Chemistry. — *"Equilibria in Ternary Systems"* VII. By Prof.
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Up to now we have only considered the occurrence of a single solid substance F; we will now take the case when a second solid substance F' also appears.

Let us first investigate what happens if a mixture of both substances F and F' is brought together.

If, at a low temperature, we introduce a mixture of the substances F and F' in an evacuated space, a vapour G is formed causing the equilibrium $F + F' + G$ to appear. The vapour G is of course represented by a point of the line FF'.

According to the composition of the vapour G or in other words according to the position of the three points in regard to each other, the following reactions can occur at a supply or withdrawal of heat or at a change in volume, P and T being constant.

1. If the point G is situated between F and F' the reaction $F + F' \rightleftarrows G$ occurs. Hence, if F and F' are placed in an evacuated space a part of each of the solid substances evaporates. We will call this a congruent sublimation.

2. If the point F' is situated between F and G the reaction $F' \rightleftarrows F + G$ takes place. Hence, if both substances are placed in an evacuated space only a part of F' will evaporate while solid F is being deposited. The formation of vapour is, therefore, accompanied by a transformation of F' into F. We will call this an incongruent or transformation sublimation.

3. If the point F is situated between F' and G the reaction $F \rightleftarrows F' + G$ occurs. This case is quite analogous to that mentioned sub 2. so we call this also an incongruent or transformation sublimation.

4. As a transition case between 1 and 2 or 3 the point G can also coincide incidentally with F' or with F.

At an elevation of temperature, the vapour pressure of the system $F + F' + G$ increases when G, of course, alters its composition; hence, in a P,T-diagram we obtain a curve such as $a''D$ of fig. 1 which we will call the sublimation curve of $F + F'$. If, between the three phases occurs the reaction mentioned sub 1 we call $a''D$ a congruent, if the reaction mentioned sub 2 or 3 takes place we call $a''D$ an incongruent or transformation sublimation curve. It is evident that the one part of a curve may be a congruent and the other part a transformation sublimation curve.

On further heating the system $F + F' + G$ a temperature T_D

and its correlated pressure P_D is attained at which an infinitesimal quantity of liquid L is formed. The sublimation curve, therefore, terminates in a point D of fig. 1 representing the temperature T_D and the pressure P_D which we will call the maximum-sublimation point of $F + F'$. The liquid L which forms in the point D will as a rule not be represented in an x,y-representation, by a point of the line FF'. As, however, the quantity of this liquid L is as yet but infinitely small, the vapour corresponding with the point D will still be represented by a point of the line FF'.

If the temperature is increased still further, still more liquid is formed and the four-phase equilibrium $F + F' + L + G$ appears. As, however, a finite quantity of liquid is now present, L and G must be in opposition in regard to the line FF'; only incidentally, L and G may fall both on this line.

At a constant P and T one of the following reactions takes place between the four phases on increase or withdrawal of heat or on a change in volume.

1. $F + F' \leftrightarrows L + G$ 2. $F'' \rightleftarrows F + L + G$ 3. $F \rightleftarrows F' + L + G$.
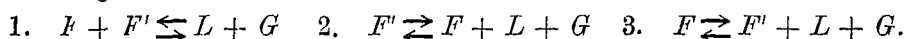
We will call the reaction 1 a congruent reaction, the reactions 2 and 3 incongruent ones. Which of these reactions takes place depends on the situation of the four points in regard to each other. As the system $F + F' + L + G$ has formed from $F + F'$ it is evident that in this four-phase equilibrium L and G are always present in such proportions that both disappear simultaneously in the above reactions.

Hence by warming the system $F + F' + G$ we have arrived on the four-phase line $F + F' + L + G$. As on this line the three components are present in four phases, this system is a monovariant one, so that to each temperature appertains a definite vapour pressure.

Hence, the four-phase line in a P, T-diagram will be represented by a curve; a part of this curve is represented in fig. 1 by DS; we shall see later that it continues in the points D and S. This curve, as we shall see meets the sublimation curve of $F + F'$ in its terminal point D.

We now take a T and P at which is formed from $F + F'$ a liquid without vapour, hence the system $F + F' + L$. The liquid will then, of course, be represented by a point of the line FF'. According to the situation of L in regard to the points F and F', the following reactions may occur at a constant P and T on a supply, or withdrawal of heat, or on a change in volume.

1. If the point L lies between F and F' the reaction $F + F' \rightleftarrows L$
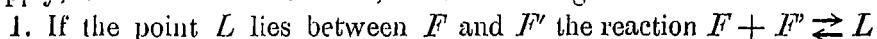
takes place. The liquid is, therefore, formed by the fusion of a part of each of the solid substances. We will call this a congruent or mutual fusion of $F + F'$.

2. If the point F' is situated between F and L the reaction $F' \rightleftarrows F + L$ occurs. Hence, the liquid is formed because a part of F' melts with separation of F. The formation of liquid is thus accompanied with a conversion of F' into F. We will call that an incongruent or transformation fusion.

3. If the point F lies between F' and L the reaction $F \rightleftarrows F' + L$ occurs. This case is quite analogous to the previous one.

If we change the temperature we must, of course, also change the pressure in order to keep together the three phases F, F', and L. The liquid L then also changes its composition. In a P, T-diagram we thus obtain a curve like $d''S$ in fig. 1, which we will call the melting point line of $F + F'$.

If between the three phases occurs the reaction mentioned sub 1 we call $d''S$ a congruent or mutual melting point line of $F + F'$; if the reaction sub 2 or sub 3 occurs we call $d''S$ an incongruent melting point line or the transformation melting point line of $F + F'$.

We now allow the system $F + F' + L$ to traverse the melting point line $d''S$ in such a direction that the pressure diminishes; at a definite pressure P_D and its correlated temperature T_D an infinitely small quantity of vapour will form so that the four-phase equilibrium $F + F' + L + G$ again appears. The complex therefore passes from the melting point line on to the four-phase line DS. The melting point line therefore terminates in the point S and, as we shall see presently, comes into contact with the four-phase line in this point. We will call S the minimum melting point, or the melting point of the complex $F + F'$ under its own vapour pressure. The vapour G forming in the point S will as a rule, not be represented by a point of the line FF', but the liquid L will, of course, still be represented by such a point.

The sublimation line $a''D$ and the melting point line Sd'' of the complex $F + F'$ are therefore connected with each other by the part DS of the four-phase curve. The fact that the points D and S will not, as a rule coincide may be perceived in the following manner. In the maximum sublimation point the points F, F', and G, in the minimum melting point F, F', and L are situated on a straight line. Hence, both points will coincide only then when incidentally the four phases of the system $F + F' + L + G$ lie on a straight line.

The course of the sublimation curve, of the four-phase curve and of the melting point line is, as we will see presently, determined

by the relation:

$$T\frac{dP}{dT}=\frac{\Delta W}{\Delta V}\quad\ldots\quad\ldots\ldots\quad(1)$$

ΔW is the quantity of heat which must be supplied, ΔV the change in volume occurring when, between the phases in equilibrium at a constant T and P, a reaction takes place in the one or in the other direction.

Let us first consider the sublimation curve $a''D$. For each of the reactions mentioned sub 1—3 taken in such a direction that vapour is formed, ΔW and ΔV are positive.

From (1) it thus follows, as drawn in fig. 1, that, at an elevation of temperature, the sublimation curve must proceed towards higher pressures. The point D lies as well on the sublimation- as on the four-phase curve. As, however, in this point D, the quantity of liquid of the four-phase equilibrium is still but infinitesimal, ΔW and ΔV are the same for both systems so that the two curves must meet in D.

Let us now consider the melting point line Sd''. We take each of the reactions mentioned sub 1—3 in such a direction that liquid is formed so that ΔW is positive. At the congruent and incongruent fusion of $F+F'$ ΔV may, however, be positive as well as negative. The melting point line can therefore, proceed from S towards the right as well as to the left; in fig. 1 the first case has been drawn. The fact that the melting point line and the four-phase line meet each other in S follows in the same manner as that given above for the meeting of the two curves in D.

In order to deduce formula (1) for the sublimation or the melting point curve, we consider the equilibrium $F+F'+G$ or $F+F'+L$. We represent the composition of F by α, β, that of F' by α', β', that of L or G by x, y. We call the volumina of these phases v, v' and V, the entropies η, η' and H, the thermodynamic potentials ζ, ζ' and Z.

As F and F' are in equilibrium with L (G) we have:

$$Z-(x-\alpha)\frac{\partial Z}{\partial x}-(y-\beta)\frac{\partial Z}{\partial y}=\zeta\quad\ldots\ldots\quad(2)$$

$$Z-(x-\alpha')\frac{\partial Z}{\partial x}-(y-\beta')\frac{\partial Z}{\partial y}=\zeta'\quad\ldots\ldots\quad(3)$$

From the condition that the three points F, F' and L (G) are situated on a straight line, follows:

$$(x-\alpha)(y-\beta')=(x-\alpha')(y-\beta)\quad\ldots\ldots\quad(4)$$

From these relations between the four variables x, y, P and T follows:

$$\{(x-\alpha)\, r + (y-\beta)\, s\}\, dx + \{(x-\alpha)\, s + (y-\beta)\, t\}\, dy = A dP - B dT \quad (5)$$

$$\{(x-\alpha')\, s + (y-\beta'\, t\}\, dx + \{(x-\alpha')\, s + (y-\beta')\, t\}\, dy = A' dP - B' dT \quad (6)$$

$$(\beta-\beta')\, dx = (\alpha-\alpha')\, dy \quad . \quad . \quad . \quad . \quad . \quad (7)$$

If from this we wish to deduce the relation between dP and dT we may divide (5) by (6). In consequence of (4) we get:

$$\frac{x-\alpha}{x-\alpha'} = \frac{A dP - B dT}{A' dP - B' dT} \quad . \quad . \quad . \quad . \quad (8)$$

or after reduction :

$$\frac{dP}{dT} = \frac{(\alpha'-\alpha)\, H + (x-\alpha')\, \eta + (x-\alpha)\, \eta'}{(\alpha'-\alpha)\, V + (x-\alpha')\, v + (x-\alpha)\, v'} \quad . \quad . \quad . \quad (9)$$

which corresponds with formula (1).

Hence, as we have seen above, if we choose the exact conditions, we can compel the complex $F + F'$ to traverse the sublimation curve $a''D$, the four-phase curve $D\,S$ and the melting point curve Sd''. We will now investigate which conditions of the complex $F + F'$ are represented by points situated outside these curves. We distinguish therein different cases.

1. The complex $F + F'$ has a congruent sublimation line, four-phase line and melting point line.

Let us first introduce the complex $F + F'$ in a point of the sublimation curve so that $F + F' + G$ is formed. From a consideration of what happens on supplying or withdrawing heat or on a change in volume we deduce: at the right of and below the line $a''D$ are situated the regions $F + G$ and $F' + G$, at the left of and above curve $a''D$ is situated the region $F + F'$.

Acting in a similar manner with points of the other curves we find :

at the left of and above $a''DSd''$ is situated the region $F + F'$. at the left of and below $a''D$ are situated the regions $F + G$ and $F'' + G$

„ „ „ „ „ „ DS „ „ „ „ $F+L+G$ and $F'+L+G$

„ „ „ „ „ „ Sd'' „ „ „ „ $F + L$ and $F' + L$.

Let us enter the region $F+L+G$ from a point of the fourphase curve in a horizontal direction. We then, at a constant pressure, raise the temperature of the system $F + L + G$. The liquid and the vapour of this system then traverse a part of the boiling point and vapour boiling point curve of the substance F.

If we enter the region $F + L + G$ from a point of the four-phase curve in a vertical direction we then, at a constant tempera-

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ture, lower the pressure of the system $F + L + G$; the liquid and the vapour of this system then traverse a part of the saturation- and vapour saturation curve of the substance F under its own vapour pressure.

The same applies if we enter the region $F' + L + G$ from a point of the four-phase curve. In order to find the limitation of the different regions we draw in fig. 1 the sublimation curve $a K$, the three-phase curve KF and the melting point curve Fd of the compound F and the same curves $a'K'$, $K'F'$ and $F'd'$ of the compound F'. We will assume that F and F' also melt with increase in volume. The curves Fe and Kf have the same significance as the homonymous curves in fig. 3 (III); the same applies to the curves $F'e'$ and $K'f'$. The question now arises· where are these curves situated in regard to the corresponding curves of the complex $F + F'$.
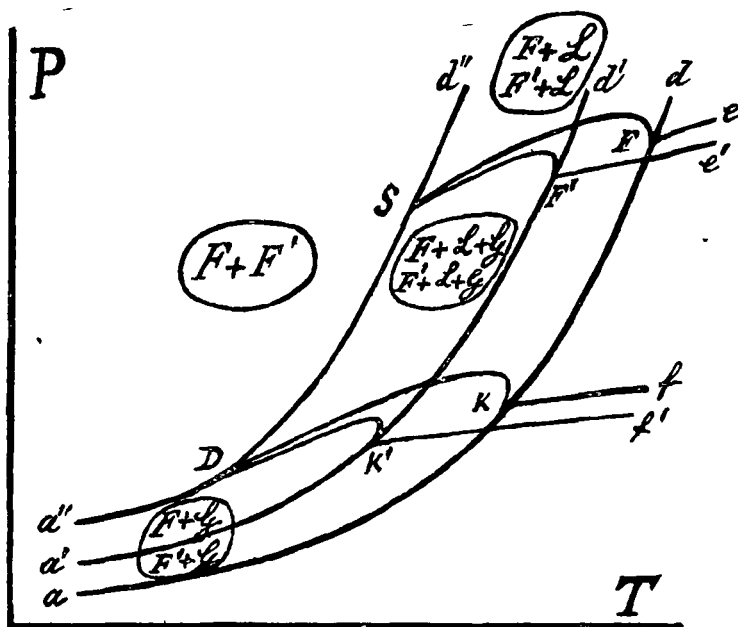

Fig. 1.

Let us first take a pressure so high that F and F' as well as their complex $F + F'$ have a melting point. Now, as is well known, the mutual melting point of $F + F'$ is situated lower than than of each of the components individually. A horizontal line intersecting the three melting point lines must therefore intersect the melting point line of $F + F'$ at lower temperature than the two other melting point lines.

In the same manner we find that a horizontal line which intersects the three sublimation curves must cut those of $F + F'$ at a lower temperature than in the case of the two other ones.

Curve $a''DSa''$ must, therefore, be situated in regard to the curves $aKFd$ and $a'K'F'd'$ as in Fig. 1.

The regions $F + L$ and $F + L + G$ are separated from each other by means of a curve, where $F + L$ appears in the proximity of an infinitesimal amount of vapour. We call this system $F + L + G°$; $G°$ signifies here that the other phases can be in equilibrium with a vapour of the composition G but that only an infinitesimal amount of that vapour is present.

If, owing to solution of large quantities of F in a small quantity of L, the system $F + L + G°$ approaches to solid $F +$ liquid $F + G°$ the system $F + L + G°$ then approaches the minimum melting point of the substance F.

If from $F + L + G°$ the solid substance F' is separated, so that the system $F + F' + L + G°$ is formed, we find ourselves in the minimum melting point of complex $F + F'$.

Hence, the P, T-curve of the system $F + L + G°$ proceeds in fig. 1 from S towards F.

In the previous communication IV we have already extensively considered this system $F + L + G°$. The liquid L of this system traverses at an elevation of temperature a straight line passing, in the x, ˙˙˙˙˙˙˙˙˙˙˙ through the point F, for instance the line ZF or Z_1F in ˙˙˙. 1 (IV). The P,T curve corresponding with this line is represented in fig. 4 (IV) by curve ZF or Z_1F. The curve SF must, therefore as a rule come into contact with the melting point line Fd in the point F. In fig. 1 it has been assumed that curve SF corresponds with branch ZF of fig. 4 (IV).

The regions $F' + L$ and $F' + L + G$ are separated from each other by a curve $F' + L + G°$; in a similar manner as above we find that this is represented by a curve SF'. In fig. 1 we have drawn the two curves SF and SF' in agreement with branch ZF of fig. 4 (IV); we might have drawn both or one of them also in agreement with branch Z_1F of this figure. The boundary curve of the regions $F + L + G$ and $F + G$ is formed by the system $F + L° + G$; that of the regions $F' + L + G$ and $F' + G$ by the system $F' + L° + G$. $L°$ signifies here that the other phases may be in equilibrium with a liquid L, but that only infinitely little of that liquid is present. In an analogous manner as above we find that the P, T-curves of these systems are represented in fig. 1 by the curves SK and SK'. These curves meet in K and K' the curves

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a d and *a' d'*. On both curves a point with a maximum pressure and one with a minimum temperature is supposed to occur.

Besides the regions whose limitations we know now we find at the right of curve *a' d'* also the regions $L + G$, L and G which, however, are not drawn in the figure.

In order to survey the connection of these regions we might draw a representation in space; for this we imagine the composition of the complex $F + F'$ to be placed perpendicularly to fig. 1. Instead of the spacial representation itself we will here consider its sections with planes.

If we place a plane perpendicularly to the concentration-axis we get a P,T-diagram which applies to a definite complex, if we place a plane perpendicularly to the T-axis we get a pressure-concentration diagram which applies to a definite temperature, and if we place a plane perpendicularly to the P-axis we get a temperature concentration diagram which applies to a definite pressure.

Let us place first a plane, which intersects the three sublimation curves, perpendicularly to the T-axis; we then obtain a section as in fig. 2 in which F and F' represent the two compounds F and F'. Perpendicularly to this line FF' is placed the P-axis.

In order to be able to indicate readily the different regions occurring in this and the following diagrams we will represent:

The liquidum region by L, the vapour region by G, the solid region by $F + F'$, the region $F + G$ by 1, $F' + G$ by 2, $F + L$ by 3, $F' + L$ by 4, $L + G$ by 5, $F + L + G$ by 6 and $F' + L + G$ by 7.

If in fig. 1 we suppose a straight line, which intersects the three sublimation curves, to be drawn parallel to the P-axis, we notice that in fig. 2 the regions $F + F'$, $1 = F + G$, $2 = F' + G$ and the region G must appear. The points s, s' and s'' represent the sublimation pressures of the solid substances F and F' and of their complex $F + F'$; the complex, therefore, has a higher sublimation pressure than each of its components by itself.

Fig. 2.

The curve ss'' represents the vapours which can be in equilibrium with solid F, curve $s's''$ those which can be in equilibrium with solid F'; these curves have in s and s' a horizontal tangent.

We now take a complex $F + F'$ of the composition c, so that the complex itself is represented by a point of the line cc'. As this line intersects the regions $F + F'$, 2 and G, then according to the pressure chosen, there
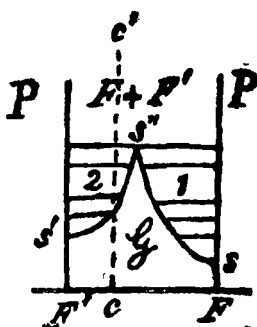
is formed either $F + F'$ or $F' + G$ or G. If the complex has such a composition that the line cc' intersects the regions $F + F'$, 1 and G either $F + F'$ or $F + G$ or G is formed.

Let us now take a pressure concentration diagram for a temperature higher than the maximum sublimation point, but lower than the minimum melting point of the complex $F + F'$. If in fig. 1 we draw a vertical line which intersects curve DS we notice that this diagram may be represented by fig. 3.

Besides the regions G, $F + F'$, 1 and 2 which appear already in fig. 2 we also find here the regions :

$$5 = L + G, \qquad 6 = F + L + G \quad \text{and} \quad 7 = F' + L + G.$$

If from $F + F'$ is formed one of the systems G, $F + G$ or $F' + G$, the vapour G always has a composition that can be represented by a point of fig. 3; the same applies to the liquid L if from $F + F'$ is formed one of the systems L, $F + L$ or $F' + L$.

If, however, $L + G$ is formed as in the systems $L + G$, $F + L + G$ and $F' + L + G$, such, as we have seen previously, is no longer the case and neither L nor G can be represented by a point of the diagram.

Let us take for example a complex K (not drawn in the figure); this complex is resolved into a liquid L and a gas G, both situated outside the plane of fig. 3. If L is situated above this plane, G lies below the same and reversedly so and in such a manner that their conjugation line intersects the region 5 in the point K.

If we take a complex K' within the region 6 (7), we then suppose this to be resolved first into $F(F')$ and a complex K of $L + G$; the complex K is, of course, represented by a point of fig. 3. To this complex now applies the same as to the complex K within the region 5.
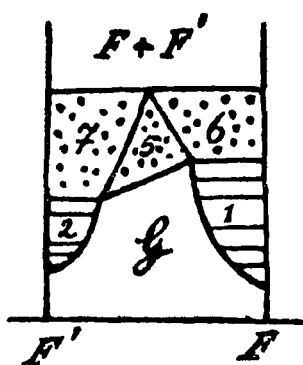

Fig. 3.

Hence, if from $F + F'$ is formed a system in which $L + G$ appears, the complex $L + G$ is certainly represented by a point of fig. 3 but L and G separately are not; one of these phases lies in front of, the other behind the plane of fig. 3. By way of distinction from the other regions, the regions 5, 6, and 7 are dotted; we may imagine that these points represent the points of intersection of fig. 3 with the conjugation lines liquid-gas. We have noticed previously that in some systems occurs only an infinitesimal quantity of L or G; of a similar complex $L^0 + G$ or $L + G^0$ the gas is

represented by a point of the diagram in the first case; the liquid in the second case.

The line of demarcation of the regions 1 and G represents the vapours which can be in equilibrium with solid F, that of the regions 2 and G those which can be in equilibrium with solid F''. The line of demarcation of the regions 5 and G represents the equilibrium $L^\circ + G$, that of the regions 5 and 6 the complex $L + G$ of the system $F + L + G$ and that of the regions 5 and 7 this same complex of the system $F'' + L + G$.

If in agreement with fig. 1 we take a temperature higher than the minimum melting point S of the complex $F + F''$ and lower than the maximum sublimation point K' of the substance F'' we obtain a diagram as in fig. 4. If in agreement with fig. 1 we take a temperature higher than the maximum sublimation point K of the substance F and lower than the minimum meltingpoint F'' of the com-
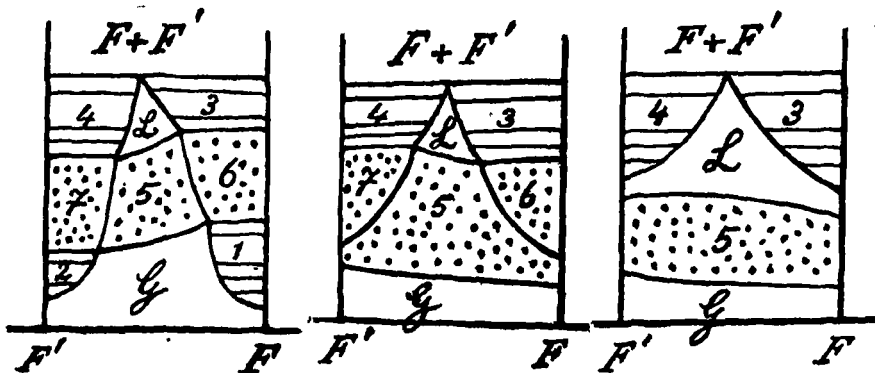

Fig. 4.   Fig. 5.   Fig. 6.

pound F'' we obtain a diagram as in fig. 5. If finally we take a temperature higher than the minimum melting point F of the compound F we obtain a diagram as in fig. 6.

Between the diagrams figs. 2—6 exist different transition forms; we must also consider the possibility that, in fig. 1, we can draw lines parallel to the P-axis which cut the curves DK, DK', SF and SF'' in two points. We will not, however, discuss here these transition forms.

When deducing the diagrams it has also been assumed that the points D, K', K, S, F'' and F are situated in regard to each other as drawn in fig. 1. But this may be different.

As a rule, the points S, F'', and F and also the points D, K' and K will lie in regard to each other as assumed in fig. 1. The minimum melting point of the complex $F + F''$ is therefore, as a

rule situated at a lower temperature and pressure than the minimum melting point of each of the substances F and F' separately.

For in fig. 1 we have assumed that curve SF corresponds with branch ZF of fig. 4 (IV) and that S is situated on the rising part of this branch and is removed far from the point with the maximum pressure. If, however, S lies on this branch somewhere between the point with the maximum pressure and that with the maximum temperature the curve SF in fig. 1 no longer exhibits a pressure maximum but only a temperature maximum; the pressure in the minimum melting point of $F + F'$ is then higher than that in the minimum melting point of F.

If S is situated on branch ZF somewhere between the point with maximum temperature and the point F, curve SF in fig. 1 proceeds from S towards lower temperatures and pressures. In that case not only the pressure but also the temperature of the minimum melting point $F + F'$ is situated higher than that of F.

From our previous considerations as to curve ZFZ_1 of fig. 4 (IV) it follows that the latter case can occur only then when the liquid formed at the minimum melting point of $F + F'$ differs but little in composition from the substance F.

From these considerations follows: at a constant pressure the melting point of the complex $F + F'$ is always lower than that of each of the substances F and F' separately. As a rule the minimum melting point of $F + F'$ is also lower than that of each of the compounds individually. By way of exception, the minimum melting point of $F + F'$ may, however, be somewhat higher than that of one or even of both of the substances F and F'.

We shall see later that in this case at the temperature of the minimum melting point of $F + F'$, the saturation curve of F or F' under its own vapour pressure is exphased.

A similar consideration applies to the maximum sublimation points of the complex $F + F'$ and the compounds F and F'.

Let us now bring a complex $F + F'$ of a definite composition c_0 to a temperature T_0 and a pressure P_0. In order to investigate in which of the 10 possible conditions this complex will now occur we take a pressure concentration diagram of the temperature T_0 and place in this the concentration c_0 and the pressure P_0 of the complex. If now the figurating point lies for instance in region 7, $F' + L + G$ is formed, if in region 3, $F + L$ is formed, if it lies in region G it is converted wholly into gas, in region L wholly into liquid, etc.

Besides the pressure concentration diagrams considered above we may also deduce from fig. 1, or its corresponding spacial represen-

tation, temperature concentration diagrams for a complex of a definite composition; I will, however, not go into this any further. -

2. The complex $F + F'$ has an incongruent sublimation line, four-phase line, and melting point line.

We will assume that both liquid and vapour have such a composition that on the sublimation curve $a''D$ (fig. 1) occurs the reaction $F' \rightleftarrows F + G$, on the four-phase curve DS the reaction $F' \rightleftarrows F + L + G$ and on the melting point curve Sd'' the reaction $F' \rightleftarrows F + L$. Hence if F' is placed in an evacuated space and if gas is generated, then according to the capacity of this space $F + F' + G$ or $F + G$ is formed or merely a vapour G of the composition F'; if liquid and vapour are generated $F + F' + L + G$ is formed, or $F + L + G$, or $L + G$; if liquid is generated $F + F' + L$ is formed or $F + L$ or merely a liquid of the composition F'.

From F' according to the conditions chosen, one of the complexes $F + F' + G$. $F + G$, G, $F + G$, $F + F' + L + G$, $F + L + G$. $L + G$, $F + F' + L$, $F + L$ or L will form or else the compound F' may remain unchanged. If only L or G is formed these will, of course have the same composition as the compound F'. Hence, we can never obtain from the compound F one of the complexes $F' + G$, $F' + L + G$ or $F' + L$ unless these appear in a meta-stable condition.

In fig. 1 all curves relating only to the compound F' ($a'K'$, $K'F'$, Fd' $F''e'$ and $K'f'$) and the regions encompassed by them, therefore represent only metastable conditions of the compound F'; hence, they cannot be realised in the stable condition. If, therefore, the compound F' is introduced into an evacuated space it will not occur in the conditions which correspond with the P, T-diagram of F', but with those corresponding with the P, T-diagram of the complex $F + F'$.

The terminal point D of the sublimation curve $a''D$ is here not only the highest sublimation point of the complex $F + F'$, but it also represents the highest pressure at which the conversion of F' into F takes place by the side of gas; the initial point S of the melting point curve Sd'' is here not only the lowest melting point of the complex $F + F'$, but represents also the lowest pressure at which the conversion of F' into F takes place in presence of liquid.

From a consideration of what happens with the complex $F + F'$ on supply or withdrawal of heat or on a change in volume we deduce:

At the left of and above $a''DSd''$ is situated the region $F + F'$

  ,, ,, right ,, ,, below $a''D$,,   ,,   ,,   ,, $F + G$

,, ,, ,, ,, ,, ,, DS ,,   ,,   ,,   ,, $F + L + G$

,. ,, ,, ,, ,, ,, Sd'' ,,   ,,   ,,   ,, $F + L.$

These regions are, therefore, situated, with regard to the curve $a''DSd''$, in the same manner as in fig. 1. It is also evident therefrom that in the P,T-diagram the regions $F' + G$, $F' + L + G$ and $F' + L$ are wanting.

In order to survey the connection of these regions we might draw a representation in space by now also placing perpendicularly to fig. 1 the composition of the complex $F + F'$. From this spacial representation we might then deduce the pressure concentration the temperature concentration and the P,T-diagrams for definite concentrations. We will, however, not go into this matter any further just now.

3. Some other cases.

Up to now, we have supposed that F and F' melt with increase in volume and that this is also the case with the congruent and incongruent melting of the complex $F + F'$; in agreement therewith, the temperature on each of the three melting point curves in fig. 1 increases with elevation of pressure.

We now see at once that there are many cases to be distinguished; the reader himself can easily introduce the necessary alterations.

Further, we have supposed sub 1 that in each point of the curve $a''DSd''$ occurs a congruent reaction and sub 2 that in each point of this curve an incongruent reaction appears. It is evident that in this respect also many cases may be distinguished of which I will briefly mention a few.

We imagine on the sublimationcurve a point l; on the part $a''l$ occurs, between the phases of the complex $F + F' + G$, the congruent reaction $F' + F \rightleftarrows G$; on the part lD the incongruent reaction $F' \rightleftarrows F + G$. In the point l itself the compound F will then take no part in the reaction but the reaction $F' \rightleftarrows G$ takes place in which G has the same composition as F'.

Hence, in the point l occurs the complex $F + F' + $ vapour F'; in l therefore, also exists the complex $F' + $ vapour F'. From this follows that l is not only a point of the sublimation curve $a''D$ but also of the sublimation curve $a'K'$.

Now, the direction of these curves in each point, therefore also in l is determined by $T\dfrac{dP}{dT} = \dfrac{\Delta W}{\Delta V}$. As, however in the point l the reaction in the two systems $F + F' + $ vapour F' and $F' + $ vapour

F'' is the same (namely, $F'' \rightleftarrows$ vapour F'') ΔW and ΔV are also the same for both systems. The curves $a''D$ and $a'K'$ must, therefore meet in the P, T-diagram in the point l.

A corresponding property holds when a corresponding point l is situated on the four-phase curve, or on the melting point curve of the complex $F + F'$.

Hence, if the sublimation line, the four-phase line or the melting point line of the complex $F + F'$ is in a part a congruent and in a part a transition curve, the curve of the complex in the P, T-diagram will meet in its transition point the corresponding curve of that compound which is being converted.

If there are two transition points, many cases may present themselves, according to their situation, the compound converted etc., which we will not discuss here any further.
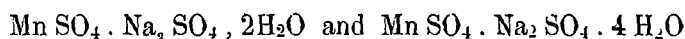
(*To be continued*).

Chemistry. — "*The system sodium sulphate, manganous sulphate and water at* 35°[1]). By Prof. F. A. H. SCHREINEMAKERS and D. J. VAN PROOIJE.

In this system occur as solid phases, which can be in equilibrium at 35° with saturated solutions: anhydrous Na_2SO_4, the hydrate $MnSO_4 . H_2O$ and the two anhydrous double salts:

$D_{9.10} = (Mn\,SO_4)_9 . (Na_2\,SO_4)_{10}$ and $D_{1.3} = Mn\,SO_4 . (Na_2\,SO_4)_3$.
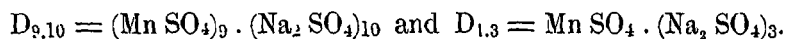
The double salts previously described:

$Mn\,SO_4 . Na_2\,SO_4 , 2H_2O$ and $Mn\,SO_4 . Na_2\,SO_4 . 4\,H_2O$

have not been found by us, whereas on the other hand those now noticed have not been described up to the present. Moreover, the accurate preparation and solubility of the salts previously described are but insufficiently known, so that it is difficult to decide whether these are perhaps metastable or whether the presence of two metastable salts was, perhaps, due to accident.

The equilibria occurring at 35° are indicated schematically in the figure; the two double salts are represented by the points $D_{9.10}$ and $D_{1.3}$, the salt $MnSO_4 . H_2O$ is represented by the point Mn_1. The isotherm consists of four branches, namely

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[1]) MARIGNAC and GEIGER, A. Min. [5] 9. 15. Mag. Pharm. 11 27.