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 plaitpoint curve meets the solubility curve, as with *ether* and *anthraquinone*. 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

Amsterdam, June 1905. *Chemical Laboratory of the University.*

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.
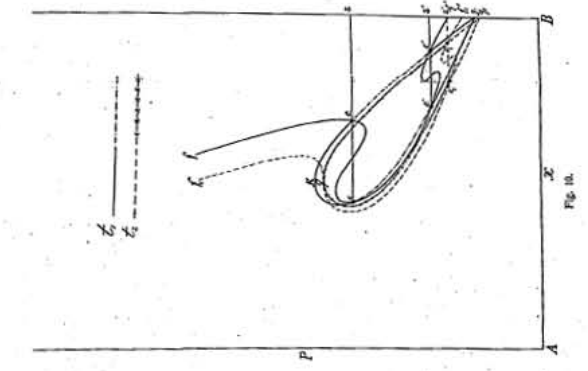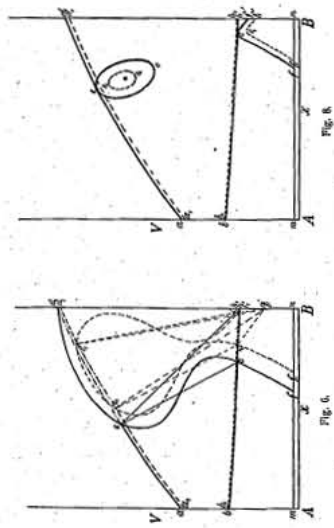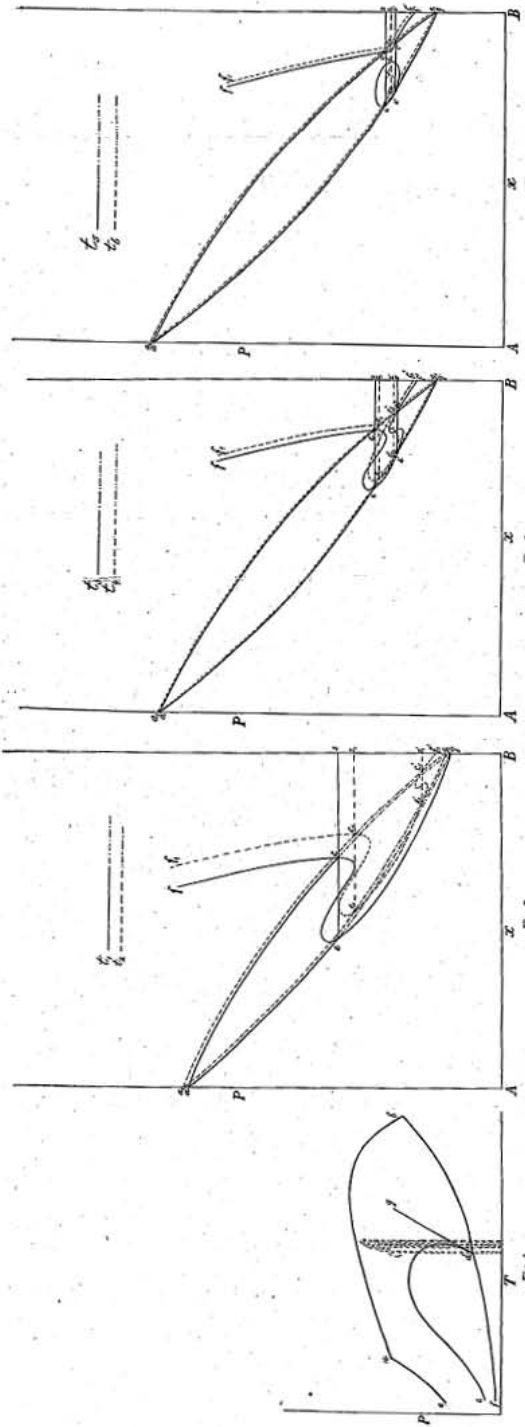
liquid and solid phase for the case that the last is a, dissociable combination.

Some of the points mentioned in what follows had already been given by him [1]), but it was not till now that they could be combined into a connected whole through the knowledge obtained during the last time (see inter alia the preceding paper).

1. For the case that two substances A and B enter into a combination, I shall distinguish three cases.

1st that the vapour tension of the combination lies between that of the components. (fig. 1).

2nd that the vapour tension of the combination is smaller than that of the components. (fig. 2).

3rd that the vapour tension of the combination is greater than that of the components. (fig. 3).

2. If we bear in mind that for the case that the combination *does not* dissociate, a p-x-section for the system $A + AB + B$ is to be considered as a junction of the two systems $A + AB$ and $AB + B$, it is not difficult to combine the p-x-sections for the system $A + AB + B$ for different temperatures into one diagram.

If we first examine case 1, where the vapour tension of AB lies between that of the components, it may be observed, that in the system $A + AB$, A is the substance with the higher and AB that with the lower vapour tension, whereas in the system $AB+B$, AB has the higher and B the lower vapour tension. Bearing this in mind, we get, led by the diagrams given by me before [2]), to fig. 1, in which the hatched regions $a\,m\,E\,E_1\,l$, $EE_1\,e\,e_1\,e_2\,d\,c_2\,c_1\,c$, $d\,c'\,E'E'_1\,e'$ and $E'E'_1\,l\,l'_1\,l'_2\,l'_3\,a'm'_3\,m'_2\,m'_1\,m'$ indicate the vapours and liquids which coexist with solid phases (A, AB, AB and B) at different temperatures. We shall call these regions henceforth the *three phase regions*; they have as base the line which joins the points E with E_1 respectively E' with E'_1 and are bounded on one side by a vapour line and on the other side by a liquid line. The latter has already been called solubility curve before. At and below the eutectic temperature the p-x-section is simplest and it consists for each of the two systems of two lines representing the vapours which can coexist with solid A or solid AB respectively with solid AB or solid B. Such a p-x-section is found in the lines $k\,o\,g_0\,E'_1\,k'$, where it must be expressly stated that $o\,g_0$ and $g_0\,E'_1$ do not form a continuous curve, but are two separate branches, which cut at g_0.

[1]) Rec. Trav. chim. 5, 335 (1886).
[2]) These Proc. Vol. VI, p. 484.

In the point o coexists a vapour with the two solid phases A and AB and the point E'_1 denotes the composition and the pressure of the vapour phase which can coexist at the eutectic temperature with a liquid E' and two solid phases AB and B.

In the second p-x-section the curves $k_1\, l, g_1\, e, g_1\, e'$ and $k'_1\, l'$ represent vapours coexisting with solid phases; the lines $m\, c$ and $m'\, c'$ denote the liquids coexisting with the vapours $e\, l$ and $e'\, l'$, while the lines $m\, s$, $c\, f$, $c_1\, f'$ and $m'\, s'$ represent liquids coexisting with solid phases.

What change this section is subjected to with rise of temperature is so easy to follow from the diagram, that it does not call for a discussion.

It may only be observed here that for the case that the combination reaches its critical point sooner than the components, we get somewhat above this temperature a p-x-section which consists of two loops $b_3\, x$ and $b'_3\, y$, in which the vapour branches have continuously passed into the liquid branches, and an opening has been formed between the two loops. This, however, does not complete the p-x-section, for, solid phases may still occur by the side of liquids at higher pressures, though above the critical temperature of $A\,B$ and the melting point of A and B, when viz. A, B and AB melt with increase of volume, as generally happens. Thus the lines $k_5\, s_4$ $g_5\, f_4$, $g_5\, f'_4$ and $k'_5\, s'_4$ represent the liquids which can coexist with a solid phase at the same temperature.

After this discussion of fig. 1, it is not necessary to give a further explanation of figs. 2 and 3, which represent the second and third case, as these figures do not present any essential differences with fig. 1.

3. It is more interesting to see what happens, when the combination $A\,B$ dissociates somewhat. In this case the total p-x-section is no longer to be considered as two separate p-x-figures joined, but as one whole and we arrive therefore at the conclusion, which sounds rather paradoxical, that the characteristic feature of a *combination* becomes apparent only when the combination is somewhat *decomposed* into its components. All the curves which meet at an angle in the figs. 1, 2 and 3 at the place of the line for the combination, now pass continuously into each other. This applies, therefore, not only to the gaslines, but also to the lines which bound the three phase regions.

With regard to the gradual transition of these three phase regions, it may be observed, that it does not take place at the point where the three phase region lines cut the line for $A\,B$, but always left

or right of this line, dependent on the mutual influence of the vapour tension of the components.

In order to elucidate this important point I have indicated in the figs. 4, 5 and 6 what shapes the three phase regions hatched in the figs. 1, 2 and 3 can assume in the neighbourhood of the line for the combination, in the case that a slight dissociation takes place in the liquid and gas phase. It is not improbable that there will also be dissociation in the solid phase in this case, but this is not taken into account here, in the first place because it is most likely exceedingly slight, and in the second place, because the diagram becomes much more intricate, when this dissociation is taken into account.

Fig. 4 corresponds to fig. 1, fig. 5 to fig. 2 and fig. 6 to fig. 3. For fig. 4 it may be remarked, that for the case that the vapour tension of the combination, lies between the vapour tensions of the components, the liquid and the vapour line draw very near to each other somewhat past the line of the combination, on the side of the component with the smaller vapour tension, but that they do not reach each other, so that there remains a gap between them, from which follows, that in the series of liquids and vapours which can coexist with solid AB, not a single point can be pointed out where vapour, liquid, and solid phase have the same concentration, nor is there a point where a vapour and a liquid phase have the same concentration.

This latter is only the case when the vapour tension of the combination lies between those of the components, for when the vapour tension of the combination is smaller or greater than those of the components, we get according to a rule of Gibbs a three phase region with a minimum, fig. 5, or with a maximum, fig. 6, and at the place of this minimum or maximum the concentration of the vapour and the liquid phase must be identical.

If we now discuss figs. 4, 5 and 6 at the same time, we may remark, that there for a special temperature the situation is indicated of the two three phase pressures ecs and $c_1e_1s_1$ and the continuous line for solid-fluid or solubility-isotherm. This line must have an horizontal tangent at the point where it cuts the line for the combination. For this case is viz. $x_f = x_s$, or the concentration of the fluid phase is the same as the concentration of the solid phase and then it appears from the equation drawn up by van der Waals for the equilibrium solid fluid:

$$\frac{dp}{dx_f} = \frac{x_s - x_f}{V_{sf}} \left(\frac{\partial^2 \zeta}{\partial x^2{}_f} \right)_{PT}$$

that

$$\frac{dp}{dx_f} = 0.$$

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If we now examine the changes with rise of temperature, it is noteworthy, as will presently become clear from the p-t-lines, that we have here to deal with changes quite analogous to those discussed in the preceding paper. The three phase pressure lines $e\,c\,s$ and $c_1\,e_1\,s_1$ approach each other and coincide at $E\,C\,S$. This coincidence takes place at the maximum temperature of the p-t-line for the three phase pressure. One of the two three phase pressure lines $s\,e\,c$ and $s_1\,e_1\,c_1$ must therefore pass through the positions indicated by $e'_1\,c'_1$ and $e'\,c'$, before it coincides with the other. Now it follows from the three phase pressure line $e'_1\,c'_1$ that the gas phase e'_1 has the same concentration as the solid combination, while the liquid phase c'_1 has another concentration. The three phase pressure line $e'\,c'$ on the other hand indicates, that the liquid phase c' and the solid phase have the same concentration, while the gas phase e' has another concentration.

We see therefore, that the three phases solid-liquid-gas have not the same concentration at any pressure, but that they become two and two equal. We may express this also in this way: When a combination dissociates in the liquid and the gas state, then this combination has no longer a triplepoint, for this point has split up into two other points where vapour and solid respectively liquid and solid get the same concentration.

After I had written this paper, I found to my surprise, that already in 1897 VAN DER WAALS had arrived at the same result by a way which I intended to discuss later on and for which the diagrams had been already drawn [1]).

4. In order to make the difference between a non-dissociating and a dissociating combination more apparent, we consider the case, that we bring the dissociating combination AB in solid condition into a vacuum, and make the temperature rise continually.

The solid substance AB will, when the volume is not too large, coexist with its vapour, till the pressure has become equal to that indicated by the point e_1'; at this moment a third phase appears, viz. liquid. As the total concentration must always be that of AB, it is necessary that the concentration of the vapour phase lies on one side, and that of the liquid phase on the other side of the line for AB; as follows from the figures 4, 5 and 6 this is really the case. With rise of temperature three phases continue to exist for some time side by side and the vapour and liquid phases coexisting with solid AB lie on the same horizontal line. The liquid phase lies on the liquid branch $c'\,c_1'$ and the vapour phase on the vapour

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[1]) Verslag Koninkl. Akad. 21 April 1897, 482.

branch $e'e_1'$, while the solid phase lies naturally on the line GG'.

With a suitable volume the three phases may now continue to exist over the whole range of pressure and temperature indicated by $e_1'c'$, but then the vapour phase must have disappeared when we have reached the point c', for in the point c' the liquid has the same concentration as the solid combination.

Beyond the maximum, respectively minimum in figs. 5 and 6 the concentration of liquid and vapour is, of course, always different, just as in fig. 4, and as the line for the combination never coincides with this maximum, respectively minimum, when there is a maximum or minimum, in the above mentioned case the two phases will necessarily only get the same concentration, when two phases coexist.

At c', we leave the three phase region, which we had entered at e_1' and coexistence of solid AB + liquid at higher temperatures can now only take place under higher pressure.

VAN DER WAALS has called the temperature of the point e_1' the *maximum sublimation temperature* and that of the point c', the *minimum melting point temperature* or the *melting point proper* of the combination.

Further it is worthy of note that as appears from the figs. 4, 5 and 6, the highest three phase temperature cannot be reached when we start from pure AB, as this temperature corresponds with a total concentration which contains more A than the combination.

It is obvious from the foregoing, that the distinguishing feature between a non-dissociating and a dissociating substance is this, that whereas for a non-dissociating substance the three phases can only exist at one temperature, they can coexist for a dissociating substance over a certain temperature range. We may express this also in this way: a non-dissociating substance has only a three phase *point*, but a dissociating substance a three phase *line.*

Before leaving figs. 4. 5 and 6 I will point out, that the solubility-isotherm at the maximum three phase temperature has a shape which is indicated by the line $f'Cf'_1$. This line touches the liquid branch at C and has an horizontal tangent at the point where it cuts the line for the combination. At higher temperature the solubility isotherm gets detached from the liquid line and moves as a whole upward.

5. It is obvious that the two three phase pressure lines ecs and $e_1 c_1 s_1$ must coincide at the maximum three phase temperature, but where the place of coincidence in the three phase regions must be drawn is a point which calls for further elucidation from the subjoined p-t-projections.

In the figs. 8, 9 and 10, I have drawn projections for the cases 1, 2 and 3. Fig. 8 corresponds to case 1, fig. 9 to case 2 and fig. 10 to case 3. The meaning of the different lines is indicated by letters; thus A denotes the solid substance A, B the solid substance B and AB the solid substance AB, L denotes liquid and G gas. E and E' are the two eutectic points, a and a' the triplepoints of pure A and B.

The p-t-projections show further that we have here a three phase line for $AB + L + G$ consisting of two branches passing continuously into each other, and that we must find here the phenomena discussed in the preceding paper, on a larger scale. As already appeared from the p-x-sections, the triplepoint has split up into two points F and F''. In the point F there is contact with the line for $AB + L$ and in F'' with the line for $AB + G$.

Though for the systems $AB + L$ and $AB + G$ we have to deal with systems of two components in two phases, they behave as monovariant systems, because the concentration of the two phases is identical. This is however not the case for the system liquid $AB +$ vapour, and this is the reason why the line for $L + G$, which begins in F, cannot be represented; at constant temperature, the pressure is here still depending on the volume.

The point F does *not* correspond to the maximum three phase temperature, and that is the cause of the analogy with the case discussed in the preceding paper.

For the cases 1 and 2 the three phase line must have the direction of the melting line at the melting point F, as VAN DER WAALS has proved. As in most cases $v_l > v_s$, the melting line runs from the melting point to the right. This involves the necessity that the point F, (see fig. 8a) lies below R, i. e. at a pressure smaller than that corresponding to the maximum three phase temperature. If we therefore proceed to higher pressure, the succession is: F'', F, R. It is also obvious from the relative situation of these three points, that in figs. 4 and 5 the pressure corresponding to the maximum three phase temperature ECS, must lie somewhat above the melting point pressure $e' c'$.

Let us now consider the rare case that $v_l < v_s$, so that the melting line runs to the left, as is represented in fig. 8b. Then the point F lies above the point R, and the succession towards higher pressure is F'', R, F. A consequence of this situation is, that in this case the two three phase pressure lines ecs and $c_1 e_1 s_1$ (figs. 4 and 5) must coincide between the pressures corresponding tot F'' and F. This, however, not being the only modification which occurs in figs. 4 and

5, I have represented in fig. 7 the figure into which fig. 4 is changed when $v_l < v_s$.

We see then, that something peculiar appears i. e. a continuous closed solubility isotherm $G e c f c_1 e_1$, which contracts more and more with rise of temperature, and disappears from the stable region at the maximum three phase pressure.

When the lower three phase pressure line $c_1 e_1 s_1$ has ascended to $e_1' c_1'$, or in other words, when we consider the temperature of the point F', the solubility isotherm has assumed the shape indicated by the line $e_2 e_1' c_1' f_1 c_2$. At this temperature the *minimum* of the solubility isotherm, which was still in the stable region before, gets into the metastable region. If we raise the temperature up to the melting point of AB or to the temperature of the point F, the former phenomenon is repeated with respect to the *maximum*, which just below this temperature was still to be found in the stable region. Accordingly at still higher temperature no maximum or minimum occurs in the portions of the solubility-isotherm passing through the stable region, and we only retain the lines $c_3 c_3'$ and $e_3 e_3'$. These lines become smaller and smaller with rise of temperature, and the two three phase pressure lines $e_3 c_3$ and $e_3' c_3'$ approach each other more and more, till they have coincided at the maximum three phase temperature in ESC. The branches of the solubility isotherm touch at this temperature exactly in the points E and C. With further rise of temperature they retreat altogether to the metastable and unstable region, after which they disappear [1]).

In the case that $v_l > v_s$ solid AB can still coexist with liquid above the maximum three phase temperature, viz. under higher pressure, but this is not the case when $v_l < v_s$, which also follows already from the figs. 8a and 8b.

We see further that in fig. 8 two three phase lines occur with a maximum temperature, in fig. 9 only one, and in fig. 10 three.

Fig. 9 shows, that the case 2, where the vapour tension of the combination is smaller than that of the components, is certainly the most interesting case, as it can yield a three phase line with a minimum and two maxima, which had been unknown up to now.

As to the situation of the two branches of this peculiar three phase line we may still remark that only one of the possible cases is drawn here. These branches may pass through each other or partially coincide, but this does not make any essential difference.

Remarkable complications present themselves, when it is assumed

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[1]) Later on I hope to discuss the course of the solubility isotherm in the metastable and unstable regions between the temperatures of F' and F more in details.

that meetings take place between solubility lines and plaitpoint lines, but to this I hope to come back afterwards.

In the lower parts of figs. 8, 9 and 10 the projections of the solubility lines on the T-x-plane or the melting curves under the varying three phase pressure are represented. From this we see that these lines, commencing at the components or the combination, must not always be drawn descending from the beginning, but that they will often first ascend, and descend after having reached a maximum.

These particularities have disappeared when we trace the melting curves at *constant pressure* or a t-x-section at constant p.

Amsterdam, June 1905. Chemical Laboratory of the University.

(August 17, 1905).
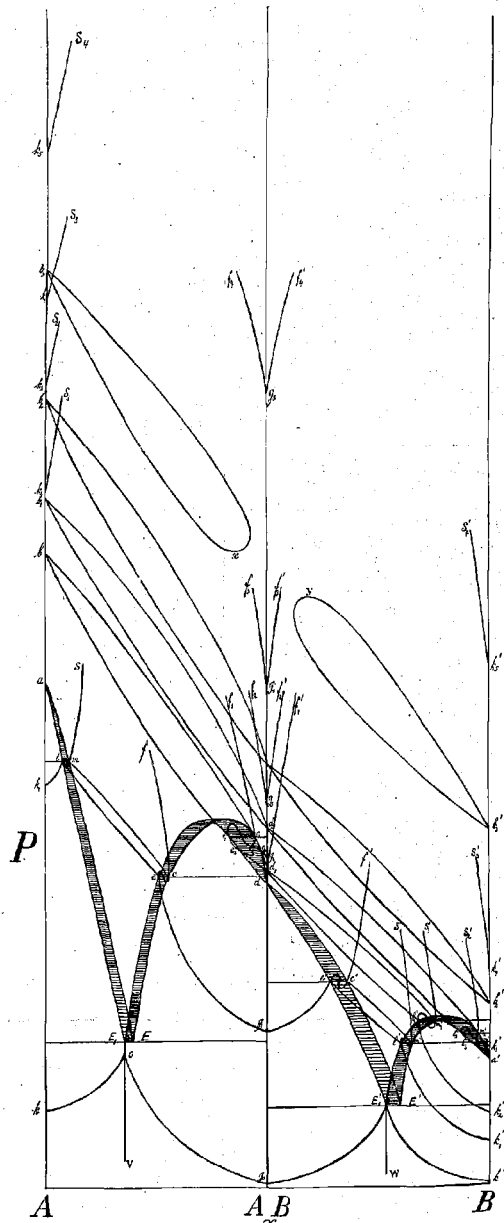
Fig. 1.
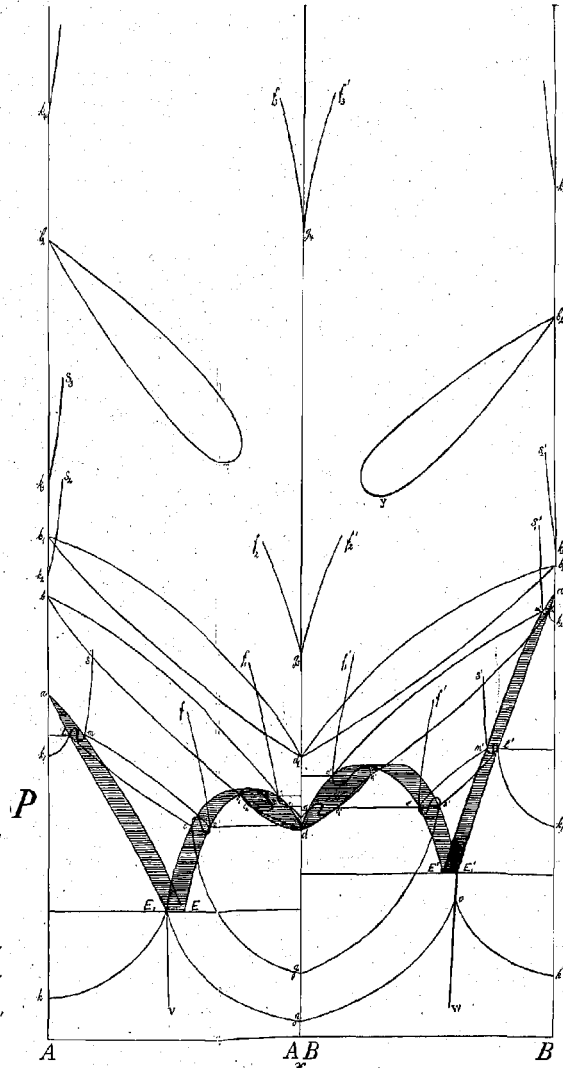
Fig. 2.
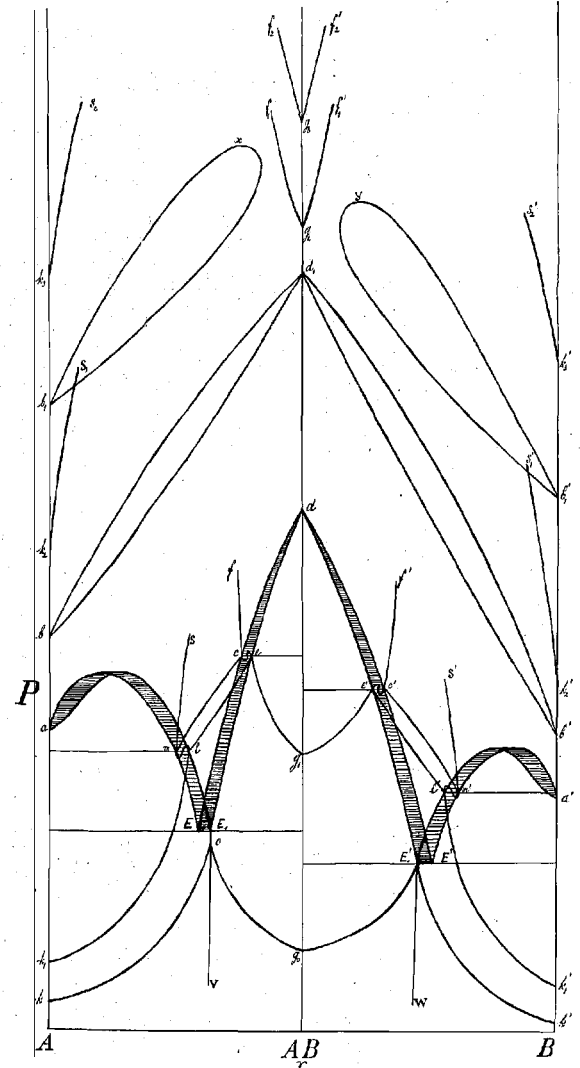
Fig. 3.

A. SMITS. "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."

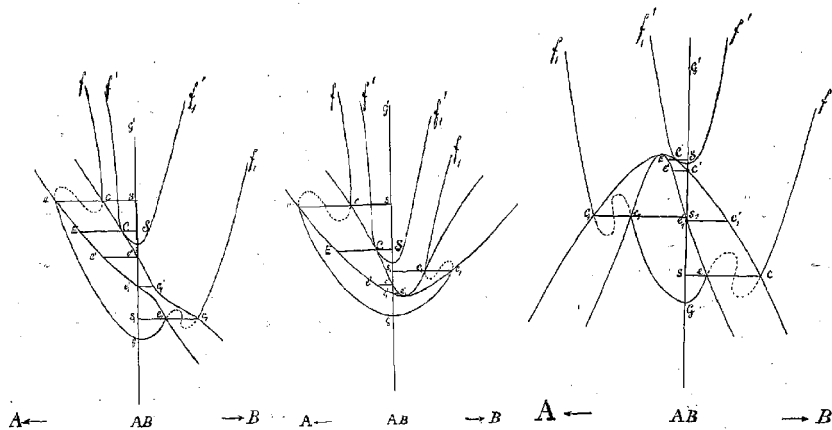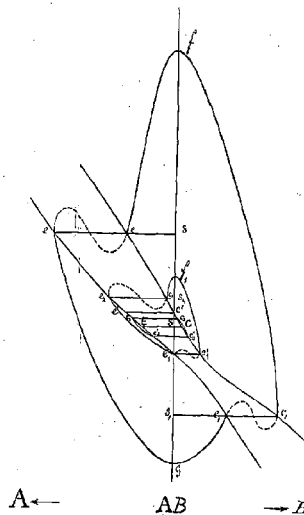Three phase regions in the neigbourhood of the line for AB, so near the melting-point temperature of AB.

Vapour tension combination *between* that of the components.

Fig. 4. Vapour tension comb. *between* that of the components.

Fig. 5. Vapour tension comb. *smaller* than that of the components.

Fig. 6. Vapour tension comb. *greater* than that of the components.

E C S corresponds to the highest three phase temperature.

Fig. 7.

Fig. 8.

Fig. 8a.

Fig. 8b.

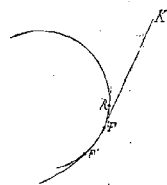Vapour tension combination *smaller* than that of the components.

Fig. 9.

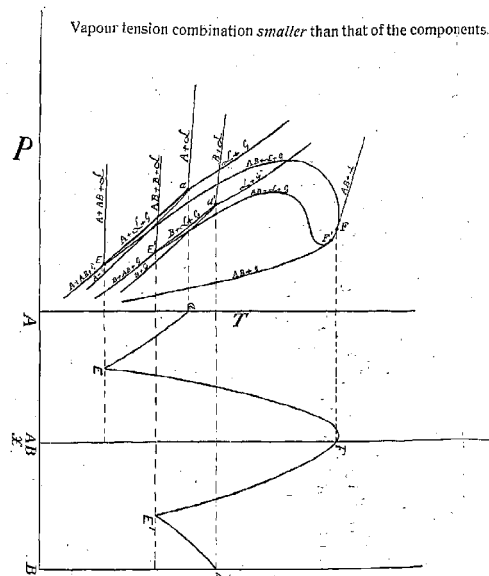Vapour tension comb. *greater* than that of the components.

Fig. 10.