial^2 \zeta'}{\partial x'^2}$, for the denominator $(1-x)\, w_1 + x w_2$ no longer vanishes for both curves at the same time. The places in the two curves where this occurred before (we may imagine them to lie between Q and Q') have henceforth disappeared. These points Q and Q' of the curves $T = f(x')$ correspond to the two cusps P and P' of the curves $T = f(x)$.

The process of detaching, described above, took place on the side of B — i. e. on the side of the highest temperature — but we shall see that the same process is repeated on the side of A, when β' still further decreases, which is represented in the figures 8 and 9.

The *second* detaching takes place at R and S and gives rise to two new rudimentary parts of the original meltingpoint curve on the lower side. The proper meltingpoint-curve is now $ARDPB$ for $T = f(x)$, and $ASDQB$ for $T = f(x')$. The two points S and S', where the curves $T = f(x')$ run horizontally in consequence of the relation $\dfrac{\partial^2 \zeta'}{\partial x'^2} = 0$ correspond with the new cusps R and R' in the lines $T = f(x)$.

It is of course important to know at what values of β' the two processes of detaching described above, take place.

In the point Q (fig. 6) we have in the first place $\dfrac{\partial^2 \zeta'}{\partial x'^2} = 0$ or $T = q_1 \beta' x' (1-x')$; but we have there also $(1-x)w_1 + x w_2 = 0$, from which follows:

$$x = \frac{w_1}{w_1 - w_2} \quad ; \quad 1 - x = \frac{-w_2}{w_1 - w_2}. \quad \ldots \quad (12)$$

In connection with the equations (6) and taking into account the equations (3) for w_1 and w_2, we may deduce from these relations a set of transcendental equations from which the quantities T, x' and β' may be solved by successive approximations. So we find for the *first* detaching with the values assumed by us for T, etc.:

$\beta' = \underline{1{,}545}$, $x' = \underline{0{,}9108}(Q)$, $x = \underline{0{,}2555}(P)$, $T = \underline{301{,}2}$.

For the *second* we find as second solution:

$\beta' = \underline{1{,}1020}$, $x' = \underline{0{,}1149}(S)$, $x = \underline{0{,}9705}(R)$, $T = \underline{268°{,}9}$.

The case of fig. 9, i. e. *just after the second detaching*, has been calculated by me point for point throughout its course, putting β'

equal to $1,1$. The following tables represent the chief branch $ARDPB$ $(T=f(x))$, corresponding with $ASDQB$ $(T=f(x'))$, and also the four rudimentary parts.

x	x'	T
(A) 0	0	1200
0.477	0.05	749
0.882	0.1	391
(R) 0.958	0.127 (S)	292
0.929	0.2	335
0.886	0 3	384
0.846	0.4	419
0.810	0.5	442
0.780	0.6	454
0.756	0.7	458^3
(D) 0.749	0.749	458^{62}
(P) 0.748	0.776 (Q)	458^{60}
0.749	0.8	461
0.795	0.9	465
0 867	0.95	476
0.911	0.97	484
0.967	0.99	494
(B) 1	1	500

x	x'	T
(A') 1	0 (B')	0
0.995	0.05	193
(R') 0.981	0.104 (S')	245
0.995	0.120	193
(A') 1	0.130 (E)	0

x	x'	T
(B') 0	1 (A')	0
$e^{-57.7}$	0.9997	16^8
(P') e^{-37}	0.990 (Q')	25^9
$e^{-57.6}$	0.970	16^8
(B') 0	0.954 (F)	0

For the exact calculations, of which these tables give the results, we refer to the more elaborate paper which will appear later. Also the figures relating to them are to be found there.

The maximum D has been calculated from the equation (9), which yields $x = x' = 0,7494$, $T = 458°,62$.

The points P and Q, etc. are calculated from (6) in connection with $\dfrac{\partial^2 \zeta'}{\partial x'^2} = 0$, or $T = q_1 \beta' x'(1-x')$. We find the following *four* solutions:

I	$x' = 0.7762$	(Q)	$x = 0.7484$	(P)	$T =$	$458°.60$
II	$x' = 0.1268$	(S)	$x = 0.9579$	(R)	$T =$	$292°.3$
III	$x' = 0.9901$	(Q')	$x = e^{-37}$	(P')	$T =$	$25° 9$
IV	$x' = 0.1035$	(S')	$x = 0.9808$	(R')	$T =$	$245°.0$

The points E and F are again determined by (10) and (10a). For E we have ($x = 1$, $T = 0$) $x' = 0,1296$; for F ($x = 0$, $T = 0$) $x' = 0,9535$.

Combining equation (6) for x_1' and x_2', we find finally for the *eutectic* point C:

$$x = 0,80673 \; ; \; x_1' = 0,08893 \; ; \; x_2' = 0,91107 \; ; \; T = 466°,41.$$

Formerly, when x' could be neglected, we have found from (8), $x = 0,809$, $T = 452°$ (see IV).

It is remarkable that the value found for x_2' is exactly equal to $1 - x_1'$. It is easy to show that this is an immediate consequence of the equations (6) (compare our previous paper).

In cases however in which our assumption $\alpha_1' = \alpha_2'$ (which follows from $b_1' = b_2'$) is not satisfied, the value of x_2' for the eutectic point will also not be equal to $1 - x_1'$.

When the amount of heat required for the mixing of the first component for $x = 1$ is equal to that of the second component for $x = 0$, then the compositions of the two solid phases at the eutectic point will be complementary.

VII. We shall now discuss the question, how the two parts ending in the cusps P and R will gradually disappear. We may follow this process step by step in the following figures.

a) In fig. 10 we see that the cusp P of the line $T = f(x)$, which till now was situated *inside* the curve $\dfrac{\partial^2 \zeta'}{\partial x'^2} = 0$, has *reached* that curve, in consequence of which the point Q of the line $T = f(x')$ coincides with P, and also with the maximum point D, which lies between P and Q. The curves $T = f(x)$ and $T = f(x')$ run therefore both *horizontally* in P, and henceforth the curve $T = f(x')$ will no longer touch the branch RP in D, but the branch PB (in a *minimum*). After the horizontal position in fig. 10 the cusp at P will be turned *upwards* instead of downwards.

This transformation is apparently determined by the relations $x = x'$, $\dfrac{\partial^2 \zeta'}{\partial x'^2}$, i. e. by

$$T = T_1 (1 - \beta' x^2) = T_2 \left(1 - \frac{q_1}{q_2} \beta' (1-x)^2 \right) = q_1 \beta' x (1-x) \quad . \quad . \quad . \quad (13)$$

This yields with the values assumed for T_1 etc.:

$$\beta' = 1,0611 \quad ; \quad x = 0,7606 \quad ; \quad T = 463°,5.$$

b. The figures 11 and 12 show a *second* peculiarity of the tran-

sition. Here the cusp P lies at the same height as C; we find therefore at the temperature of the eutectic point for the first time four values of x': x_1' and x_2' corresponding to C, and the coinciding points x_3' and x_4' corresponding to P. These latter two points still represent *unstable* conditions. A moment later P has risen above C and the two coinciding points x_3' and x_4' have separated (fig. 12). The values x_1' and x_2' always correspond to C, x_3' and x_4' to two other points of the line $T = f(x)$. The phase to which x_3' relates, is *unstable*, that to which x_4' relates *metastable*.

The transition of fig. 11 is determined in combination of (6) for x_1' and x_2' (with x_c), for x_3' (with x_p), in connection with the relation $T = q_1 \beta' x_3' (1 - x_3')$. By means of these relations we may determine $T, x_c, x_{,}, x_1', x_2', x_3', \beta'$, if we moreover take into account $x_2' = 1 - x_1'$ (compare VI above).

c. The figures 13 and 14 represent a new and very important case of transition. Formerly the branch AR intersected the branch BP always *on the left* of the maximum (or minimum) D in the eutectic point C; in fig. 13 it passes *exactly through the point D*. From this follows, that the point x_4' coincides in C with x_2' (both $= x$), which point represents a *stable* phase from this moment. Afterwards the minimum D lies *on the left* of the eutectic point C (see fig. 14) in consequence of which *the realizable part* of the meltingpoint curve begins to show *a totally different shape*, namely *with a minimum* (see fig. 14a). The point x_2' which till now lay *on the left* of C, lies in future *on the right* of that point. On the other hand x_4' has got on the left of C and it corresponds to a point of the line $T = f(x)$ between B and D.

It will not escape our notice that the case drawn in fig. 14a occurs to some extent in the mixtures of $Ag\,NO_3$ and $Na\,NO_3$, investigated by Mr. HISSINK (see fig. 14b). The difference is only that the minimum D in the line $T = f(x)$ in the case of fig. 14b appears beyond $x = 1$ and has therefore already disappeared. In our case we have supposed this to occur in a later stage.

The case of transition of fig. 13 is calculated from the equations (6) for x_1' and x_2', taking into account $x = x_2'$, and moreover $x_2' (= x_4') = 1 - x_1'$. The numerical solution of these equations yields the following values:

$$\beta' = \underline{0,9247} \; ; \; x_1' = \underline{0,1940} \; ; \; x_2' = x_4' = x_c = \underline{0,8060} \; ; \; T = \underline{479°,1}.$$

We may then calculate x_3' and x_3 from equation (6).

d. Finally the figures 15 and 16 represent the most important case of transition.

Here Q and S coincide with the summit of the curve $\dfrac{\partial^2 \zeta'}{\partial x'^2} = 0$, and so also P and R with C. The parts with the cusps have now disappeared once for all through the eutectic point.

The points x_1', x_3' and x_2' coincide with the *horizontal* tangent in the *point of inflexion* Q,S. This point Q,S lies apparently at $x' = \frac{1}{2}$, as the curve $\dfrac{\partial^2 \zeta'}{\partial x'^2} = 0$ or $T = q_1 \beta' x' (1-x')$ is perfectly symmetrical on either side of the summit at $x' = \frac{1}{2}$ according to our supposition $\alpha_1' = \alpha_2'$ (in consequence of $b_1' = b_2'$).

Not before this instant we may say that the meltingpoint curve has obtained a perfectly normal course, running continuously without any cusp from A to B with a *minimum* in D where $x = x'$ (fig. 16). The point of inflexion with a horizontal tangent has passed into an ordinary point of inflexion with an oblique tangent. This point of inflexion also will gradually disappear when β' continues to diminish, and for still smaller values the minimum also will disappear from the melting-point line which will then show a continuously ascending course from B to A. It is of course possible that the minimum has disappeared already before, of which fig. 14b gives an example.

The transition of fig. 15 is determined by the equations (6) for x' $(x_1' = x_2' = x_3') = \frac{1}{2}$, in connection with $\dfrac{\partial^2 \zeta'}{\partial x'^2} = 0$ or $T = \dfrac{1}{4} q \beta'$.

We find:

$\beta' = \underline{0,8226}$; $x = \underline{0,8030}$; $T = \underline{492°,6}$. $(x_1' = x_2' = x_3' = 0,5)$.

The points x_4' and x_4 may further be calculated from equation (6).

e). The *minimum disappears* apparently (see III equation (5bis)), when

$$\beta' \lessgtr \frac{T_1 - T_2}{T_1} \qquad . \qquad . \qquad . \qquad . \qquad . \qquad . \qquad (14)$$

For with $\beta = 0$ formula (5 bis) passes into $-\beta' < \dfrac{T_2 - T_1}{T_1}$ or $\beta' > \dfrac{T_1 - T_2}{T_1}$. This formula expresses the condition for the occurrence of a minimum. Formula (14) expresses consequently that *no* minimum will occur.

The minimum disappears therefore in our case as soon as β' becomes equal to $\dfrac{7}{12}$ or $\underline{0,5823}$.

f. In the above considerations we have lost sight of the rudimentary pieces which have been detached (compare VI).
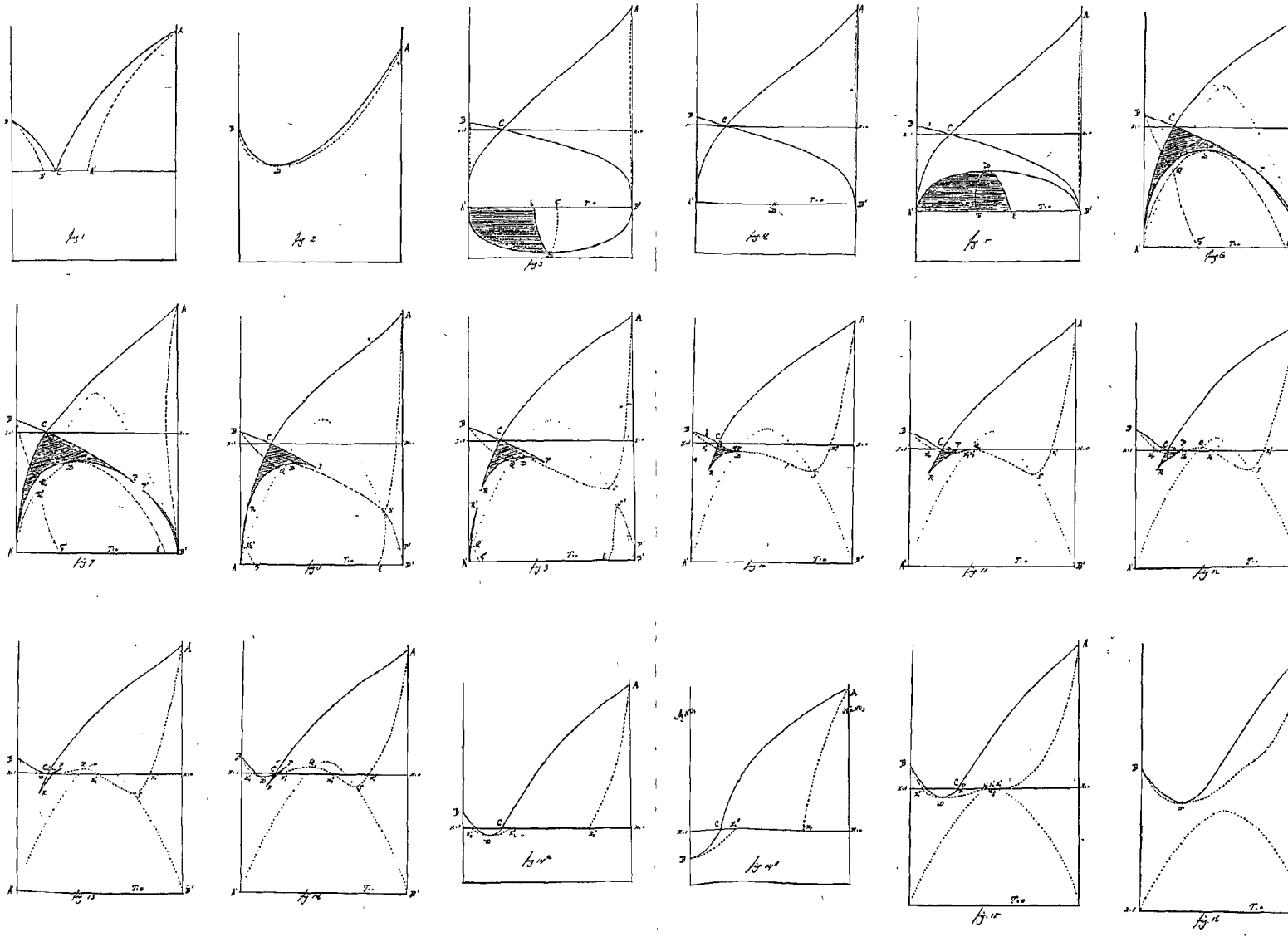
We shall now investigate when they also disappear. Apparently this is the case, when the summits P' and Q', R' and S' lie at $T=0$; i.e. when these points coincide with B' and A'. These summits are determined by the equations (6), in connection with $T=q_1 \beta' x' (1-x')$. Now P' coincides with B and Q' with A, if these equations are satisfied by $T = 0$, $x = 0$, $x' = 1$. It is clear that this requires $\underline{\beta'=1}$. Further R' coincides with A' and S' with B', if the equations are satisfied by $T = 0$, $x = 1$, $x' = 0$. And this can only be the case when $\beta' = \dfrac{q_1}{q_2}$, in our case $\beta' = \dfrac{5}{6} = \underline{0,8333}$.

VIII. It is easy to see that the results of the above investigation would remain unchanged *qualitatively*, if we had not neglected the quantity r in the term ax^2, and if we had not omitted the quantity β for the liquid phase by the side of the corresponding quantity β' (β being nearly always very small compared with β'). Then all the values given for β', x, x' and T would be slightly changed *numerically*, but the transformations and transitions which we have discussed, would have occurred in the same order and exactly in the same way as we have described above.

We conclude from the above considerations, that the occurrence of a *eutectic* point and the *apparent* interruption in the series of the solid mixtures caused by it, necessarily follow from the theory represented by the equations (2) or (6), which teaches that high values of β' (or a'), i. e. of the heat required for the mixing of the solid phase, cause the occurrence of *unstable* conditions. In reality the curve is *continuous*, as is shown in the different figures, but in general only *a part* of the continuous meltingpoint-curve is liable to be realized. And only *this* part of course is found by means of the experiments.

Finally I regard it as an agreeable duty to express my thanks to Prof. BAKHUIS ROOZEBOOM, who has encouraged me to undertake this investigation, and who has given me many a useful hint also for my former papers on the meltingpoint-curves of amalgams and alloys.

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