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Chemistry. — “*In-, mono- and divariant equilibria.*” XI. By Prof. F. A. H. SCHREINEMAKERS.

(Communicated in the meeting of October 28, 1916).

18. *Binary systems with two indifferent phases.*

After the general considerations [Communication X] about systems with two indifferent phases, we shall apply them now to binary systems.

When in the invariant point of a binary system occurs the equilibrium: $F_1 + F_2 + F_3 + F_4$, then only one type of P, T -diagram exists; we find it in fig. 2 (I).

When in a binary system, however two indifferent phases occur and, therefore, also two singular phases, then two types of P, T -diagram exist [figs. 1 and 2]. We may deduce them in different ways.

When in the concentration-diagram of fig. 2 (I) F_3 and F_4 are the indifferent phases, then F_1 and F_2 are the singular ones; F_1 and F_2 have then the same composition, so that the points F_1 and F_2 coincide [fig. 1]. Then we have the singular equilibria:

$$(M) = F_1 + F_2 \quad [\text{Curve } (M) \text{ in fig. 1}]$$

$$(F_3) = F_1 + F_2 + F_4 \quad [\text{Curve } (3) \text{ in fig. 1}]$$

$$(F_4) = F_1 + F_2 + F_3 \quad [\text{Curve } (4) \text{ in fig. 1}]$$

and further the equilibria:

$$(F_1) = F_2 + F_3 + F_4 \quad [\text{Curve } (1) \text{ in fig. 1}]$$

$$(F_2) = F_1 + F_3 + F_4 \quad [\text{Curve } (2) \text{ in fig. 1}].$$

We may deduce the type of P, T -diagram from fig. 2 (I). As (3) and (4) are the singular curves, they must, therefore, coincide. It follows from our previous considerations that this coincidence may take place in fig. 2 (I) only in such a way that curve (3) coincides with the prolongation of (4) and therefore also curve (4) with the prolongation of (3). Then we obtain a type of P, T -diagram, as in fig. 1, in which curve (M) is bidirectionable. This diagram contains two bundles of curves; the one bundle consists of the curves (1), (4) and (2), the other only of curve (3). Curve (M) is a middlecurve of the (M)-bundle.

We are able to find the bivariant regions in this P, T -diagram in the same way as in other diagrams. Between the curves (1) and (4) is situated the region (14) = 23, between the curves (1) and (2) we find the region (12) = 34, etc. In fig. 1 those regions are indicated; they are the same as in fig. 2 (I), with this difference, how-

ever, that the region 12 from fig. 2 (I) is missing in fig. 1 and is replaced by the singular curve $(M) = F_1 + F_2$.

We have seen in the previous communication that each region which extends over the stable or metastable part of a singular curve, contains the two indifferent phases. In fig. 1 the region 34 extends over the singular curves; and therefore it contains the two indifferent phases F_3 and F_4 .

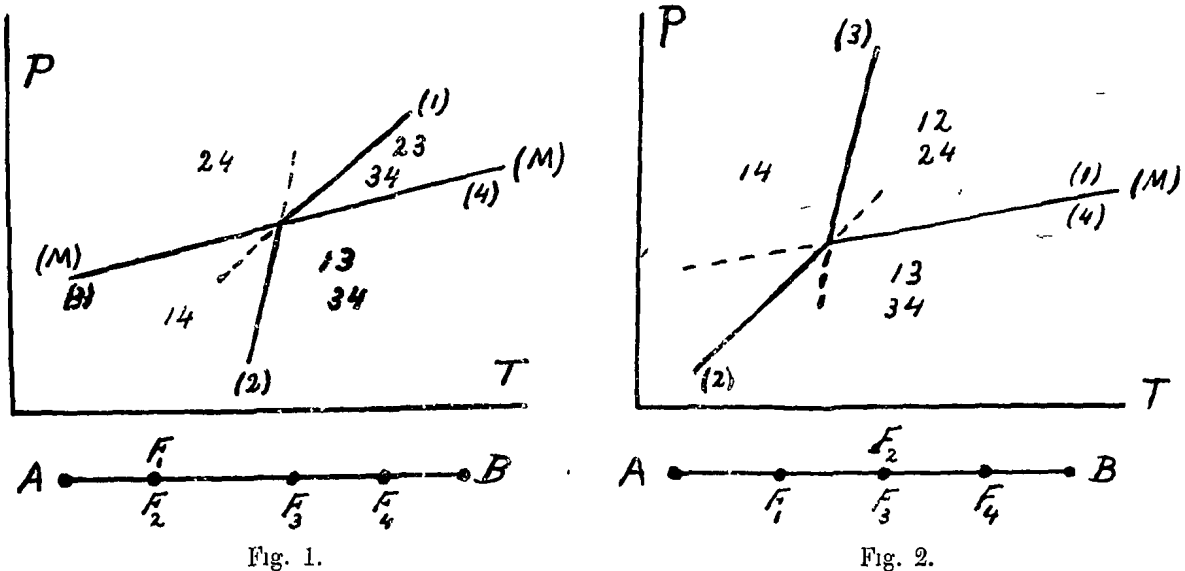


Fig. 1.

Fig. 2.

When in the concentration diagram of fig. 2 (I) F_1 and F_2 are the indifferent phases, then F_3 and F_4 are the singular phases, F_3 and F_4 have then the same composition, so that the points F_3 and F_4 coincide [fig. 2]. Then we have the singular equilibria:

$$(M) = F_3 + F_4 \quad [\text{Curve } (M) \text{ in fig. 2}]$$

$$(F_1) = F_3 + F_4 + F_1 \quad [\text{Curve } (1) \text{ in fig. 2}]$$

$$(F_2) = F_1 + F_3 + F_4 \quad [\text{Curve } (2) \text{ in fig. 2}]$$

and further the equilibria:

$$(F_3) = F_1 + F_2 + F_4 \quad [\text{Curve } (3) \text{ in fig. 2}].$$

When we wish to deduce the type of P, T -diagram from fig. 2 (I) then, as (1) and (2) are the singular curves, we have to let them coincide. Then we obtain fig. 2. The three singular curves (M) , (1) and (2) coincide now in the same direction; the (M) -curve is, therefore, monodirectionable. Consequently the P, T -diagram consists of three onecurval bundles.

In order to find the bivariant regions, we have to bear in mind that between the curves (1) and (3) the region $(13) = 24$ is situated,

between the curves (1) and (2) the region (12) = 34; etc.; then we find the regions indicated in fig. 2. Those regions are the same as in fig. 2 (I); only the region 23 from fig. 2 (I) is missing in fig. 2, it is replaced by the singular curve $(M) = F_2 + F_3$.

In fig. 2 the region 14 extends itself over the metastable parts of the singular curves (M) , (1) and (4); indeed this region contains the two indifferent phases F_1 and F_4 .

Now we have let the phases F_1 and F_2 coincide and also F_2 and F_3 in the concentration-diagram of fig. 2 (I), we might as well have made F_3 and F_4 coincide. Then we obtain however a same type of P, T -diagram as in fig. 1. Consequently only two different types of P, T -diagram may occur; they are represented in figs. 1 and 2.

We are able to deduce the types of P, T -diagram also in the following way. In communication X we have viz. seen that we may distinguish three main types, viz. I, IIA and IIB.

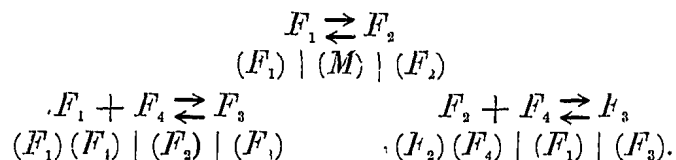
In main type I curve (M) is monodirectionable; the P, T -diagram of a binary system has then the same appearance as that of a unary system. Therefore, it consists, as in fig. 2, of three one-curvical bundles; one of these curves represents then the three singular curves. [In fig. 2 they are the curves (M) , (1) and (4).]

In main type IIA curve (M) is bidirectionable and a middle curve of the (M) -bundle [fig. 3 (X)], we obtain then for a ternary system a type of P, T -diagram as in fig. 1.

In main type IIB curve (M) is bidirectionable and a side-curve of the (M) -bundle [fig. 4 (X)]. As in this type, besides the (M) -curve, still five curves at least have to occur, in binary systems a P, T -diagram of this type cannot exist.

We can also find the types of P, T -diagram with the aid of the reactions, which may occur between the phases of the invariant point.

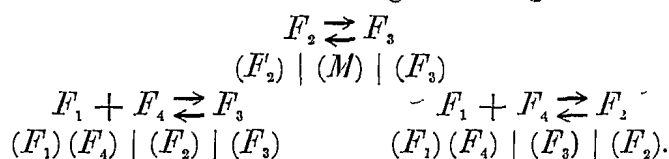
In order to find the type of P, T -diagram, which belongs to the concentration-diagram of fig. 1, we consider the reactions, which may occur between the phases and the partition of the curves, resulting from those.



We see that this partition of the curves is in accordance with

fig. 1. It is evident that we can also find easily the type of P, T -diagram with the aid of this partition of the curves.

We find from the concentration-diagram of fig. 2



Hence we find a type of P, T -diagram as in fig. 2.

We are also able to deduce the types of P, T -diagram with the aid of the series of signs. In order to find the series of signs, we have to know two reactions, each between the four phases of the invariant point. We can easily deduce those reactions from the concentration-diagrams of figs. 1 and 2; for the concentration-diagram of fig. 1 we find then series of signs 1, for that of fig. 2 the series of signs 2.

Series of signs 1 (fig. 1)

F_1	F_3	F_4	F_2
+	-	+	+
0	-	+	+
-	0	0	+
-	+	-	0

Series of signs 2 (fig. 2)

F_2	F_1	F_4	F_3
+	-	-	+
0	-	-	+
-	0	0	+
-	+	+	0

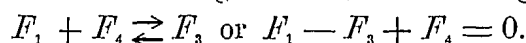
In series of signs 1 F_3 and F_4 , in series of signs 2 F_1 and F_4 are the indifferent phases; they have opposite signs in series of signs 1 and they have the same sign in series of signs 2. The positions of the curves with respect to one another as in the figs. 1 and 2 follow immediately from those series of signs.

It is apparent from the previous considerations that two types of P, T -diagram [figs. 1 and 2] may occur in binary systems with two indifferent phases. Those types are in accordance with the rules which we have deduced in the general considerations [Communication X]. We found amongst others:

1. The two indifferent phases have the same sign or in other words: the singular equilibrium (M) is transformable into the invariant equilibrium (M) and reversally. Curve (M) is monodirectional; the three singular curves coincide in the same direction. [fig. 1 (X)].

2. The two indifferent phases have opposite sign or in other words: the singular equilibrium (M) is not transformable. Curve (M) is bidirectional, the two other singular curves coincide in opposite direction [fig. 2 (X)].

In order to examine whether the two indifferent phases F_3 and F_4 in fig. 1 have the same sign or not, we take e.g. the reaction:

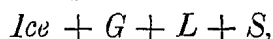


Hence it appears that F_3 and F_4 have opposite signs so that the singular equilibrium $(M) = F_1 + F_2$ is not transformable. Moreover the latter appears also at once from fig. 1; it appears viz. from the position of the points F_1, F_2, F_3 , and F_4 with respect to one another, that a complex of the phases F_1 and F_2 can never be converted into the invariant equilibrium $F_1 + F_2 + F_3 + F_4$.

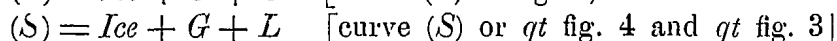
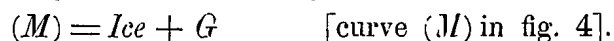
In accordance with rule 2 curve (M) must be therefore bidirectional and the two other singular curves [(3) and (4)] have to coincide in opposite direction. We see that this is in accordance with fig. 1.

In the same way it appears that the indifferent phases F_1 and F_4 from fig. 2 have the same sign and that the singular equilibrium $(M) = F_2 + F_3$ is transformable. In accordance with rule 1 curve (M) must then be monodirectional and the three singular curves have to coincide in the same direction. This is in accordance with fig. 2.

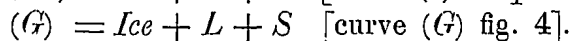
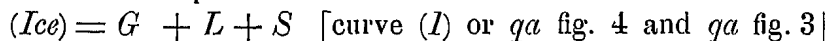
Now we shall contemplate more in detail some P, T -diagrams. We take a binary system: water + a salt S , of which we may assume that S is not volatile; consequently the gasphase G consists of water-vapour only. When no hydrates of the salt S occur, then we find in the cryohydratic point the invariant equilibrium:



in which L is the solution saturated with ice + S . As the water-vapour G and the ice I [fig. 4] have the same composition, G and Ice are the singular phases, L and S the indifferent ones. Consequently we have the singular equilibria:



and further the equilibria:



In fig. 3 a concentration-temperature diagram of this binary system is drawn; W and S represent the two components, q is the cryohydratic solution L . The curves qt and qa go towards higher temperatures starting from q ; qt is the ice-curve, it represents the solutions of the equilibrium $(S) = Ice + G + L$; qa represents the solutions, saturated with the salt S , viz. the solutions of the equilibrium

(Ice) = $G + L + S$. Curve qt terminates in the point t : the melting-point of ice under its own vapour-pressure, consequently the triple-point: water + vapour + ice. Curve qa terminates in the melting-point a of the salt S .

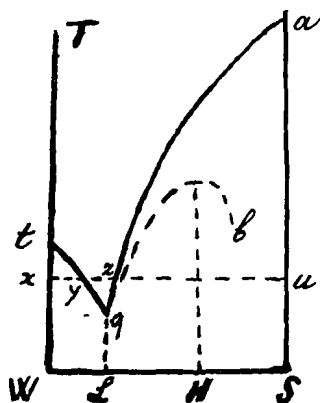


Fig. 3.

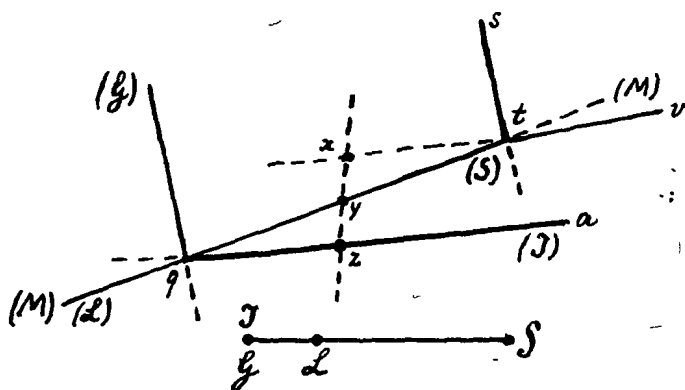


Fig. 4.

We find in fig. 4, besides the P, T -diagram, also the concentration-diagram; as ice and watervapour have the same composition, in this the points I and G coincide.

We find in fig. 4 besides the curves (M) , (L) , (S) , (I) and (G) also the triplepoint t of the water. Three curves start from this triplepoint; tv is the evaporationcurve (equilibrium: water + vapour); ts is the meltingcurve of the ice (equilibrium: ice + water); tq is the sublimationcurve of the ice (equilibrium: ice + vapour). This sublimationcurve tq of the ice is, therefore, at the same time the singular curve $(M) = \text{Ice} + G$ of the binary system.

This (M) -curve is bidirectionable, for the invariant point q of course cannot be a terminating-point of this curve; at the one side of the point q it coincides with the singular curve $(S) = \text{Ice} + G + L$, at the other side of the point q with the singular curve $(L) = \text{Ice} + G + S$.

The reaction $\text{Ice} + S \rightleftharpoons L$ may occur between the phases of curve $(G) = \text{Ice} + S + L$; consequently curve (G) is the common melting-curve of ice and salt S . In general it proceeds upwards starting from the point q fairly parallel to the P -axis. When at the reaction $\text{Ice} + S \rightarrow L$ the volume increases; then it goes starting from q towards higher temperatures; when the volume decreases, it goes towards lower temperatures. In fig. 4 we have assumed that it proceeds, just as the melting-line ts of the ice, starting from q towards lower temperatures.

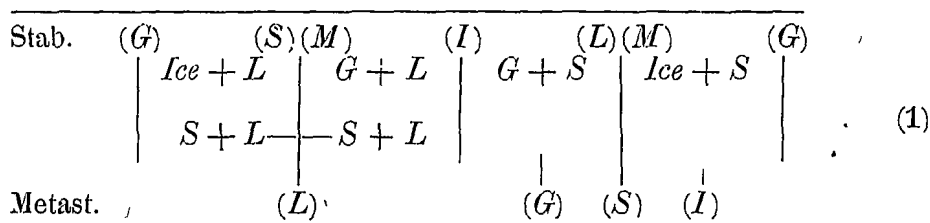
It follows from fig. 3 that in fig. 4 curve qa must be situated

below qt . For this we draw a horizontal line $xyzu$ in fig. 3; we assume that all the points of this line represent liquids. (Those liquids are then partly stable, partly metastable). In the point x this liquid is water, while the percentage of salt increases starting from x towards u . Consequently the vapourpressure decreases along this line starting from x towards u .

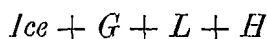
The horizontal line $xyzu$ is represented in fig. 4 by the vertical line $xyzu$, as the vapourpressure in the point u is practically zero, this point has not been drawn in fig. 4; it is situated in the immediate vicinity of the T -axis. The point x is situated on the metastable part of curve tv , point y on curve $(qt) = (S)$ and point z on curve $qa = (I)$. Hence it is apparent that curve qa must be situated, therefore, below qt .

As the concentration-diagram of fig. 4 is the same as that of fig. 1, the P, T -diagram of fig. 4 must belong also to the same type as that of fig. 1. We see that this is the case; both P, T -diagrams [fig. 1 and 4] consist viz. of a threecurvical and a onecurvical bundle; in both diagrams curve (M) is also a middle-curve of the (M) -bundle.

Just as the P, T -diagram of fig. 1 the reader may deduce also that of fig. 4 in different ways; just as in fig. 1 we are able to draw the bivariant regions also in fig. 4. As this figure would be then overfilled with letters, I give in (1) a symbolical representation. [Compare communication IV], The reader may indicate them in a P, T -diagram, which is drawn on a larger scale.



When in the binary system: water + salt S occurs a hydrate H , then the equilibrium:



may occur in the cryohydratic point q . When this point H is situated as in fig. 3, in which qb represents the solutions, which are saturated with H under their own vapourpressure, then the P, T -diagram is the same as in fig. 4; in this we have only to replace (S) by (H) and a by b . Curve qb in fig. 4 obtains then in its further proceeding

first a point of maximum pressure and afterwards a point of maximum temperature.

The hydrate H however may be situated also as in fig. 5; curve $aqmb$ of this figure represents the solutions, saturated with H under their own vapour pressure; the solutions of the dotted part bmq are then metastable. Now we have the following singular equilibria:

$$(M) = Ice + G \quad [\text{Curve } (M) \text{ fig. 6}]$$

$$(L) = Ice + G + H \quad [\text{Curve } (L) \text{ fig. 6}]$$

$$(H) = Ice + G + L \quad [\text{Curve } (H) \text{ or } qt \text{ in fig. 6 and } qt \text{ in fig. 5}]$$

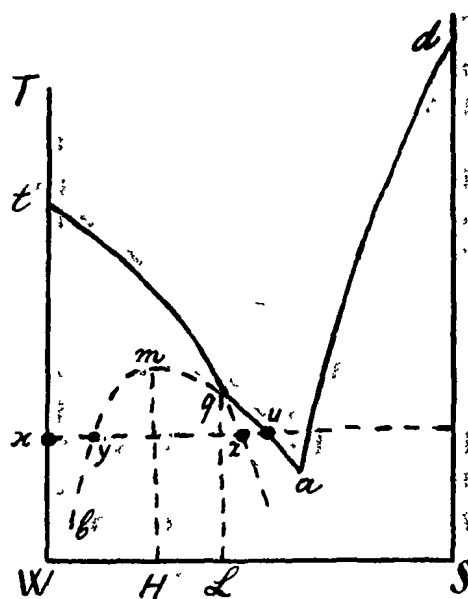


Fig. 5.

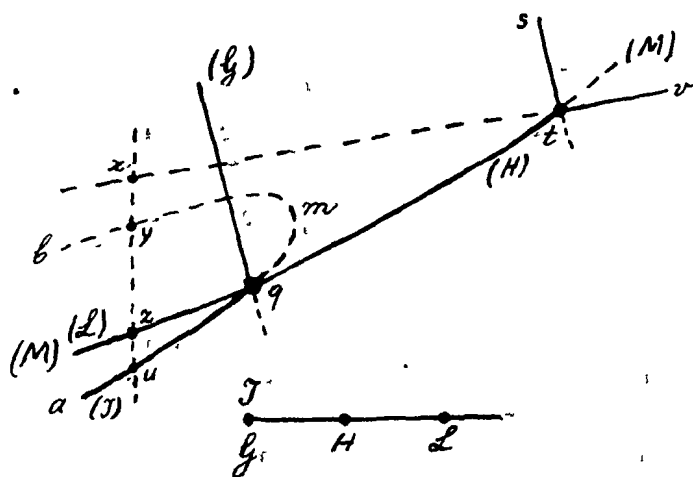


Fig. 6.

and further the equilibria

$$(Ice) = G + L + H \quad [\text{Curve } (I) \text{ or } qa \text{ fig. 6 and } qa \text{ fig. 5}]$$

$$(G) = Ice + L + H \quad [\text{Curve } (G) \text{ fig. 6}]$$

Besides the curves (M) , (L) , (H) , (I) and G we find in fig. 6 also the triplepoint t of the water, ts : the melting-curve of the ice and tw the evaporationcurve of the water.

It appears from a comparison of the figs. 4 and 6 that curve $(S) = qt$ from fig. 4 is replaced in fig. 6 by curve $(H) = qt$. Curve $(L) = qa$, which represents the equilibrium $G + L + H$, proceeds in fig. 4 from q towards higher T and P , in fig. 6 this curve proceeds, however, starting from q towards lower T and P . The metastable part qmb of this curve has its point of maximum temperature in the vicinity of the point m [figs. 5 and 6].

When we draw in fig. 5 the horizontal line $xyzu$ and in fig. 6 the vertical line $xyzu$ corresponding with this then we see that the different curves must be situated with respect to one another, as is drawn in fig. 6.

As the concentrationdiagram of fig. 6 is the same as that of fig. 1, the P, T -diagram of fig. 6 must therefore, belong to the same type as that of fig. 1. We see that this is really the case.

Now we take the binary system: water + salt S , of which S occurs in two modifications S_α and S_β . In fig. 7 q is the solution, saturated with the two modifications under its own vapourpressure. Consequently we have the equilibrium:



Curve $(q\beta)$ [fig. 7] represents the solutions of the equilibrium $G + L + S_\beta$; it terminates in the meltingpoint β of the modification S_β . Curve dq represents the solutions of the equilibrium $G + L + S_\alpha$, the metastable prolongation qa of this curve terminates in the metastable meltingpoint α of the modification S_α .

Curve qo represents the solutions of the equilibrium $S_\alpha + S_\beta + L$; with this we have assumed that this curve proceeds starting from q towards higher temperatures.

We have the singular equilibria:

$$(M) = S_\alpha + S_\beta \quad [\text{Curve } (M) \text{ fig. 8}]$$

$$(L) = S_\alpha + S_\beta + G \quad [\text{Curve } (L) \text{ fig. 8}]$$

$$(G) = S_\alpha + S_\beta + L \quad [\text{Curve } (G) \text{ or } qo \text{ fig. 8 and } qo \text{ fig. 7}]$$

and further the equilibria:

$$(S_\alpha) = G + L + S_\beta \quad [\text{Curve } (S_\alpha) \text{ or } q\beta \text{ fig. 8 and } q\beta \text{ fig. 7}]$$

$$(S_\beta) = G + L + S_\alpha \quad [\text{Curve } (S_\beta) \text{ or } qd \text{ fig. 8 and } qd \text{ fig. 7}]$$

When S_α and S_β are not volatile, then G consists of watervapour only. If they are volatile, then G contains also S . The more S is contained in G , the more the point G shifts towards the right in the concentration-diagram of fig. 8. As long as the four phases with respect to one another are situated, however, as in fig. 8, the P, T -diagramtype remains the same.

As it appears from the change in volume at the reaction $S_\alpha \rightleftharpoons S_\beta$ which is generally small, the (M) -curve proceeds general fairly parallel to the P -axis; it terminates towards lower pressures in the

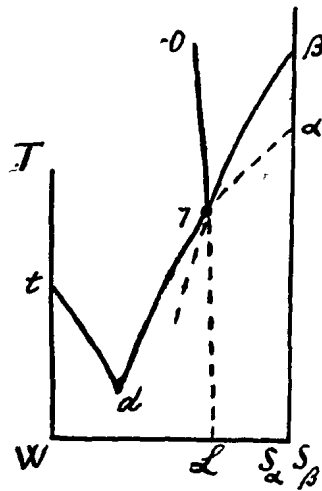


Fig. 7.

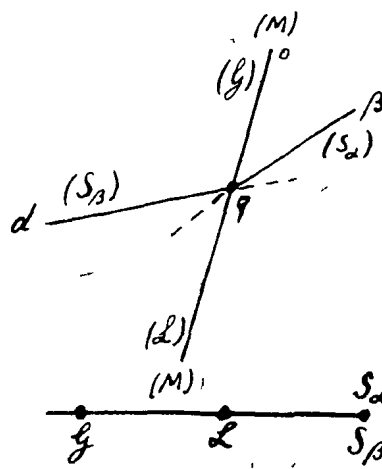


Fig. 8.

triplepoint. $S_\alpha + S_\beta + \text{vapour } S$. It may proceed from this triplepoint as well towards higher as towards lower temperatures; in figs. 7 and 8 we have assumed that it goes towards higher T .

The position of the curves $q\beta$ and qd with respect to one another in fig. 8 follows from fig. 7; for this we have to draw a horizontal line, which intersects the stable part of the one and the metastable part of the other curve.

As the concentration-diagrams of figs. 1 and 8 belong to the same type, this must also be the case with the P, T -diagrams of both figures. We see that this is really the case.

Now we shall discuss a binary system, in which occurs a P, T -diagram of the type of fig. 2. For this we take the system: water + salt S , in which a hydrate H occurs in the two modifications H_α and H_β [fig. 9].

When we represent the solutions of the equilibrium $G + L + H_\alpha$

in a concentration-temperature-diagram, then we obtain a curve $dqaq_1c$ [fig. 9], which has its maximum of temperature in the vicinity of the point α . The curve, which represents the solutions of the equilibrium $G + L + H_\beta$, is represented by $xq\beta q_1z$ (fig. 9); it has its point of maximum temperature in the vicinity of the point β . The curves intersect one another in q and q_1 (fig. 9); in this we have assumed $T_q > T_{q_1}$. The dotted parts of the curves represent metastable conditions.

Now we have two invariant equilibria, viz.

$$\text{in the point } q : G + L_q + H_\nu + H_\beta$$

$$\text{in the point } q_1 : G + L_{q_1} + H_\nu + H_\beta$$

In fig. 9 the solutions of the equilibria $G + L + H_\nu$ and $G + L + H_\beta$ are represented by $dqaq_1c$ and $xq\beta q_1z$; in the P, T -diagram of fig. 10 those equilibria are represented by the same curves. As we have assumed in fig. 9 $T_q > T_{q_1}$, this must also be the case in fig. 10.

The position of those curves in fig. 10 with respect to one another follows from fig. 9. On the horizontal line $dxzc$ viz. the vapour-tension of the liquids decreases starting from d towards c ; in the P, T -diagram the points d, x, z and c must be situated, therefore, with respect to one another, as in fig. 10. When we draw in fig. 9 also other horizontal lines, then we see that the position of the curves dac and $x'z$ in fig. 10 is in accordance with that in fig. 9.

In the point q we have the singular equilibria:

$$(M) = H_\nu + H_\beta \quad [\text{Curve } (M) \text{ fig. 10}]$$

$$(L) = H_\nu + H_\beta + G \quad [\text{Curve } (L) = qq_1 \text{ fig. 10}]$$

$$(G) = H_\nu + H_\beta + L \quad [\text{Curve } (G) = qo = qo_1 \text{ fig. 10} \\ \text{and Curve } qo \text{ fig. 9}]$$

and further the equilibria, already discussed:

$$(H_\nu) = G + L + H_\beta \quad [\text{Curve } q\beta \text{ figs. 9 and 10}]$$

$$(H_\beta) = G + L + H_\nu \quad [\text{Curve } qd \text{ figs. 9 and 10}].$$

In distinction of the equilibria occurring in q , we give to the equilibria occurring in q_1 the index 1. Then we have in the point q_1 the singular equilibria:

$$(M)_1 = H_\nu + H_\beta \quad [\text{Curve } (M) \text{ fig. 10}]$$

$$(L)_1 = H_\nu + H_\beta + G \quad [\text{Curve } (L)_1 = q_1q \text{ fig. 10}]$$

$$(G)_1 = H_\nu + H_\beta + L \quad [\text{Curve } (G)_1 = q_1o_1 = q_1o \text{ fig. 10} \\ \text{and Curve } q_1o_1 \text{ fig. 9}]$$

and further the equilibria, already discussed:

$$(H_\nu)_1 = G + L + H_\beta \quad [\text{Curve } q_1\beta \text{ figs. 9 and 10}]$$

$$(H_\beta)_1 = G + L + H_\nu \quad [\text{Curve } q_1c \text{ figs. 9 and 10}].$$

Let us imagine the singular equilibrium $(M) = (M)_1 = H_\nu + H_\beta$ in the point q . It appears from fig. 9 that a complex $H_\nu + H_\beta$ can not be converted into the invariant equilibrium of the point q viz. into $G + L_q + H_\alpha + H_\beta$. [We assume that the gas G consists of watervapour only, so that point G coincides with W]. The singular equilibrium $(M) = (M)_1$ is, therefore, not transformable into the invariant equilibrium q ; curve (M) is consequently bidirectionable and does not terminate, therefore, in the point q , but it goes through that point.

Let us now imagine the singular equilibrium $(M) = (M)_1$ in the point q_1 . It appears from fig. 9 that a complex $H_\nu + H_\beta$ may be-

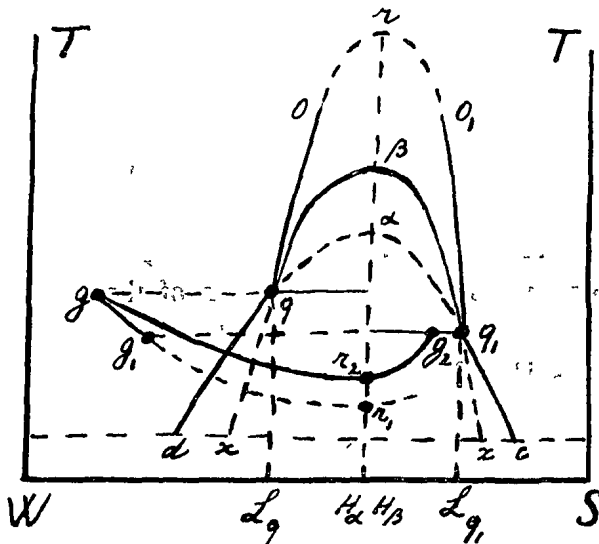


Fig. 9.

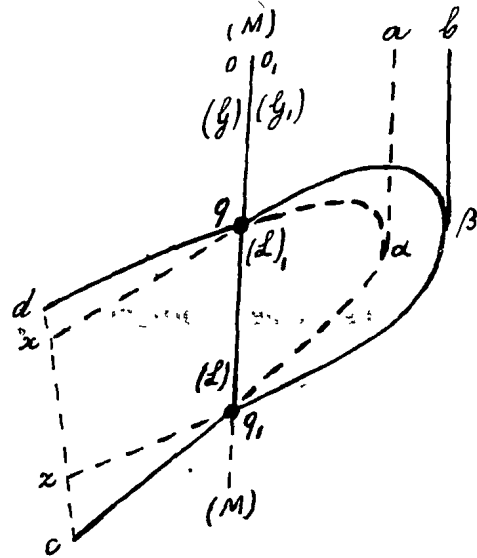


Fig. 10.

converted into the invariant equilibrium of the point q_1 viz. into $G + L_{q_1} + H_\nu + H_\beta$. The singular equilibrium $(M) = (M)_1$ is, therefore, transformable into the invariant equilibrium q_1 ; consequently curve (M) is monodirectionable and terminates in the point q_1 . The (M) -curve is represented, therefore, in fig. 10 by curve $q_1q_0 = q_1q_0_1$.

Further the singular equilibria

$$(L)_1 = H_\nu + H_\beta + G \quad \text{and} \quad (G)_1 = H_\nu + H_\beta + L$$

start from the point q_1 ; as the (M) -curve is monodirectionable in q_1 , the three singular curves (M) , $(L)_1$ and $(G)_1$ coincide in the same direction. The curves $(L)_1$ and $(G)_1$ go, therefore, also, starting from q_1 in the direction towards q .

As the equilibrium $(L)_1 = H_\alpha + H_\beta + G$ may be converted in the point q into the invariant equilibrium q viz. into $G + L_q + H_\alpha + H_\beta$, curve $(L)_1$ terminates in the point q . Consequently curve $(L)_1$ is represented in fig. 10 by curve q_1q .

The equilibrium $(G)_1 = H_\alpha + H_\beta + L$ may not be converted in the point q into the invariant equilibrium $q = G + L_q + H_\alpha + H_\beta$; curve $(G)_1$ does not terminate, therefore, in the point q , but it proceeds further. It is represented in fig. 10 by curve $q_1qo = q_1qo_1$. When we represent the solutions of the equilibrium $(G)_1 = H_\alpha + H_\beta + L$ in fig. 9, then we get a curve as q_1o_1 .

The singular equilibria

$$(L) = H_\alpha + H_\beta + G \quad \text{and} \quad (G) = H_\alpha + H_\beta + L$$

start from the point q . As the (M) -curve is bidirectionable in q , the singular curves (L) and (G) go in opposite direction. Consequently curve (L) goes starting from q towards lower pressures and it terminates in q_1 . Curve (G) goes starting from q towards higher pressures, it is represented in fig. 10 by $qo = qo_1$. The solutions of the equilibrium $(G) = H_\alpha + H_\beta + L$ are represented in fig. 9 by curve qo .

Let us now consider the P, T -diagram in the vicinity of the point q . In this point the equilibrium: $G + L_q + H_\alpha + H_\beta$ occurs, it appears from the position of those phases with respect to one another in fig. 9 that the P, T -diagram must belong to the type of fig. 1. We see that this is really the case.

In the point q_1 the equilibrium $G + L_{q_1} + H_\alpha + H_\beta$ occurs. In accordance with the position of those phases with respect to one another in fig. 9, it is apparent that the P, T -diagram belongs to the type of fig. 2 in the vicinity of the point q_1 in fig. 10.

The curves $qo = (G) = H_\alpha + H_\beta + L$ and $q_1o_1 = (G)_1 = H_\alpha + H_\beta + L$ are no separate curves in fig. 9, but parts of one single curve $qo_1o_1q_1$; this curve has a point of maximum- or of minimum-temperature in its point of intersection r with the line $\alpha\beta$ (viz. with the prolongation of this line). In fig. 9 we have assumed that T is a maximum. In this point r the equilibrium: $H_\alpha + H_\beta + L_{\alpha\beta}$ occurs, in which $L_{\alpha\beta}$ represents a liquid of the composition $H_\alpha = H_\beta$.

In fig. 10 the point r has not been drawn, of course it is situated somewhere on that part of the (M) -curve, which ascends starting from the point q , for we have assumed in fig. 9 $T_1 > T_q$. This point r is the stable terminating-point of the curves qo and q_1o_1 and, as we shall see further, the common point of intersection of three curves viz. of the (M) -curve, of the melting-line of H_α and of the melting-line of H_β .

In the point r viz. the equilibrium: $H_\nu + H_\beta + L_{\alpha\beta}$ occurs; as the melting-line of H_ν represents the equilibrium $H_\alpha + L_{\nu,\beta}$, r is, therefore, also a point of this melting-line. In the same way it appears that r is also a point of the melting-line of H_β .

The melting-line of H_α is represented in fig. 10 by $\alpha\alpha$, that of H_β by $\beta\beta$. The three curves $\alpha\alpha$, $\beta\beta$ and (M) , therefore must go in fig. 10 through a same point r .

In the deduction of fig. 10 we have assumed that the gas-phase G consists of watervapour only; now we shall briefly discuss the case that the compounds H_β and H_ν are also volatile.

Then G contains, besides the watervapour, still the substance S .

When we represent in fig. 9 the compositions of the gas-phases which may be in equilibrium with the liquids of curve dac , then a curve $d'a'c'$ arises, which is not drawn in fig. 9. This curve is the vapourcurve belonging to dac . Also a vapourcurve $x'\beta'z'$ which is not drawn belongs to curve $x\beta z$. Now we assume firstly that the vapours, which are in equilibrium with the liquids, contain less of the substance S than the liquids. Branch $d'a'$ is then situated in fig. 9 more towards the left than $d\alpha$, branch $c'a'$ more than $c\alpha$, branch $x'\beta'$ more than $x\beta$ and branch $z'\beta'$ more than $z\beta$.

The two vapourcurves $d'a'c'$ and $x'\beta'z'$ intersect one another in fig. 9 in g and g_1 ; the vapour g is in equilibrium with the liquid g ; the vapour g_1 with the liquid g_1 . The point g is always situated at the left of the line $\alpha\beta$, the point g_1 may be situated also, however, just as e. g. g_2 at the right of the line $\alpha\beta$. We first consider the case that the vapour, which is in equilibrium with the liquid g_1 , is represented by g_1 .

In the same way as we have deduced above fig. 10, we now find that the P, T -diagram keeps the form of fig. 10.

The vapours of the equilibrium $(L) = H_\nu + H_\beta + G$ and of $(L)_1 = H_\nu + H_\beta + G$ are represented in fig. 9 by curve gg_1 . The equilibrium $H_\nu + H_\beta + G$ has a point of maximum- or of minimum-temperature, when the vapour G has the composition $H_\alpha = H_\beta$. When we produce in fig. 9 curve gg_1 until it meets in r_1 the line $\alpha\beta_1$, then the tangent in r_1 is horizontal. Consequently in r_1 the equilibrium $H_\nu + H_\alpha + G_{\nu,\beta}$ occurs, in which $G_{\nu,\beta}$ represents a vapour of the composition $H_\nu = H_\beta$.

In fig. 10 this point r_1 is situated somewhere on the metastable part of the (M) -curve, viz. on the part, descending starting from the point g_1 . This point r_1 is the metastable terminating-point of the curves (L) and $(L)_1$; at the same time it is, as we easily see,

a common point of intersection of three curves viz. of the (M)-curve, of the sublimation-curve of H_α and of that of H_β . It appears from the position of the vapour-curves $d'a'c'$ and $x'\beta'z'$ with respect to the line $\alpha\beta$ in fig. 9, that the points in which the sublimation-curves come in contact with the curves $d'ac$ and $x\beta z$ in fig. 10, are situated at the left of q_1 .

As long as the vapour, which is in equilibrium with the liquid q_1 is represented in fig. 9 by a point q_1 at the left of the line $\alpha\beta$, the P, T -diagram keeps a form as in fig. 10. The P, T -diagram changes, however, when the vapour is represented by a point q_2 at the right of the line $\alpha\beta$. The singular equilibrium (M) = $H_\alpha + H_\beta$ is then viz. no more transformable into the invariant equilibrium $q_1 = H_\alpha + H_\beta + G_{q_1} + L_{q_1}$. Curve (M) is then bidirectionable not only in point q but also in q_1 (fig. 10); consequently it proceeds now also in stable condition below the point q_1 . Curve (G)₁ = $H_\alpha + H_\beta + L$ continues to be represented in fig. 10 by q_1o_1 ; curve (L)₁ no more goes now, however, starting from q_1 upwards, but downwards.

The vapours of the equilibria (L) = $H_\alpha + H_\beta + G$ and (L)₁ = $H_\alpha + H_\beta + G$ are represented in fig. 9 by curve gr_2g_2 , which has in r_2 a minimum-temperature. In fig. 10 this point r_2 is situated somewhere on the (M)-curve below the point q_1 . This point r_2 is the stable terminating-point of the curves (L) and (L)₁. [Now curve (L)₁ viz. as has already been said above ascends no more starting from q_1 but it descends]. Point r_2 is also now again the common point of intersection of three curves, viz. of the (M)-curve, the sublimation-curve of H_α and that of H_β . The point in which the sublimation-curve of H_α comes in contact with curve $d'ac$, is situated at the left of q_1 ; the point in which the sublimation-curve of H_β touches curve $x\beta z$, is situated, however, at the right of q_1 .

Now the reader may easily draw the changes in the figures 9 and 10, when the vapours, which are in equilibrium with the liquids, contain more of the substance S than the liquids.

(To be continued.)

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