Huygens Institute - Royal Netherlands Academy of Arts and Sciences (KNAW)

have to enter fully into the very heart of the matter, as I cannot assume the reader to be fully acquainted with the details of these investigations. But then I should think I abused the hospitality which this Academy so courteously extends in its publications also to non-members. So I think that the above will suffice. If Mr. VAN LAAR should, however, wish to pursue this discussion elsewhere, I am willing, though not desirous, to continue it.

Chemistry. — *"The equilibrium solid-liquid-gas in binary systems which present mixed crystals."* By Dr. H. R. KRUYT. (Communicated by Prof. P. VAN ROMBURGH.) First communication.

In the Archives Néerlandaises [2] 5 (Jubilee number in honour of Prof. LORENTZ) p. 360 (1900) Prof. BAKHUIS ROOZEBOOM published an article "Sur l'équilibre de cristaux mixtes avec la phase vapeur" in which he described and illustrated the ptx surface of a binary system when exclusively homogeneous mixed crystals occur as a solid phase. He treats the case of unlimited miscibility in all phases and especially for a system in which the melting point line proceeds without a maximum or a minimum. He has, moreover, limited himself to the case that the three-phase line solid-liquid-gas (SLG) also occurs without a maximum or a minimum.

These matters have not been further investigated theoretically [1]; there was in fact no inducement to do so, as there has been an almost entire absence of experimental research. Only two investigators, SPERANSKI [2] and KÜSTER [3] furnished material as to the equilibrium of mixed crystals with a gas-phase, whereas the researches of HOLLMAN [4] belong to a category of more complicated phenomena.

I intend to carry out a series of investigations in order to extend our knowledge of the systems showing a miscibility in the solid condition. First of all, I will accept the facts already known and, therefore will discuss at present, *theoretically*, the various possibilities of the progressive change of the three-phase line indicated by ROOZEBOOM (l.c.) and communicate later the results of an *investigation*

---

[1]) The results obtained by A. SMITS (Proc. (1908) XI p. 165, and Zeitschr. f. physikal. Chem. (1909) 67, 464) do not differ from those of ROOZEBOOM. The only paper I know connected with this subject is a communication of MEYERHOFFER : "Ueber Reifkurven", Zeitschr. f. physikal. Chem. 46, 379 (1903).

[2]) Zeitschr. f. physikal. Chem. 46, 70 (1903) and 51, 45 (1905).

[3]) Ibid. 51, 222 (1905).

[4]) Ibid. 37, 193 (1901),

as to the three-phase equilibria in the system p-dichlorobenzene —
p-dibromobenzene, the same system of which, thanks to Küster
and Speranski (l.c.), we already know a series of solid-gas equilibria.
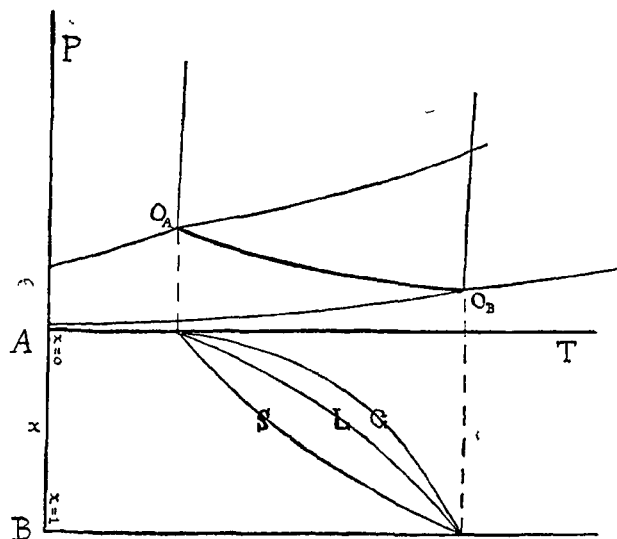

Fig. 1.

Fig. 1 is a combined PT and Tx-projection: O_A and O_B are the
triple points of the components. They are connected by the three-
phase line. In the Tx projection this line divides into three branches
which indicate, respectively, the composition of the solid (S) liquid
(L) and gas (G) phases.

Since the influence of the pressure on the equilibrium LS, is
very trifling and as triple-point pressures are comparatively low,
the branches S and L may, usually, be taken as being equal
respectively to the melting-point curve and the freezing-point curve[2])
at 1 atmosphere.

In fig. 1 is assumed $Po_A > Po_B$[1]) which case we will call chief
type I. We will now ascertain under what conditions three con-
ceivable cases might occur, namely:

case a with a maximum pressure in the three-phase line
,, b ,, ,, minimum ,, ,, ,, ,, ,,
,, c without a max. or min. ,, ,, ,, ,,

To get an insight as to the change of the pressure with the tem-

---

[1]) A (as is customary) is the name of the component with the lowest melting
point and with a vapour pressure greater than that of B at the same temperature.

[2]) In what follows we shall speak of these curves "as the branches of the
melting diagram."

perature we must first of all proceed in the direction indicated by Prof. VAN DER WAALS[1]) where he treats of the three-phase equilibria of a binary compound with liquid and vapour.

To the ψvx-surface of the liquid and vapour condition another one has to be added which shows the connection between those quantities in the homogeneous solid phase. If we consider the case occurring most frequently that the fusion takes place with an increase in volume this surface will be found between the liquid-vapour surface and the ψx-plane.

As to the form of this new ψvx-surface it should be observed that it will practically be a plane with descriptive lines proceeding from the ψv-plane for $x = 0$, to that for $x = 1$. For the mixing of two solid substances to a homogeneous solid phase takes place either *without* a change in volume or *with a hardly appreciable* one [2]).

If we now wish to know which are the coexisting phases we must allow tangent planes to move over these surfaces and thus cause the appearance of the derived surfaces and connodal lines [3]).
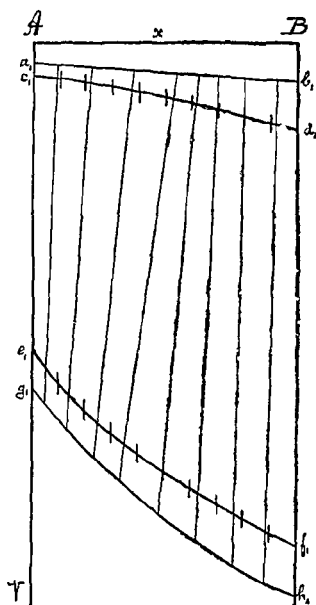

Fig. 2.

Let us commence by considering a surface for a temperature below the triple-point temperatures of the components. The surface for the solid condition will then be situated very low, the tangent plane will rest both on this surface and on the vapour part of vapour-liquid surface. The lines $a_1 b_1$ and $g_1 h_1$ in fig. 2 indicate the connodal lines so formed. The derived surface thus obtained will be situated lower than the derived surface which rests on the two parts of the vapour-liquid surface and which, therefore, does not represent stable conditions, but the vapour equilibria of "super-cooled" liquids. The connodal lines ($c_1 d_1$ and $e_1 f_1$) proceeding therefrom are situated between the connodal lines of the solid-vapour equilibrium.

If we proceed to a higher temperature the correlated connodal lines

---

[1]) Verslagen Kon. Akad. V, p. 482, (1897).

[2]) Cf. RETGERS, Zeitschr. f. physikal. Chem. 3, 497 (1889) and

GOSSNER, „ „ Kristallographie 44, 417 (1908).

[3]) In what follows, the question whether a minimum or a maximum pressure is possible for the coexistence of two phases has not been considered. All nodal lines are therefore supposed to proceed in the same sense.

approach each other; and also the stable
and metastable branches on the vapour part
especially at the side of the component
melting at the lowest temperature [1]). For
if we approach the temperature of the
triple point of this component the points
e_1 and g_1 of fig. 2 will have coincided
to the point $e_2 g_2$ in fig. 3, which is
intended for the temperature of O_A (fig. 1).
The two derived surfaces intersect each
other in the ψv-plane of the component
A; that intersecting line is, of course,
the tangent to the ψ-line for the gas-liquid
condition of A and just the one which
is also tangent to the ψ-line of solid A
(triple point A).

By consulting fig. 4 it will be easily
seen what happens at a temperature
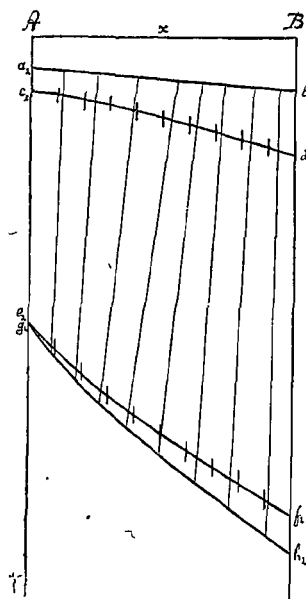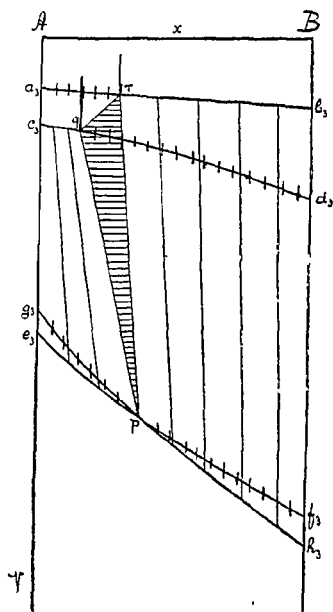situated between that of the two triple

Fig. 3.

Fig. 4.

points. The rolling tangent plane coming
from the A side will now rest first on
the liquid- and vapour parts; but if a
certain nodal line pq is thus reached the
tangent plane will rest also on a point
r of the surface of the solid phase. The
angular points of the three-phase triangle
pqr give us the composition of the three
possible coexisting G, L, and S phases at
that temperature. By further motion of the
tangent plane a derived surface for GS
equilibria is formed, whilst also a similar
movement over the liquid part of the fluid
surface and over the surface of the solid
phase is possible in the direction of the
small volumina. Hence a new system of
connodal lines for LS equilibria is formed
starting from r and q. Fig. 4, however,
will be plainly understood without further
comment and a discussion of the configurations at higher temperatures
will also be superfluous.

---

[1]) The non-related connodal lines ab (solid) and cd (liquid) diverge from each
other because as a rule the coefficient of expansion of a substance is smaller in
the solid than in the liquid state.

Prof. VAN DER WAALS (1. c. p. 490) has also taught us how to deduce an expression showing the relation between p,t and x.

From the three equations

$$V_S dp - \eta_S dt = dM_1 \mu_1 + x_S d(M_2 \mu_2 - M_1 \mu_1)$$
$$V_L dp - \eta_L dt = dM_1 \mu_1 + x_L d(M_2 \mu_2 - M_1 \mu_1)$$
$$V_G dp - \eta_G dt = dM_1 \mu_1 + x_G d(M_2 \mu_2 - M_1 \mu_1)$$

follows

$$\frac{dp}{dt} = \frac{\begin{vmatrix} x_S & \eta_S & 1 \\ x_L & \eta_L & 1 \\ x_G & \eta_G & 1 \end{vmatrix}}{\begin{vmatrix} x_S & V_S & 1 \\ x_L & V_L & 1 \\ x_G & V_G & 1 \end{vmatrix}} = \frac{x_S(\eta_L - \eta_G) + x_L(\eta_G - \eta_S) + x_G(\eta_S - \eta_L)}{x_S(V_L - V_G) + x_L(V_G - V_S) + x_G(V_S - V_L)}.$$

This gives us a *quite general expression* for the three-phase line in the systems described. It will, however, not be easy to arrive through it to the desired elucidations. If, for instance, we wish to know when $\frac{dp}{dt}$ will be equal to 0 the numerator thus becoming nought, the question first arising is what do $\eta_L - \eta_G$ etc. really represent. KOHNSTAMM [1] has rightly observed that such differences must not be simply called heat of condensation etc. because η_L and η_G do not relate to the same mixture. And the second question as to the numerical value of those quantities in a system to be investigated is still much more difficult to answer.

In order to get a first insight into these systems, I have taken another course though of less general applicability. We will see how the pressure changes in regard to the triple-point pressure of A, when the liquid phase has the composition x_L assuming that x_L has a very small value, in other words that but a very small quantity of B has been added to A.

The temperature T_2 at which that liquid is in equilibrium with a solid phase, the composition of which is x_S, is found from ROTH-MUND's formula [2] for very dilute mixtures:

$$T_2 = T_1 + \frac{RT_1^2}{q}(x_S - x_L) \quad \ldots \quad \ldots \quad (1)$$

[1]) Proc. Kon. Akad. IX p. 647 (1907).

[2]) Zeitschr. f. physikal. Chem. **24**, 710 (1897).

in which T_1 is the temperature of the triple point O_A.

The vapour, pressure P_2 at the temperature T_2 is the sum of the partial pressures of the components p_A and p_B:

$$P_2 = p_A + p_B$$

for which we may write

$$P_2 = (1-x_L) P_{T_2} + p_B \quad \cdots \cdots \quad (2)$$

if P_{T_2} represents the vapour pressure of liquid A at that temperature. If now we call P_{T_1} the vapour pressure of A at' its triple point and use VAN DER WAALS' well known formula for the saturated vapour pressure we may write

$$l\frac{P_k}{P_{T_1}} = f\frac{T_k - T_1}{T_1}$$

$$l\frac{P_k}{P_{T_2}} = f\frac{T_k - T_2}{T_2}.$$

By subtraction we get:

$$l\frac{P_{T_2}}{P_{T_1}} = f\frac{T_2 - T_1}{T_1}$$

$$l P_{T_2} = f\frac{T_2 - T_1}{T_1} + l P_{T_1}$$

If now we substitute the value found in (1) for T_2 we obtain

$$P_{T_2} = P_{T_1} e^{f\frac{RT_1}{q}(x_S - x_L)}$$

thus writing (2) in this form:

$$P_2 = (1-x_L) P_{T_1} e^{f\frac{RT_1}{q}(x_S - x_L)} + p_B \quad \cdots \quad (3)$$

If now case Ia (maximum pressure) is to occur, the three-phase line must rise from O_A to higher values of P and therefore $P_2 > P_{T_1}$. The chance of seeing this case realised in a certain system, therefore depends on P_2 having as great as possible a value in regard to P_{T_1} and relation (3) shows us when this will be the case. For the first term $\dfrac{T_1}{q}$ and $x_S - x_L$ will then be characteristic. The value of $x_S - x_L$ is indicated by the difference in initial direction of the branches of the melting point lines for solid and liquid and this difference is determined precisely by $\dfrac{T}{q}$ [1]). When therefore we pay special attention to $x_S - x_L$,

---

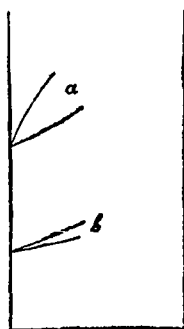[1]) Compare VAN LAAR, Zeitschr. f. physikal. Chem. 64, 257 (1908).

the first term of (3) will be large if $x_S — x_L$ is large, that is to say when the initial directions of the branches of the melting diagram line differ greatly (Fig. 5a).

The second term of (3) the partial pressure of the component B will as a rule be greater [1]) when this component gets more volatile; as in the case of this chief type I we have assumed that its triple point pressure is smaller than that of A we shall have the most advantageous conditions when they differ as little as possible.

Fig. 5.

For the case Ia is, therefore, required 1. a type of melting diagram with greatly diverging branches near the A-axis and 2. about equal triple point pressures.

Case Ib (minimum pressure) makes two demands: from O_A an initial fall, but followed by a rise; if this second demand is not fulfilled we are dealing with Ic. This second demand means, of course, a small difference of the triple point pressures; the first demand, a small P_2 is, therefore, in regard to the value of p_B in (3), opposed to the second and is, in consequence, determined altogether by the first term of (3). In order that this may be as small as possible it is, of course, required that $x_S — x_L$ shall approach 0 as closely as possible, a demand which is complied with in a melting diagram with branches almost coinciding in the initial direction. (Fig. 2b).

We arrive at an identical result if we start from the triple point of B and examine the vapour pressure $P_2{}'$ of a liquid containing a little of A, when that liquid can also coexist with a solid phase. In this case the relations (1), (2), and (3) become:

$$T'_2 = T'_1 - \frac{RT'^{2}_1}{q'}(x_S - x_L). \quad \ldots \ldots \quad (1bis)$$

$$P'_2 = p_A + x_L P'_{T_2} \quad \ldots \ldots \ldots \ldots \quad (2bis)$$

$$P'_2 = P'_{T_1} e^{-\frac{RT''_1}{q'}(x_S - x_L)} + p_A \quad \ldots \ldots \quad (3bis)$$

which will be readily understood on considering that the accentuated signs have the same significance for B as the non-accentuated ones had above for A.

In the case of Ib the three-phase line must descend from B, therefore $P'_2 < P'_{T_1}$. Now first of all p_A should be at a minimum

---

[1]) Apart, therefore, from special differences in the critical quantities and of special influences of the components on each other.

which, on the same supposition as above, again demands about equal triple-point pressures for A and B; secondly, the exponent of e with a negative sign should be as large as possible, which requires widely diverging branches in the melting diagram at the side of the component B.

These demands put from two sides are brought into agreement by a conclusion of VAN LAAR (loc. cit. p. 265) that closely adjacent branches in the melting diagram at the side of the one component cannot meet a similar configuration at the side of the other.[1]) If this were possible, the occurrence of a maximum *and* a minimum in one three-phase line would be quite possible.

In the case of Ib we therefore, require:

1. Melting diagram with branches nearly coinciding at the side of the A-axis and 2. about equal triple-point pressures.

Case Ic finally occurs as an intermediate case between the two previous extreme cases. Of course, the line $O_A O_B$ may be concave or convex in regard to the temperature axis; this depends on whether the conditions for Ia or Ib have been partially fulfilled. Let us call these cases Ic_1 and Ic_2 respectively. For definite forms of the melting diagram points of inflection may probably occur, but our mode of treatment is inadequate for their investigation.

A single remark may be made as to the chance of observing a fall of the three-phase line starting from O_A. As stated, the following condition is required:

$$(1 - x_L) P_{T_1} e^{f \frac{RT_1}{q} (x_S - x_L)} + p_B < P_{T_1}.$$

If now we imagine the most favourable circumstance, in which p_B may be neglected (because the components differ, for instance, very much in their melting temperature) the factor $(1 - x_L)$ will cause a decrease and the factor $e^{f \frac{RT_1}{q} (x_S - x_L)}$ an increase in the value of the first member in regard to that of the second one. For $1 - x_L$ is always < 1; the other factor is > 1 and only in the case of $x_S = x_L$ it is equal to 1: in that case a fall may be expected, but as soon as x_S and x_L differ in value the enlarging factor appears and the said difference occurs therein *exponentially*. The enlarging influence will, therefore, very soon exceed the other, so that the chance for realising the case Ic will be diminished and that for Ib will be reduced to a minimum.

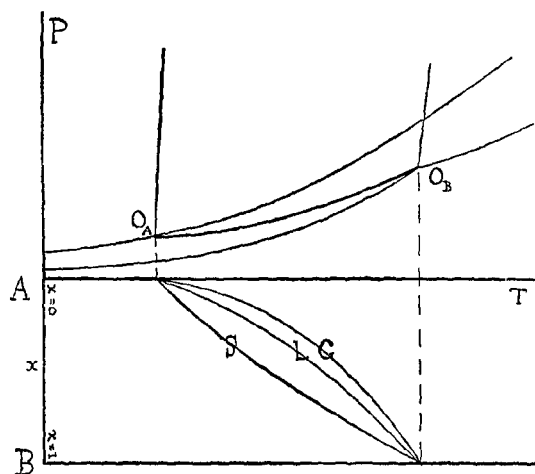[1]) At least when we make the same suppositions as in the footnote on p. 543,

Fig. 6.

Let us now consider a second category of possibilities, namely $Po_A < Po_B$ which case we will call chief type II.

We again distinguish three possibilities, viz.

    a. maximum   pressure in the three-phase line

    b. minimum   ,,   ,, ,,   ,,   ,,

    c. no max: or min.   ,,   ,, ,,   ,,   ,,

It will be superfluous to repeat the previous arguments when we examine the initial directions in the equations (3) and (3*bis*). The conclusions arrived at are that we require for:

Case II*a*: a melting diagram with closely joined branches at the side of the component *B*, and but slightly differing triple-point pressures.

Case II*b*: a melting diagram with closely joined branches at the side of the component *A*, and but slightly differing triple-point pressures.

Case II*c* will be again the intermediate case between the two previous ones; a concave (II*c₁*) and a convex (II*c₂*) course will again be possible.

In a future paper, I hope to communicate the results of an experimental investigation of the system *p*-dichlorobenzene — *p*-dibromobenzene which has been going on already for a considerable time.

November 1909.   *Utrecht*, van 't Hoff-laboratory.

ERRATA.

p. 438 line 16 from the top: for 1000 read 10000.

(January 26, 1910).