Physics. — *"On the hidden equilibria in the p-x-diagram of a binary system in consequence of the appearance of solid substances."* By Dr. A. SMITS. (Communicated by Prof. J. D. VAN DER WAALS).

1. Some time ago Prof. VAN DER WAALS [1]) showed that in a binary mixture (A, B) one of the two p-T-lines for the three phase pressure, viz. that which runs from the eutectic point to the higher-melting substance (B), can present some particularity.

It proved, namely, that at the triplepoint this p-t-line must have the direction of the melting line (of B).

As for most substances $v_l > v_s$, or in other words the substance expands when melting, increase of pressure causes as a rule a rise of the melting point.

If in the p-t-projection, (Fig. 1), the triplepoint of the substance B is denoted by d, then the melting line dg will in most cases run from the triplepoint to the right, and as the three phase line cd must have the direction of dg at d, this three phase pressure line will have to present the particularity, that it does not only possess a maximum of pressure, but also a maximum of temperature, as is represented in Fig. 1 in an exaggerated manner.

2. As has been shown before [2]) and will be further discussed in the second paper, in a dissociating composition the same course may be found on a larger scale, and it is this part of the three phase line, that is the most important in compositions. Therefore it seemed desirable to me to examine the p-x-diagrams from the triplepoint to higher temperatures for the simple case discussed just now, and to treat the compositions afterwards.

3. The p-x-diagram at the triplepoint, and at a temperature slightly higher are presented in Fig, 2.

As appears from Fig. 1, we find a double section of the three phase line for the first time at the triplepoint, when coming from lower temperatures, and a consequence of this is, that besides at the triplepoint pressure, three phases may also occur at a much higher pressure. This case is more closely defined in Fig. 2 by the p-x-diagram corresponding to the temperature t_1. The lowest three phase pressure or the triplepoint pressure is repre-

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[1]) These Proc. Vol. VI, p. 230.

[2]) BAKHUIS ROOZEBOOM, Zeitschr. f. phys. Chem. 4. 31.

STORTENBEKER,   „   „   „   „   3. 71.

sented by the point g, where the liquid curve $a\,c\,g$, the vapour curve $a\,e\,g$ and the solubility isotherm $f\,c\,e\,g$ meet.

The second three-phase pressure is represented by the curve $e\,c\,s$ and lies considerably higher. The coexisting phases have here different concentration, and are denoted by e, c and s. Here c is the saturated liquid phase and e the vapour phase which coexists with the solid phase s.

If we now start from these three phases, and lower the pressure at constant temperature, we reach the region for solid $B +$ vapour, as Fig. 1 represents. So below the three phase pressure $e\,c\,s$ and above the triplepoint pressure of B, only vapour can occur by the side of solid B in stable condition, and the curve representing the vapours which can coexist with solid B is the lowest branch of the continuous solubility isotherm, viz. $e\,g$.

The line $a\,c$ denotes the unsaturated liquids coexisting with the vapours lying on the line $a\,e$. The lines $c\,g$ and $e\,g$ represent metastable conditions, viz. supersaturated solutions with their coexisting vapours. The curve $c\,f$, the upper part of the solubility isotherm represents the liquids coexisting with solid B.

The second p-x-diagram, represented in Fig. 2, corresponds with a somewhat higher temperature t_2. We are now above the triplepoint temperature and the lowest three phase pressure is not a triplepoint pressure now, but perfectly comparable with the highest three phase pressure. A result of this is, that we get below the lowest three phase pressure a reflection of what takes place above the highest three phase pressure. The solubility isotherm $f_1\,c_1\,e_1\,e'_1\,c'_1\,f'_1$ cuts, as it were, a portion out of the region for liquid $+$ vapour, on account of which between the two occurring three phase pressures indicated by the curves $e_1\,c_1\,s_1$ and $e'_1\,c'_1\,s'_1$, only solid B can coexist with vapour in stable condition. The line $c'_1\,f'_1$, like $c_1\,f_1$ represents now the liquids coexisting with solid B, and the portion $e_1\,e'_1$ the vapours coexisting with solid B.

As to the whole course of the solubility isotherm it may be observed that this line has now two maxima, two minima and four vertical tangents. For the portion $f_1\,c_1\,e_1$ the points of contact of the vertical tangents lie in the metastable or the stable region, whereas those for the second piece $e'_1\,c'_1\,f'_1$ are situated in the unstable region.

At higher temperatures the three phase pressures draw nearer and nearer to each other and coincide finally, as may be seen from fig. 1.

When we examine this change in the p-x-diagram it appears that the points e_1 and c_1 move downward and at the same time to the right, whereas the points e'_1 and c'_1 move upward and to the left,

As to the points a_1 and y_1, they move upward with increase of temperature.

The result of these shiftings must of course be, as has been just said, that at the maximum temperature of the three phase line (see Fig. 1) the two three phase pressures become equal, and the points c_1 and c'_1, like e_1 and e'_1, coincide; then the solubility isotherm does not cut the liquid line any longer, but just touches it in the point where c_1 and c'_1 have coincided, after which no three phase pressure is possible and the solubility isotherm has got detached from the liquid line.

Though all this seems very simple, the representation of the inter-mediate stages presented some difficulties, which Prof. V. D. WAALS was kind enough to remove by allowing me to examine some T-x-diagrams corresponding with pressures respectively smaller, equal and larger than the three phase pressure, in which exactly the same succession of states occurred [1]).

What has been drawn in accordance with this in the figs. 3, 4 and 5, may be brought into words in the following way:

When the two three phase pressures have drawn so near, that the two branches of the solubility isotherm *would touch*, *intersection* takes place, and we get a curve as is indicated by $f_1\,c_1\,e'_1\,e_1\,c'_1\,f'_1$ in Fig. 3. Immediately afterwards, i.e. at somewhat higher temperature a portion gets detached, as represented in Fig. 4 and we get two solubility isotherms; one is $f\,c\,c'\,f'$ and the other forms a closed curve $e\,e'\,d$, a part of which ($e\,e'$) runs through the stable region.

At the maximum temperature of the three phase line the two three phase pressures $e\,c\,s$ and $e'\,c'\,s'$ have coincided, as is represented in the diagram corresponding with the temperature t_6, in Fig. 4, and the solubility isotherm $f_1\,c_1\,f_1'$ no longer *cuts* the liquid curve, but only *touches* it in the point c_1.

With the exception of this one point it runs therefore wholly through the stable region. The other *closed* branch no longer *cuts* the vapour curve, but only touches it in e_1; further this branch as a whole has contracted through the shifting of d to d_1. This second branch of the solubility isotherm lies therefore at the maximum three phase pressure partly in the unstable region, partly in the metastable region.

At a temperature slightly above the maximum temperature of the three phase curve t_r, the solubility isotherm $f\,f'$ is quite detached from the liquid curve, as is represented in Fig. 5; in the same

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[1]) See the foregoing paper by VAN DER WAALS.

way the closed branch has got detached from the vapour branch, and has further contracted. At the temperature t_3 the distance between the solubility isotherm $f_1 f'_1$ and the liquid curve has increased, and the closed branch has vanished, after having contracted to a point.

4. In the figs. 6, 7 and 8 I have drawn the v-x-sections of the v-x-t-space diagram for the case discussed here; they follow immediately from the v-x-sections, given by me last year [1]).

The section indicated by continuous lines in Fig. 6 holds for the triplepoint temperature t_1. There $a\,e\,c\,b$ is the region for liquid + vapour, $e\,h\,c$ the three phase triangle, $h\,e\,d$ the region for solid B + vapour, $b\,c\,f\,m$ the liquid region and $c\,h\,n\,f$ the region for solid B + liquid.

The curve for solid-fluid or the solubility isotherm $d\,e\,c\,f$ meets the metastable vapour branch $e\,d$ exactly on the line for the substance B, because at the triplepoint temperature of B the vapour which is in equilibrium with solid B, is perfectly the same as that which is in equilibrium with liquid B.

At a somewhat higher temperature the curve for solid-fluid cuts the vapour and liquid curve twice each, just as was the case in the p-x-diagram. The curve for solid-fluid has then a shape as is indicated by the dotted line $f_1 c_1 e_1 e'_1 c'_1 f'_1$ in fig. 6 [2]). Just as in the p-x-diagram, this line cuts a piece out of the liquid-vapour region; in consequence we get two separated regions for liquid and vapour viz. $a_1 e_1 c_1 b_1$ and $e'_1 d_1 h_1 c'_1$. From this particular situation ensues further the existence of two three phase triangles, viz. $c_1 e_1 g_1$ and $c'_1 e'_1 g_1$, between which is situated the region for solid B + gas $g_1 e_1 e'_1$, two liquid regions $b_1 c_1 f_1 m$ and $h_1 c'_1 f_1'$ and two regions for solid B + liquid viz. $g_1 c_1 f_1$ and $g_1 c'_1 f_1'$.

With increase of temperature the line solid B + fluid assumes the shape of a loop, as is indicated by the line $f c e' e c' f'$ in fig. 7; on this follows immediately detaching of a part, splitting up into two branches, viz. into the line $f'_1 c'_1 c_1 f_1$ and the closed line $e_1 e'_1 o$. At the maximum three phase temperature (fig. 8) the line $f c f'$ touches the liquid line and the closed line $e\,o\,e$ touches the vapour line. Above this temperature the two lines get detached from the liquid, respectively the vapour line and the closed line $e_1 o_1 e_1$ disappears as a point in the metastable region.

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[1]) These Proc. Vol. VI, p. 484.

[2]) At a temperature, only very little higher than the triplepoint temperature, a part of the branch $e'_1 c'_1 f'_1$ will fall outside the line for B.

5. Fig. 9 represents the most interesting part of the projection of the p-t-x-space diagram on the p-T-plane for the case that the plait-point curve meets the solubility curve, as with *ether* and *anthra-quinone*. In this fig. the possibility has moreover been assumed, that the second plaitpoint temperature t_2 of a saturated solution lies above the triplepoint temperature t_3. Fig. 10 represents for this case the p-x-sections corresponding with the temperatures t_1 and t_2 (see fig. 9).

The section for t_1 differs from the second section in Fig. 2 only in this, that the liquid branch passes continuously into the vapour branch with the point K as plaitpoint. If we now pass on to lower temperatures, the downmost three phase pressure becomes smaller and the upmost greater, while the plaitpoint pressure diminishes. In consequence of these last two changes the points e, c and K get nearer and nearer to each other, and when we have descended to the temperature t_2, the points e, c and K have coincided or in other words the upmost three phase pressure has become a plaitpoint pressure; this circumstance is accounted for in the p-x-section, corresponding with the temperature t_2 (Fig. 10).

At the temperature t_3, the triplepoint temperature, for which no p-x-section is drawn here, because it immediately follows from that for t_2, the remaining downmost three phase pressure has become triplepoint pressure, and the points e'_1, c'_1 and g_1 have coincided.

Below this temperature the p-x-sections over a certain temperature-range consist only of a solubility isotherm of the shape of $e'_1 q f_1$ in Fig. 10, as has been discussed before.
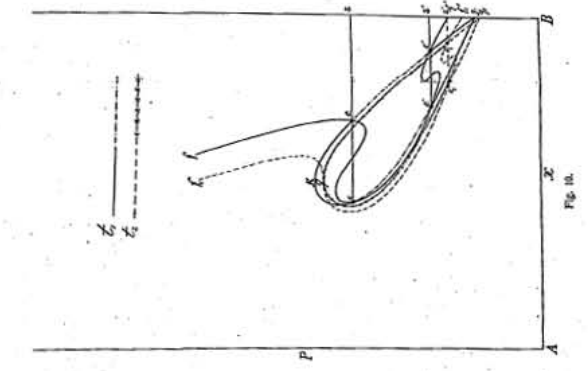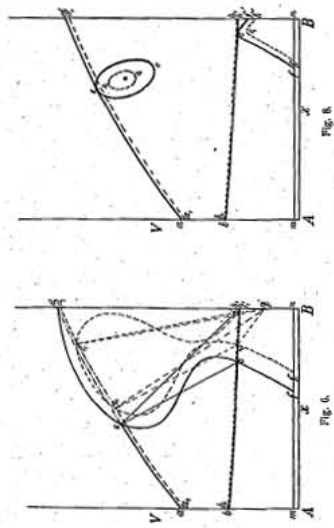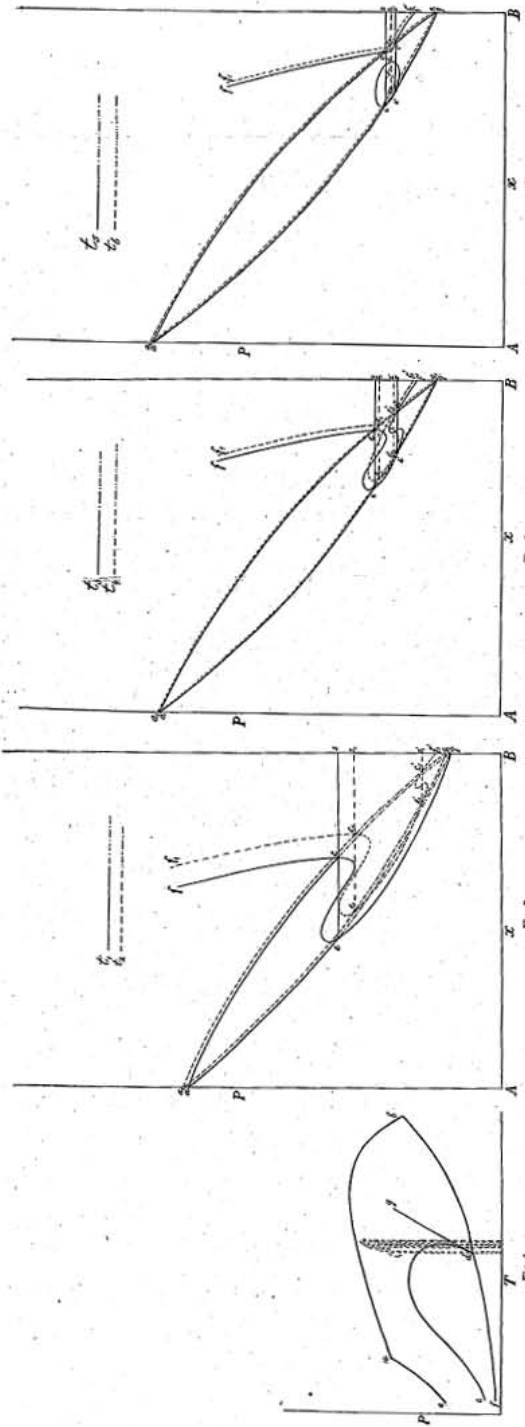
That the case assumed in Fig. 9 is not often to be realized, is obvious, but that it is a possible case, is, in my opinion, not doubtful

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Physics. — *"Contribution to the knowledge of the px- and the pT-lines for the case that two substances enter into a combination which is dissociated in the liquid and the gasphase."* By Dr. A. Smits. (Communicated by Prof. J. D. van der Waals).

The purpose of the following paper is to give a connected representation which is in logical connection with the p,x,t-diagram which has been recently drawn up by Bakhuis Roozeboom and in which it is assumed that only the components can occur as solid phases, for the most important particularities of the equilibria between a vapour,

A. SMITS: "On the hidden equilibria in the p—x diagrams of a binary system in consequence of the appearance of solid substances."

Fig. 1.

Fig. 2.

Fig. 3.

Fig. 4.

Fig. 5.

Fig. 6.

Fig. 7.

Fig. 8.

Fig. 9.

Fig. 10.

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