

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

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*Equilibria of  $n$  components in  $n + 1$  phases, when the quantity of one of the components approaches to zero. The influence of a new substance on an invariant equilibrium.*

For the equilibrium:

$$E = F_1 + F_2 + \dots + F_{n+1} \dots \dots \dots (1)$$

of  $n$  components in  $n + 1$  phases, as we have seen furtherly, are valid the equations:

$$Z_i - x_i \frac{\partial Z_i}{\partial x_i} - y_i \frac{\partial Z_i}{\partial y_i} - \dots = K \dots \dots \dots (2)$$

wherein

$$i = 1, 2, \dots (n + 1)$$

and further:

$$\left. \begin{aligned} \frac{\partial Z_1}{\partial x_1} = \frac{\partial Z_2}{\partial x_2} = \dots = \frac{\partial Z_{n+1}}{\partial x_{n+1}} = K_x \\ \frac{\partial Z_1}{\partial y_1} = \frac{\partial Z_2}{\partial y_2} = \dots = \frac{\partial Z_{n+1}}{\partial y_{n+1}} = K_y \end{aligned} \right\} \dots \dots \dots (3)$$

to which still must be added the corresponding equations for the variables  $z_1, z_2, \dots, u_1, u_2, \dots$  etc. As it is apparent from the number of equations (viz.  $n^2 + n$ ) and the number of variables (viz.  $n^2 + n + 1$ ), this equilibrium is monovariant, consequently, in the  $P, T$ -diagram we represent it by a curve, which we call  $E$ .

When in this equilibrium  $E$  all phases with constant composition contain together only  $n - 1$  of the  $n$  components, so that in these phases one of the components f.i.  $X$  is missing, then, in the phases with variable composition the quantity of this component  $X$  may approach to Zero.

Then the equilibrium  $E$  passes into an equilibrium, that we call  $E(x=0)$  which consists of  $n - 1$  components in  $n + 1$  phases and that, consequently is invariant; in the  $P, T$ -diagram it is represented therefore, by a point which we shall call  $i(x=0)$ . This point is the invariant terminating — or beginning — point of curve  $E$ .

As we do approach the quantity of the component  $X$  to zero, we put again:

$$Z_1 = Z'_1 + RTx_1 \log x_1 \quad Z_2 = Z'_2 + RTx_2 \log x_2 \quad . \quad (4)$$

etc. In similar way as we have done formerly, now we find:

$$H_i dT - V_i dP + RTx_i + y_i d \left( \frac{\partial Z'}{\partial y} \right)_i + \dots = -dK \quad . \quad (5)$$

$$i = 1, 2, \dots (n + 1)$$

$$x_2 = \mu_2 x_1 \quad x_3 = \mu_3 x_1 \dots x_{n+1} = \mu_{n+1} x_1 \quad . \quad (6)$$

$$d \frac{\partial Z'_1}{\partial y_1} = d \frac{\partial Z'_2}{\partial y_2} = \dots = d \frac{\partial Z'_{n+1}}{\partial y_{n+1}} = dK_y \quad . \quad (7)$$

To these equations (7) must be added the corresponding equations for the variables  $z, z_2, \dots u, u_2$ . The sign  $d$  indicates that there must be differentiated with respect to all variables.

Now we add to one another the  $n+1$  equations (5) after having multiplied the first with  $\lambda_1$ , the second with  $\lambda_2$ , etc. Then we obtain:

$$\left. \begin{aligned} \Sigma (\lambda H) \cdot dT - \Sigma (\lambda V) \cdot dP + RT \Sigma (\lambda x) + \Sigma (\lambda y) dK_y + \\ + \Sigma (\lambda z) \cdot dK_z + \dots = - \Sigma (\lambda) \cdot dK \end{aligned} \right\} \quad (8)$$

Now we put:

$$\left. \begin{aligned} \Sigma (\lambda) = 0 \text{ of } \lambda_1 + \lambda_2 + \dots + \lambda_{n+1} = 0 \\ \Sigma (\lambda x) = 0 \text{ of } \lambda_1 x_1 + \lambda_2 x_2 + \dots + \lambda_{n+1} x_{n+1} = 0 \\ \Sigma (\lambda y) = 0 \text{ of } \lambda_1 y_1 + \lambda_2 y_2 + \dots + \lambda_{n+1} y_{n+1} = 0 \end{aligned} \right\} \quad . \quad (9)$$

etc. but *not*  $\Sigma (\lambda H)$  and  $\Sigma (\lambda V)$ .

Then we have  $n$  equations, so that that the  $n$  ratio's between  $\lambda_1, \lambda_2, \dots, \lambda_{n+1}$  are defined. The reaction:

$$\lambda_1 F_1 + \lambda_2 F_2 + \dots + \lambda_{n+1} F_{n+1} = 0 \quad . \quad . \quad . \quad (10)$$

which may occur in the monovariant equilibrium  $E$ , when the quantity of the component  $X$  is infinitely small, is, therefore, also defined. We shall call this equilibrium, which differs extremely little from  $E(x=0)$  the equilibrium  $E$  ( $Lim x=0$ ) or shortly the equilibrium  $E(x)$ . With the aid of (9) now (8) passes into:

$$\left( \frac{dP}{dT} \right)_x = \frac{\Sigma (\lambda H)}{\Sigma (\lambda V)} \quad . \quad . \quad . \quad . \quad (11)$$

wherein  $\lambda_1, \lambda_2$  are defined by (9).

Consequently the direction of the tangent to curve  $E$  in its invariant point of beginning or terminating  $i(x=0)$  is defined by (11). The relation (7) (XIX) is, therefore, true also when the quantity of one of the components approaches to zero.

Now we put:

$$\left. \begin{aligned} \Sigma(\lambda) = 0 \text{ conseq. } \lambda_1 + \lambda_2 + \dots + \lambda_{n+1} &= 0 \\ \Sigma(\lambda y) = 0 \text{ ,, } \lambda_1 y_1 + \lambda_2 y_2 + \dots + \lambda_{n+1} y_{n+1} &= 0 \\ \Sigma(\lambda z) = 0 \text{ ,, } \lambda_1 z_1 + \lambda_2 z_2 + \dots + \lambda_{n+1} z_{n+1} &= 0 \\ \dots &\dots \\ \Sigma(\lambda V) = 0 \text{ ,, } \lambda_1 V_1 + \lambda_2 V_2 + \dots + \lambda_{n+1} V_{n+1} &= 0 \end{aligned} \right\} \quad (12)$$

but *not*  $\Sigma(\lambda x)$  and  $\Sigma(\lambda H)$ . The  $n$  relations between  $\lambda_1, \lambda_2, \dots, \lambda_{n+1}$  are then defined again. Those relations now define the isovolumetrical reaction in the invariant equilibrium  $E(x=0)$ .

Now it follows from (8)

$$(dT)_x = - \frac{RT \Sigma(\lambda x)_V}{\Sigma(\lambda H)_V} \dots \dots \dots (13)$$

wherein the index  $V$  indicates that  $\lambda_1, \lambda_2, \dots, \lambda_{n+1}$  must be calculated from (12) consequently from the isovolumetrical reaction.

Also we may put:

$$\left. \begin{aligned} \Sigma(\lambda) = 0 \text{ conseq. } \lambda_1 + \lambda_2 + \dots + \lambda_{n+1} &= 0 \\ \Sigma(\lambda y) = 0 \text{ ,, } \lambda_1 y_1 + \lambda_2 y_2 + \dots + \lambda_{n+1} y_{n+1} &= 0 \\ \Sigma(\lambda z) = 0 \text{ ,, } \lambda_1 z_1 + \lambda_2 z_2 + \dots + \lambda_{n+1} z_{n+1} &= 0 \\ \dots &\dots \\ \Sigma(\lambda H) = 0 \text{ ,, } \lambda_1 H_1 + \lambda_2 H_2 + \dots + \lambda_{n+1} H_{n+1} &= 0 \end{aligned} \right\} \quad (14)$$

but *not*  $\Sigma(\lambda x)$  and  $\Sigma(\lambda V)$ . The relations between  $\lambda_1, \lambda_2, \dots, \lambda_{n+1}$  are, therefore, defined and by this also the isentropical reaction, which may occur in the invariant equilibrium  $E(x=0)$ . Now it follows from (8):

$$(dP)_x = \frac{RT \Sigma(\lambda x)_H}{\Sigma(\lambda V)_H} \dots \dots \dots (15)$$

wherein the index  $H$  indicates that  $\lambda_1, \lambda_2, \dots, \lambda_{n+1}$  must be calculated from the isentropical reaction, therefore from (14).

From (11), (13) and (15) follows the relation

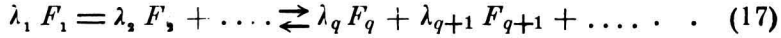
$$\Sigma(\lambda V) \cdot \Sigma(\lambda H)_V \cdot \Sigma(\lambda x)_H + \Sigma(\lambda H) \cdot \Sigma(\lambda V)_H \cdot \Sigma(\lambda x)_V = 0 \quad (16)$$

While the direction of the tangent to curve  $E$  in the point  $i(x=0)$  follows from (11), formula (13) is determining whether this curve is going from this point towards heigher or towards lower temperatures and (15) is determining whether it is going from this point to higher or lower pressures.

We may express all this also in the following way. When we add a new substance to an invariant equilibrium, then it becomes monovariant, the partition of this substance between the different

phases is defined by (6). By (13) is defined whether the temperature is rising or falling; by (15) is defined whether the pressure is increasing or decreasing.

We write the isovolumetrical reaction:



wherein all reaction-coefficients have been taken positive. Now we have:

$$\Sigma(\lambda H)_V = \lambda_q H_q + \lambda_{q+1} H_{q+1} + \dots - \lambda_1 H_1 - \lambda_2 H_2 - \dots$$

$$\Sigma(\lambda x)_V = \lambda_q x_q + \lambda_{q+1} x_{q+1} + \dots - \lambda_1 x_1 - \lambda_2 x_2 - \dots$$

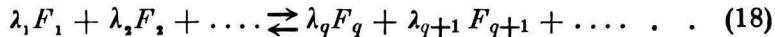
Now we assume that we have written reaction (17) in such a way that it proceeds on addition of heat from the left to the right; consequently  $\Sigma(\lambda H)_V$  is positive. In order to determine the sign of  $\Sigma(\lambda x)_V$  we have to dissolve  $\lambda_1, \lambda_2, \dots$  from (12) and we must know the partition of the new substance between the different phases; this may be found from (6).

In some cases the sign of  $\Sigma(\lambda x)_V$  is known, however, at once without this calculation. When f.i. the new substance occurs only in one or more of the phases, which arise in (17) on addition of heat, consequently in  $F_q, F_{q+1}, \dots$ , then is  $x_1 = 0, x_2 = 0, \dots, x_{q-1} = 0$  and, therefore  $\Sigma(\lambda x)_V$  is positive. It follows then from (13) that  $(dT)_x$  is negative.

When, however, the new substance occurs only in one or more of the phases, which arise in (17) on withdrawing heat, then  $x_q, x_{q+1}, \dots$  are zero, so that  $\Sigma(\lambda x)_V$  is negative. Then it follows from (13) that  $(dT)_x$  is positive.

When, however, the new substance occurs in both groups of phases, then only a calculation more in detail may decide on the sign of  $\Sigma(\lambda x)_V$  and consequently also on the sign of  $(dT)_x$ .

Now we represent the isentropical reaction also by



However, we have to take in mind, that  $\lambda_1, \lambda_2, \dots$  in this case, must not be dissolved from (12) but from (14). Consequently in (18)  $\lambda_1, \lambda_2, \dots$  shall have not only other values than in (17), but one or more of them may have also other signs, so that they must be transferred from the one part to the other. Now we have:

$$\Sigma(\lambda V)_H = \lambda_q V_q + \lambda_{q+1} V_{q+1} + \dots - \lambda_1 V_1 - \lambda_2 V_2 - \dots$$

$$\Sigma(\lambda x)_H = \lambda_q x_q + \lambda_{q+1} x_{q+1} + \dots - \lambda_1 x_1 - \lambda_2 x_2 - \dots$$

Now we assume that reaction (18) is written in such a way that it is proceeding from left to right with increase of volume. Consequently  $\Sigma(\lambda V)_H$  is positive. When the new substance occurs only

in one or more of the phases which arise at increase of volume, then  $\Sigma(\lambda x)_H$  is positive and, in accordance with (15) therefore also  $(dP)_x$ .

When, however, the new substance occurs only in one or more of the phases which arise on decrease of volume, then  $\Sigma(\lambda x)_H$  is negative and therefore, also  $(dP)_x$  is negative.

Hence we may deduce the following rules:

When we add a new substance to an invariant equilibrium  $E(x=0)$  then a monovariant equilibrium  $E$  occurs, which we represent in a  $P, T$ -diagram by a curve  $E$ ; when the new substance occurs only in one or more of the phases, which arise at the isovolumetrical reaction on addition (withdrawal) of heat, then the temperature is lowered (raised); consequently curve  $E$  proceeds starting from its invariant beginning-point towards higher (lower) pressures.

In some cases we may also deduce something on the direction of curve  $E$  in its invariant beginning-point in the following way. We assume that the new substance which is added to the invariant equilibrium:

$$E(x=0) = F_1 + F_2 + \dots + F_q + F_{q+1} + \dots + F_{n+1}$$

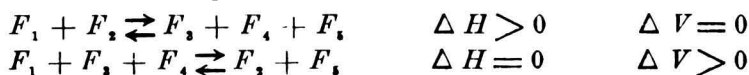
occurs only in the phases  $F_{q+1} \dots F_{n+1}$  and, therefore, not in  $F_1, F_2, \dots, F_q$ . This is surely the case when  $F_1 \dots F_q$  are phases of constant composition. When we take away from the equilibrium  $E$  the phases  $F_{q+1} \dots F_{n+1}$ , then we keep an plurivariant equilibrium  $F_1 \dots F_q$ ; this is represented in the  $P, T$ -diagram by a plurivariant region. As curve  $E$  must be situated in this region, hence follows the said-above. In the special case that the new substance occurs in one of the phases only, curve  $E$  coincides, therefore, with one of the monovariant equilibria of the equilibrium  $E(x=0)$ .

Before applying those considerations to some cases, firstly I will draw the attention to some points, which have been already discussed before. When we know of the isovolumetrical and isentropical reaction the ratio of the coefficients  $\lambda_1, \lambda_2, \dots$  and also in which direction those reactions proceed on addition of heat or on increase of volume, then we shall say that those reactions are known quantitatively. When we know, however, only the signs of  $\lambda_1, \lambda_2, \dots$  and also in which direction the reactions are proceeding on addition of heat or on increase of volume, then we shall say that the reactions are known qualitatively. Then we only know which phases are at the one side and which at the other side of the reaction-sign.

When we know of each phase of the invariant equilibrium  $E(x=0)$  the entropy, the volume and the composition, then with the aid of (12) and (14) we may define the isovolumetrical and isentropical reaction quantitatively. Consequently we are able to draw exactly the direction of the different monovariant curves in the  $P, T$ -diagram, we call it a quantitative  $P, T$ -diagram.

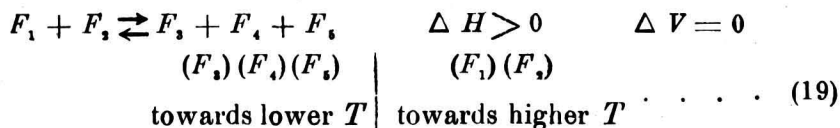
When we only know both reactions qualitatively, then we can define only whether the monovariant curves proceed, starting from the invariant point towards higher or lower temperatures and towards higher or lower pressures; but then their situation with respect to one another is still undefined; this we call a qualitative  $P, T$ -diagram.

We take for example the reactions:

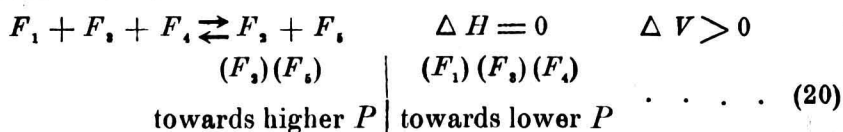


of a ternary invariant equilibrium. The first is, according to the supposition  $\Delta V = 0$ , the isovolumetrical reaction and it takes place, according to the supposition  $\Delta H > 0$  from left to right on addition of heat. It appears from  $\Delta H = 0$  and  $\Delta V > 0$  that the second one is the isentropical reaction and that the volume increases from left to right.

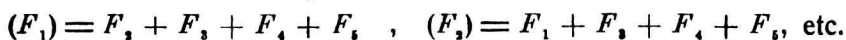
In accordance to our former considerations, now we have:



Further we have:



In accordance to our previous notation, herein is:



Now we know qualitatively the  $P, T$ -diagram; we know viz. that from the invariant point curve  $(F_1)$  is going towards higher  $T$  and lower  $P$ ; curve  $(F_2)$  goes towards higher  $T$  and at the same time towards higher  $P$ , etc.

Inversely we can also find from a qualitative  $P, T$ -diagram the qualitative isovolumetrical and isentropical reaction. When we know f.i. that the curves  $(F_1)$  and  $(F_2)$  go towards higher temperatures and  $(F_3)$   $(F_4)$  and  $(F_5)$  towards lower temperatures, then we have to construe (19) in the inverse direction viz. from the bottom to the top, in order to find the isovolumetrical reaction.

When we know that  $(F_2)$  and  $(F_3)$  go towards higher temperatures, and  $(F_1)$ ,  $(F_3)$  and  $(F_4)$  towards lower pressures, then we find at once, by construing (20) in the inverse direction the isentropical reaction.

Firstly we shall apply those considerations to a simple case viz. to the addition of a new substance to the invariant unary equilibrium  $E(x=0) = F + L + G$ . The  $P, T$ -diagram may belong to two types, viz. when the volume decreases, on melting of the solid substance, then fig 1 is true; when the volume increases, then fig 2 is valid. The regions in which occur the phases  $F$ ,  $L$  and  $G$  are indicated by the same letters, but in a circle; the curves are represented by  $(F)$ ,  $(L)$  and  $(G)$ ; in accordance with our notation is  $(F) = L + G$ , etc.

When we add to  $E(x=0)$  a new substance, which occurs only in the liquid, then the monovariant equilibrium  $E = F + L + G$  arises; when we take away from it  $L$ , then we keep the equilibrium  $F + G = (L)$ .

Curve  $E$  coincides therefore in figs 1 and 2 with curve  $(L)$  of the invariant unary equilibrium  $E(x=0)$ .

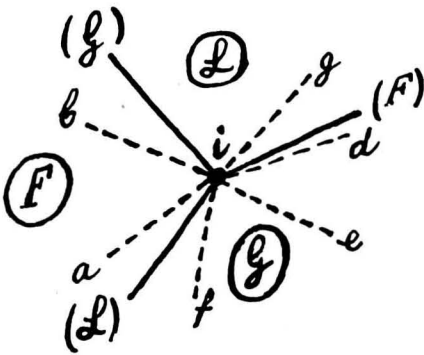


Fig. 1.

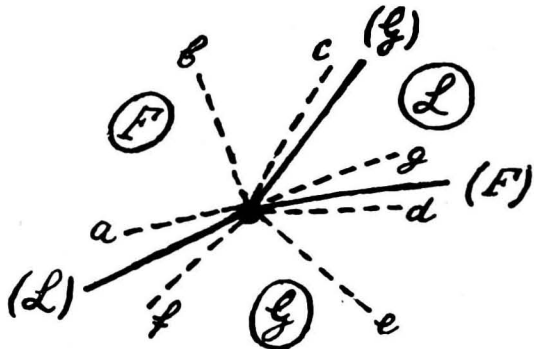


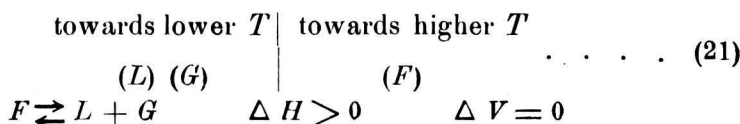
Fig. 2.

When we add a volatile substance, then we must take away from the monovariant equilibrium the phases  $L$  and  $G$ , so that we keep  $F$  only. Therefore, curve  $E$  must be situated in the region  $F$ , as f. i.  $ia$ ,  $ib$  and  $ic$  in the figs 1 and 2.

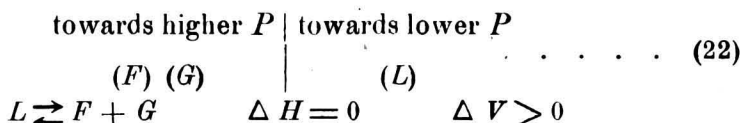
When we add a substance, which is not volatile, which gives, however, mixed-crystals with  $F$ , then we must take away from the equilibrium  $E$  the phases  $F$  and  $L$ , so that the vapour  $G$  only remains. Therefore, curve  $E$  must be situated in the region  $G$ .

We may obtain also these results by using the qualitative isovolumetrical and isentropical reaction, which we can deduce easily

from the figs 1 and 2. It follows from the position of the curves in fig 1.



and



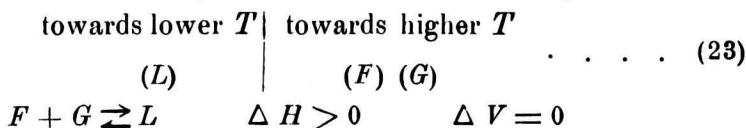
so that both reactions are known qualitatively.

Now we add to this equilibrium  $E(x=0) = F + L + G$  a substance, which occurs in the liquid only. As in the isovolumetrical reaction (21)  $L$  is placed at the right side of the reaction-sign, consequently, in accordance with our rules,  $T$  is lowered; as in the isentropical reaction (22)  $L$  is placed at the left side of the reaction-sign, the pressure is also lowered, therefore.

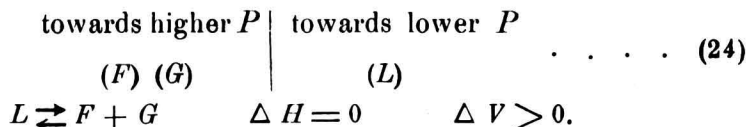
Consequently in fig. 1 curve  $E$  proceeds starting from point  $i$  towards lower  $T$  and  $P$ ; this is in accordance with the deduced above, that curve  $E$  coincides with curve  $(L)$  in this case.

When we add a volatile substance, than it occurs in  $L$  and  $G$ . As both those phases are placed in (21) at the right side of the reaction-sign, consequently  $T$  is lowered. As  $L$  and  $G$  are placed in (22) at different sides of the reaction-sign, the pressure may be as well increased as decreased. Therefore, curve  $E$  may be represented by  $ia$  or  $ib$  in fig. 1. Which of these curves may occur in a definite case, cannot be deduced in this manner; we are able to do this, as we shall see further, with the aid of the quantitative reactions.

In order to deduce the qualitative reactions from fig. 2, we write:



and



When we add a new substance, which occurs in  $L$  and  $G$ , then we find that curve  $E$  may be represented in fig. 2 by  $ia$ ,  $ib$  or  $ic$ .

It is apparent from the previous that by simple considerations we may deduce already something about the direction of curve  $E$  from the qualitative  $P, T$ -diagram of an invariant equilibrium  $E(x=0)$ .



When, however, we know the quantitative reactions, then we are able to deduce not only the quantitative  $P, T$ -diagram for the equilibrium  $E(x=0)$  but also  $(dT)_x$  and  $(dP)_x$  for the equilibrium  $E$  and consequently we can define exactly the direction of curve  $E$ .

When we represent entropy and volume of  $F$  by  $H$  and  $V$ , of  $L$  by  $H_1$  and  $V_1$  and of  $G$  by  $H_2$  and  $V_2$ , and when we assume that the substance melts on decrease of volume, then we have:

$$H_2 > H_1 > H \text{ and } V_2 > V > V_1 \dots (25)$$

We write the isovolumetrical reaction:

$$F + \lambda_1 L + \lambda_2 G = 0 \dots (26)$$

As, in accordance with (12):

$$1 + \lambda_1 + \lambda_2 = 0 \text{ and } V + \lambda_1 V_1 + \lambda_2 V_2 = 0 \dots (27)$$

it follows:

$$\lambda_1 = -\frac{V_2 - V}{V_2 - V_1} \text{ and } \lambda_2 = -\frac{V - V_1}{V_2 - V_1} \dots (28)$$

so that  $\lambda_1$  and  $\lambda_2$  are both negative. Instead of (26) we now write:

$$F \rightleftharpoons \lambda_1 L + \lambda_2 G \dots (29)$$

wherein

$$\lambda_1 = \frac{V_2 - V}{V_2 - V_1} \text{ and } \lambda_2 = \frac{V - V_1}{V_2 - V_1} \dots (30)$$

and

$$\Sigma(\lambda H)_V = \lambda_1 H_1 + \lambda_2 H_2 - H \dots (31)$$

Now we may prove that  $\Sigma(\lambda H)_V$  is generally positive, so that, on addition of heat the isovolumetrical reaction (29) proceeds from left to right.

In a similar way we find for the isentropical reaction:

$$\mu_1 L \rightleftharpoons F + \mu_2 G \dots (32)$$

and

$$\Sigma(\lambda V)_H = V + \mu_2 V_2 - \mu_1 V_1$$

wherein

$$\mu_1 = \frac{H_1 - H}{H_2 - H_1} \text{ en } \mu_2 = \frac{H_1 - H}{H_2 - H_1} \dots (33)$$

so that  $\mu_1$  and  $\mu_2$  are both positive.

As  $\Sigma(\lambda V)_H$  is positive, reaction (32) proceeds from left to right with increase of volume.

With the aid of reactions (29) and (32), as is discussed in previous communications we now can deduce the  $P, T$ -diagram quantitatively; then we find fig. 1.

Now we add a new substance which occurs in the liquid only.

When we call its concentration  $x_1$ , then we have:

$$\Sigma (\lambda x)_V = \lambda_1 x_1 \text{ and } \Sigma (\lambda x)_H = -\mu_1 x_1$$

so that, in accordance with (13) and (15):

$$(dT)_x = \frac{-RT \lambda_1 x_1}{\Sigma (\lambda H)_V} \text{ and } (dP)_x = \frac{-RT \mu_1 x_1}{\Sigma (\lambda V)_H} \dots (34)$$

Consequently in fig. 1 curve  $E$  proceeds, starting from point  $i$  towards lower  $P$  and  $T$ .

It follows from (33):

$$\left(\frac{dP}{dT}\right)_x = \frac{\mu_1}{\lambda_1} \cdot \frac{-H + \lambda_2 H_2 + \lambda_1 H_1}{V + \mu_2 V_2 - \mu_1 V_1} = \frac{H_2 - H}{V_2 - V} \dots (35)$$

Hence it appears that in fig. 1 curve  $E$  coincides with curve  $(L)$ . Also we may find (34) at once with the aid of (9) and (11). We put viz.:

$$\Sigma (\lambda) = 1 + \lambda_1 + \lambda_2 = 0 \text{ and } \Sigma (\lambda x) = \lambda_1 x_1 = 0$$

so that  $\lambda_1 = 0$  and  $\lambda_2 = -1$ . Hence it follows:

$$\Sigma (\lambda H) = H - H_2 \text{ and } \Sigma (\lambda V) = V - V_2,$$

consequently for (11) the same value as in (34).

When the new substance occurs in liquid and vapour with the concentrations  $x_1$  and  $x_2$ , then we have:

in accordance with (29):  $\Sigma (\lambda x)_V = \lambda_1 x_1 + \lambda_2 x_2$

and in accordance with (32):  $\Sigma (\lambda x)_H = -\mu_1 x_1 + \mu_2 x_2$

so that  $(dT)_x$  and  $(dP)_x$  are known again. We see that  $(dT)_x$  is negative, but that  $(dP)_x$  may be as well positive as negative. Curve  $E$ , therefore, may be situated in fig. 1 as  $ia$  or  $ib$ .

When we put:

$$\frac{\mu_1}{\mu_2} = \frac{H_2 - H}{H_1 - H} = K \dots (36)$$

then is

$$\Sigma (\lambda x)_H = \mu_2 (x_2 - Kx_1) \dots (37)$$

wherein, in accordance to (35),  $K > 1$ .

Now we find:

for  $\frac{x_2}{x_1} > K$  is  $(dP)_x > 0$ ; consequently curve  $E$  goes, starting from point  $i$  towards higher pressures;

for  $\frac{x_2}{x_1} < K$  is  $(dP)_x < 0$ ; consequently curve  $E$  goes, starting from point  $i$  towards lower pressures.

When f.i. is  $K = 5$ , then the concentration of the new substance in the vapour must be at least five times as large as in the liquid, that curve  $E$  is proceeding towards higher pressures, starting from  $i$ .

In order to define the direction of curve  $E$  we define the values of  $\lambda_1$  and  $\lambda_2$  according (9) from:

$$1 + \lambda_1 + \lambda_2 = 0 \quad \text{and} \quad \lambda_1 x_1 + \lambda_2 x_2 = 0$$

(11) then passes into:

$$\left(\frac{dP}{dT}\right)_x = \frac{x_2 (H_1 - H) - x_1 (H_2 - H)}{x_2 (V_1 - V) - x_1 (V_2 - V)} \dots \dots \dots (38)$$

by which the direction of curve  $E$  is defined. This direction, as follows from (37), is dependent on the partition ( $x_2 : x_1$ ) of the new substance between gas and liquid. Also it follows from (37) that curve  $E$  must be situated between the curves ( $L$ ) and ( $G$ ).

We now add a new substance which forms mixed-crystals with  $F$ , but which does not occur in the vapour. When we represent its concentration in  $F$  and  $L$  by  $x$  and  $x_1$  then it follows from (29) and (32):

$$\Sigma (\lambda x)_V = \lambda_1 x_1 - x \quad \text{and} \quad \Sigma (\lambda x)_H = x - \mu_1 x_1$$

consequently:

$$(dT)_x = \frac{RT(x - \lambda_1 x_1)}{\Sigma (\lambda H)_V} \quad \text{and} \quad (dP)_x = \frac{RT(x - \mu_1 x_1)}{\Sigma (\lambda V)_H} \dots \dots (39)$$

It is apparent from (30) and (33) that  $\lambda_1 < 1$  and  $\mu_1 > 1$ , but also that  $\lambda_1$  differs very little only from 1. It follows from (39):

$$\text{for } \frac{x}{x_1} > \mu_1 \quad \text{is} \quad (dT)_x > 0 \quad \text{and} \quad (dP)_x > 0;$$

Curve  $E$  is situated then, f.i. like curve  $id$  in fig. 1

$$\text{for } \mu_1 > \frac{x}{x_1} > \lambda_1 \quad \text{is} \quad (dT)_x > 0 \quad \text{and} \quad (dP)_x < 0;$$

Curve  $E$  is then situated, f.i. like curve  $ie$  in fig. 1

$$\text{for } \frac{x}{x_1} < \lambda_1 \quad \text{is} \quad (dT)_x < 0 \quad \text{and} \quad (dP)_x < 0;$$

Curve  $E$  then is situated f.i. as curve  $if$  in fig. 1.

In order to define the direction of curve  $E$  we take in accordance with (9):

$$\Sigma (\lambda) = 1 + \lambda_1 + \lambda_2 = 0 \quad \text{and} \quad \Sigma (\lambda x) = x + \lambda_1 x_1 = 0.$$

With the values of  $\lambda_1$  and  $\lambda_2$  which follow from this we find for (11):

$$\left(\frac{dP}{dT}\right)_x = \frac{x_1 (H_2 - H) - x (H_2 - H_1)}{x_1 (V_2 - V) - x (V_2 - V_1)} \dots \dots \dots (40)$$

so that the direction of curve  $E$  is defined.

Also it is apparent from (39) that  $E$  must be situated between the curves ( $F$ ) and ( $L$ ).

Finally we shall assume that the new substance divides itself over the three phases, we call its concentration in  $F$   $L$  and  $G$   $x_1$  and  $x_2$ . We now have according to (29) and (32):

$$\Sigma (\lambda x)_V = -x + \lambda_1 x_1 + \lambda_2 x_2 \text{ and } \Sigma (\lambda x)_H = x - \mu_1 x_1 + \mu_2 x_2,$$

wherein  $\lambda_1 + \lambda_2 = 1$  and  $\mu_1 = 1 + \mu_2$ , so that  $(dT)_x$  and  $(dP)_x$  are known.

We now put:

$$\Sigma (\lambda x)_V = r \text{ and } \Sigma (\lambda x)_H = s \dots \dots \dots (41)$$

As we are able to satisfy (40), independent on the values of  $r$  and  $s$ , by positive values of  $x_1$  and  $x_2$ , it follows that curve  $E$  may go in every direction starting from point  $i$ . It may be situated, therefore, not only in one of the regions  $F$  and  $G$ , but also, like f. i. curve  $ig$ , in the region  $L$ . Of course its situation is dependent on the partition of the new substance between the three phases.

The same considerations as for fig 1 are also valid for fig 2, for this we have to examine however more in detail the occurrence of curve  $ic$ .

Instead of (25) we have for fig 2:

$$H_2 > H_1 > H \text{ and } V_2 > V_1 > V \dots \dots \dots (42)$$

As  $\lambda_2$  is negative now, in accordance with (30) the isovolumetrical reaction passes into:



wherein:

$$\lambda_1 = \frac{V_2 - V}{V_2 - V_1} \text{ and } \lambda_2 = \frac{V_1 - V}{V_2 - V_1}$$

so that

$$\Sigma (\lambda H) = \lambda_1 H_1 - H - \lambda_2 G$$

is generally positive; reaction (43) is proceeding therefore, on addition of heat from left to right.

When we now add a new substance, which occurs in liquid and vapour, then we have:  $\Sigma (\lambda x)_V = \lambda_1 x_1 - \lambda_2 x_2$ . In order that  $(dT)_x$  is positive,  $\Sigma (\lambda x)_V$  must be negative, consequently:

$$\frac{x_2}{x_1} > \frac{\lambda_1}{\lambda_2} \text{ or } \frac{x_2}{x_1} > \frac{V_2 - V}{V_1 - V} \dots \dots \dots (44)$$

As in general  $V_2 - V$  is some thousand times larger than  $V_1 - V$  curve  $ic$  therefore can, occur only in the very special case that the concentration of the new substance is some thousand times larger in the vapour than in the liquid.

We may summarize some of the previous deductions in the following way.

When we add a new substance to an invariant unary equilibrium  $E(x=0) = F + L + G$ , then an equilibrium  $E = F + L + G$  arises that is represented in the  $P, T$ -diagram by a curve  $E$ ; this curve begins in the invariant point  $i$  of the equilibrium  $E(x=0)$ .

When the new substance occurs in the liquid only, then curve  $E$  coincides with curve  $(L) = F + G$  of the system  $E(x=0)$ .

When the new substance is occurring in liquid and vapour then curve  $E$  is situated in the region  $F$ ; its direction is defined by the partition of the new substance between vapour and liquid. A curve, like  $ic$  in fig. 2 may, however, occur only in very special circumstances.

When the new substance is occurring in liquid and solid phase (consequently with formation of mixed crystals) then curve  $E$  is situated in the region  $G$ ; its direction is defined by the partition of the new substance between mixed crystals and liquid.

When the new substance occurs in the three phases, then curve  $E$  may be situated in each of the three regions; its direction is defined by the partition of the new substance between the three phases.

*(To be continued).*

*Leiden, Lab. of Inorganic Chemistry.*

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