Chemistry. — *"In-, mono- and divariant equilibria."* XXIII. By Prof. F. A. H. Schreinemakers.

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. (Continuation).

We write the isovolumetrical reaction of an equilibrium $E(x=0)$:

$$\lambda_1 F_1 + \lambda_2 F_2 + \ldots = 0 \quad \Sigma (\lambda H)_V > 0 \quad \Sigma (\lambda V) = 0. \quad (1)$$

and the isentropical reaction:

$$\mu_1 F_1 + \mu_2 F_2 + \ldots = 0 \quad \Sigma (\mu H) = 0 \quad \Sigma (\mu V)_H > 0. \quad (2)$$

Consequently in reaction (1) are formed on addition of heat and in reaction (2) on increase of volume those phases, which have a negative reaction-coefficient. We have, therefore:

$$\Sigma (\lambda x)_V = -\lambda_1 x_1 - \lambda_2 x_2 - \text{ en } \Sigma (\mu x)_H = -\mu_1 x_1 - \mu_2 x_2 - \ldots$$

When we subtract both reaction-equations (1) and (2) from one another, after having multiplied the first one with μ_1 and the second one with λ_1, then we find the reaction:

$$(\mu_1 \lambda_2 - \lambda_1 \mu_2) F_2 + (\mu_1 \lambda_3 - \lambda_1 \mu_3) F_3 + \ldots = 0 \quad (3)$$

wherein the change of entropy is $\mu_1 \Sigma (\lambda H)_V$
and the change of volume is $-\lambda_1 \Sigma (\mu V_H)$.

As (3) represents the reaction, which may occur in the equilibrium $(F_1) = F_2 + F_3 + \ldots$, we have

$$\left(\frac{dP}{dT} \right)_1 = -\frac{\mu_1}{\lambda_1} \cdot \frac{\Sigma (\lambda H)_V}{\Sigma (\mu V)_H}. \quad \ldots \ldots (4)$$

Herein $\left(\dfrac{dP}{dT} \right)_1$ indicates the direction of curve (F_1) in the invariant point. In the same way we find:

$$\left(\frac{dP}{dT} \right)_2 = -\frac{\mu_2}{\lambda_2} \cdot \frac{\Sigma (\lambda H)_V}{\Sigma (\mu V)_H}; \left(\frac{dP}{dT} \right)_3 = -\frac{\mu_3}{\lambda_3} \frac{\Sigma (\lambda H)_V}{\Sigma (\mu V)_H} \text{ etc.} \quad (5, 6)$$

As we are able to deduce from (1) and (2) also the direction of temperature and pressure of the different monovariant curves, the P, T-diagram is, therefore, quantitatively defined.

Now we add to the equilibrium a new substance X, which occurs

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in the phases $F_1 F_2 \ldots$ with the concentrations $x_1 x_2 \ldots$ In accordance with (13) and (15) (**XXII**) we now have:

$$\frac{\Sigma (\lambda H)_V}{RT} \cdot (dT)_x = \lambda_1 x_1 + \lambda_2 x_2 + \ldots = - \Sigma (\lambda x)_V. \quad (7)$$

$$\frac{\Sigma (\mu V)_H}{RT} \cdot (dP)_x = - \mu_1 x_1 - \mu_2 x_2 \ldots = \Sigma (\mu x)_H \quad (8)$$

With the aid of (4) etc. we may also write for this:

$$\frac{\Sigma (\mu V)_H}{RT} \cdot (dT)_x = - x_1 \mu_1 \left(\frac{dT}{dP}\right)_1 - x_2 \mu_2 \left(\frac{dT}{dP}\right)_2 - \ldots \quad (9)$$

$$\frac{\Sigma (\lambda H)_V}{RT} \cdot (dP)_x = x_1 \lambda_1 \left(\frac{dP}{dT}\right)_1 + x_2 \lambda_2 \left(\frac{dT}{dP}\right)_2 + \ldots \quad (10)$$

It follows from (8) and (9):

$$\left(\frac{dT}{dP}\right)_x = - \frac{x_1 \mu_1}{\Sigma (\mu x)_H} \cdot \left(\frac{dT}{dP}\right)_1 - \frac{x_2 \mu_2}{\Sigma (\mu x)_H} \cdot \left(\frac{dT}{dP}\right)_2 - \ldots \quad (11)$$

from (7) and (10) it follows:

$$\left(\frac{dP}{dT}\right)_x = - \frac{x_1 \lambda_1}{\Sigma (\lambda x)_V} \cdot \left(\frac{dP}{dT}\right)_1 - \frac{x_2 \lambda_2}{\Sigma (\lambda x)_V} \cdot \left(\frac{dP}{dT}\right)_2 - \ldots \quad (12)$$

and from (7) and (8):

$$\frac{\Sigma (\mu V)_H}{\Sigma (\lambda H)_V} \cdot \left(\frac{dP}{dT}\right)_x = - \frac{\mu_1 x_1 + \mu_2 x_2 + \ldots}{\lambda_1 x_1 + \lambda_2 x_2 + \ldots} \quad (13)$$

From (7) we see that we are able to express $(dT)_x$ with the aid of the isovolumetrical reaction (1); it is apparent from (9), that, however, we cannot express $(dT)_x$ with the aid of the isentropical reaction (2) only, but that we must know also the directions of the monovariant curves $(F_1) (F_2) \ldots$ of the equilibrium $E (x = 0)$.

It appears from (8) that we are able to express $(dP)_x$ with the aid of the isentropical reaction (2); we see, however, from (10) that we cannot define $(dP)_x$ with the aid of the isovolumetrical reaction only but that we must know for this also again the directions of the curves $(F_1) (F_2) \ldots$

The direction of the monovariant curve E can be defined, as is apparent from (13), with the aid of the isovolumetrical and isentropical reaction; it follows from (11) and (12) that it can also be defined with the aid of the directions of the curves $(F_1) (F_2) \ldots$ and one of both reactions.

When we add a new substance X which occurs in one of the phases only, f.i. in F_1 than we must put in (7)—(13) $x_2 = 0$ $x_3 = 0 \ldots$ As now $\Sigma (\lambda x)_V = - \lambda_1 x_1$, it follows from (12):

$$\left(\frac{dP}{dT}\right)_x = \left(\frac{dP}{dT}\right)_1 \quad (14)$$

which follows of course immediately from (11). Consequently curve E and (F_1) have the same tangent in the invariant point. It follows from (7) and (8) that they go also in the same direction of temperature and pressure, starting from this point. When viz. λ_1 is positive, then it follows from reaction (1) that curve (F_1) goes towards higher temperatures, starting from the invariant point. As it follows, however, from (7) that $(dT)_x$ is then positive also, consequently curve E goes also towards higher T. When λ_1 is negative, then the curves (F_1) and E go both towards lower T. It follows from (2) and (8) that both curves have also the same direction of pressure.

In accordance with previous papers (Communication XXII) we, therefore, find: when the new substance occurs in the phase F_1 only, then curve E coincides with curve (F_1).

When the new substance occurs in the phases F_1 and F_2 only, then (12) passes into:

$$\left(\frac{dP}{dT}\right)_x = \frac{\lambda_1}{\lambda_1 + K\lambda_2}\left(\frac{dP}{dT}\right)_1 + \frac{K\lambda_2}{\lambda_1 + K\lambda_2}\left(\frac{dP}{dT}\right)_2 . \quad . \quad . \quad (15)$$

wherein $K = \dfrac{x_2}{x_1}$. Hence it follows:

$$d\left(\frac{dP}{dT}\right)_x = \frac{\lambda_1 \lambda_2}{(\lambda_1 + K\lambda_2)^2}\left[\left(\frac{dP}{dT}\right)_2 - \left(\frac{dP}{dT}\right)_1\right]dK. \quad . \quad . \quad (16)$$

For fixing the ideas we assume that $\left(\dfrac{dP}{dT}\right)_2$ is greater than $\left(\dfrac{dP}{dT}\right)_1$. Now we distinguish two cases.

1. λ_1 and λ_2 have the same sign. The following is apparent from (15) and (16). When K changes from 0 tot ∞ then $\left(\dfrac{dP}{dT}\right)_x$ increases from $\left(\dfrac{dP}{dT}\right)_1$ to $\left(\dfrac{dP}{dT}\right)_2$ without becoming maximum, minimum or discontinuous.

2. λ_1 and λ_2 have opposite sign. When K changes from 0 to ∞, then $\left(\dfrac{dP}{dT}\right)_x$ decreases without becoming maximum or minimum from $\left(\dfrac{dP}{dT}\right)_1$ till $-\infty$, then it proceeds discontinuously towards $+\infty$ and afterwards it decreases to $\left(\dfrac{dP}{dT}\right)_2$.

When λ_1 and λ_2 are both positive, then, in accordance with reaction (1) both curves (F_1) and (F_2) go towards higher tempera-

tures starting from the invariant point; when λ_1 and λ_2 are both negative, then both curves go towards lower T; when λ_1 and λ_2 have opposite sign, then both curves go, starting from the invariant point in opposite direction of temperature.

It follows from all this that the tangent to curve E is situated within the angle, which is formed by the curves (F_1) and (F_2). [Of course we mean that angle wich is smaller than 180°]. As in the case of $K = 0$ (consequently $x_2 = 0$) curve E coincides with (F_1) and in the case of $K = \infty$ (consequently $x_1 = 0$) curve E coincides with (F_2) consequently the property follows, which we have deduced already in the previous communication also, viz:

Curve E is situated between the curves (F_1) and (F_2) or in other words: in the region $(F_1 F_2)$.

Yet also we find, however:

Curve E is situated nearer curve (F_1) in proportion as the concentration of the new substance in the phase F_1 is larger with respect to that in F_2; curve E is situated nearer to curve (F_2) in proportion as the concentration of the new substance in the phase F_2 is greater with respect to that in F_1.

When the new substance occurs only in the phases $F_1 F_2$ and F_3, then we find, in accordance with previous papers that curve E is situated in the region $(F_1 F_2 F_3)$.

When one of the curves, f.i. (F_3) is between the other two (F_1) and (F_2) then curve E is situated also between (F_1) and (F_2). When, however, none of the three curves is situated between the other two, then curve E may go, starting from the invariant point in every arbitrary direction.

Now we consider the binary equilibrium

$$E (x = 0) = F + L_1 + L_2 + G$$
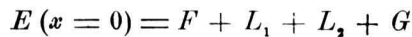
we represent the composition, the entropy and the volume of

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\begin{array}{llllll}
F & \text{by } y & 1—y & H & \text{and} & V \\
L_1 & ,, & y_1 & 1—y_1 & H_1 & \text{and} & V_1 \\
L_2 & ,, & y_2 & 1—y_2 & H_2 & \text{and} & V_2 \\
G & ,, & y_3 & 1—y_3 & H_3 & \text{and} & V_3
\end{array}
$$

When we add a new substance X, then we call its concentration in those phases $x\ x_1\ x_2$ and x_3.

In order to deduce the isovolumetrical and isentropical reaction we take two arbitrary reactions; for this we choose:

$$F + a L_2 \rightleftharpoons (1 + a) L_1 \qquad \Delta H \; \Delta V \quad . \quad . \quad . \quad (17)$$

$$(1 + b) L_2 \rightleftharpoons F + b G \qquad \Delta H' \; \Delta V' \quad . \quad . \quad . \quad (18)$$

Herein is:

$$\Delta H = (1 + a) H_1 - H - a H_2, \qquad \Delta \cdot H' = H + b H_3 - (1 + b) H_2$$

$$\Delta V = (1 + a) V_1 - V - a V_2 \qquad \Delta V' = V + b V_3 - (1 + b) V_2$$

In (17) and (18) a and b may be as well positive as negative. It follows from (17) and (18) for the isovolumetrical reaction:

$$(\Delta V + \Delta V') F - (1 + a) \Delta V' L_1 + [a \Delta V' - (1 + b) \Delta V] L_2 + b \Delta V . G = 0$$
$$\Delta H \; \Delta V' - \Delta H' . \Delta V \qquad 0 \quad . \quad . \quad . \quad . \quad (19)$$

and for the isentropical reaction:

$$-(\Delta H + \Delta H') F + (1 + a) \Delta H' . L_1 - [a \Delta H' - (1 + b) \Delta H] L_2 - b \Delta H . G = 0$$
$$0 \qquad \Delta H \; \Delta V' - \Delta H' \Delta V \quad . \quad . \quad . \quad . \quad (20)$$

We now add to this equilibrium $E(x = 0)$ a new substance X, which occurs in the two liquids L_1 and L_2 only. With the aid of (19) and (20) it then follows from (7) and (8):

$$M . (dT)_x = -(1 + a) \Delta V' . x_1 + [a \Delta V' - (1 + b) \Delta V] x_2 . \quad (21)$$

$$M . (dP)_x = -(1 + a) \Delta H' . x_1 + [a \Delta H' - (1 + b) \Delta H] x_2 . \quad (22)$$

wherein:

$$M = (\Delta H . \Delta V' - \Delta H' . \Delta V) : R T$$

It follows from (21) and (22): when we add to the equilibrium $E(x = 0)$ a new substance which occurs only in the two liquids, then the temperature as well as the pressure may be increased or decreased.

We now shall assume that the four phases are situated with respect to one another, as on the line YZ in fig. 1. Then we have:

$$y > y_1 > y_2 > y_3.$$

It follows from (17) and (18) for the determination of a and b:

$$y + a y_2 = (1 + a) y_1 \qquad (1 + b) y_2 = y + b y_3$$

$$a = \frac{y - y_1}{y_1 - y_2} \qquad b = \frac{y - y_2}{y_2 - y_3} \quad . \quad . \quad . \quad . \quad (23)$$

so that a and b are positive. Further we assume that F and L_1 and also that L_1 and L_2 are not situated very close to one another, so that a is neither very small nor very large. When F and L_2 and also L_2 and G are not situated very close to one another, then also b is not very small and not very large.

As now $\Delta V'$ is positive and very large with respect to ΔV, M is positive.

Further we may distinguish the following cases.

a)
$$\Delta H > 0 \qquad \Delta V \gtreqless 0 \qquad \Delta H' > 0 \qquad \Delta V' > 0$$
$$a\,\Delta H' - (1+b)\,\Delta H > 0 \qquad a\,\Delta V' - (1+b)\,\Delta V > 0 \qquad (24)$$

b)
$$\Delta H > 0 \qquad \Delta V \gtreqless 0 \qquad \Delta H' > 0 \qquad \Delta V' > 0$$
$$a\,\Delta H' - (1+b)\,\Delta H < 0 \qquad a\,\Delta V' - (1+b)\,\Delta V > 0 \qquad (25)$$

c)
$$\Delta H > 0 \qquad \Delta V \gtreqless 0 \qquad \Delta H' < 0 \qquad \Delta V' > 0$$
$$a\,\Delta H' - (1+b)\,\Delta H < 0 \qquad a\,\Delta V' - (1+b)\,\Delta V > 0 \qquad (26)$$

In each of the three cases, mentioned above, is in (21) the coefficient of x_1 negative and of x_2 positive; consequently we have:

$$(dT)_x \gtreqless 0 \quad \text{when} \quad \frac{x_2}{x_1} \gtrless \frac{(1+a)\,\Delta V'}{a\,\Delta V' - (1+b)\,\Delta V} \quad \cdot \quad \cdot \quad (27)$$

As $\Delta V'$ is very large with respect to ΔV it follows from this approximately with the aid of (23):

$$(dT)_x \gtreqless 0 \quad \text{when} \quad \frac{x_2}{x_1} \gtrless \frac{y - y_2}{y - y_1} \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (28)$$

In the case, mentioned sub b in (22) the coefficients of x_1 and x_2 are negative, so that $(dP)_x$ is also negative; consequently the pressure is lowered.

In order to examine more in detail the sign of $(dP)_x$ we write for (22)

$$M\,(dP)_x = \left[x_2 - \frac{\Delta H'}{\Delta H' - \dfrac{1+b}{a}\,\Delta H} \cdot \frac{1+a}{a}\,x_1 \right] N \quad \cdot \quad \cdot \quad (29)$$

wherein:

$$N = a\,\Delta H' - (1+b)\,\Delta H$$

When we put herein the value of a from (23) then we may write for (29):

$$M \cdot (dP)_x = \left[\frac{x_2}{x_1} - \frac{\Delta H'}{\Delta H' - \dfrac{1+b}{a}\,\Delta H} \cdot \frac{y - y_2}{y - y_1} \right] N x_1 \quad \cdot \quad \cdot \quad (30)$$

When we consider the three cases a, b and c mentioned above, then we may write for (30):

a)
$$(dP)_x = \left[\frac{x_2}{x_1} - (1+K)\frac{y - y_2}{y - y_1} \right] L \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (31)$$

b)
$$(dP)_x = -\left[\frac{x_2}{x_1} + K\frac{y - y_2}{y - y_1} \right] L \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (32)$$

c)
$$(dP)_x = \left[-\frac{x_2}{x_1} + (1-K)\frac{y - y_2}{y - y_1} \right] L \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (33)$$

wherein L, K, $1 + K$ and $1 - K$ are positive. In each of the three formula's L and K have different values.

In order to apply the above we take the figs. 1 and 2, wherein XY is a side of the components-triangle XYZ. The points $FL_1 L_2$ and G represent the four phases of the invariant binary equilibrium $E(x = 0) = F + L_1 + L_2 + G$. When we add a new substance X then the ternary equilibrium $E = F + L_1 + L_2 + G$ arises. The liquids L_1 and L_2 then proceed along the curves $L_1 q_1 r_1$ and $L_2 q_2 r_2$; as the new substance is not volatile, G follows a part of the line XZ. When we add only a little of the new substance, then the liquids are represented by the points q_1 and q_2 in the immediate
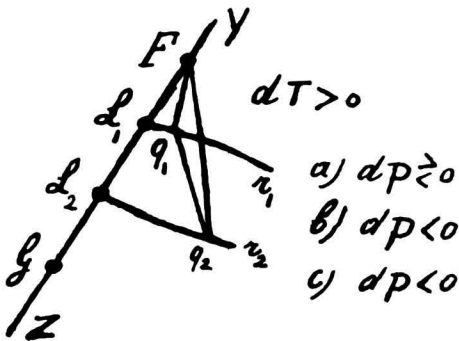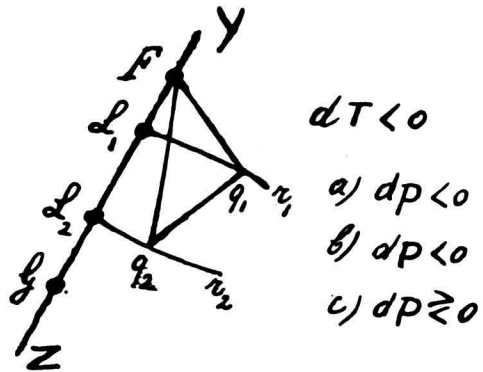

Fig. 1.   Fig. 2.

vicinity of L_1 and L_2; for the sake of clearness they have been drawn in the figures on greater distance.

In fig. 1 is:

$$\frac{x_2}{y - y_2} > \frac{x_1}{y - y_1} \quad \text{or} \quad \frac{x_2}{x_1} > \frac{y - y_2}{y - y_1} \quad . \quad . \quad . \quad (34)$$

consequently in accordance with (28): $(dT')_x > 0$ as is also indicated in the figure. It follows from (31)—(33):

$$\text{in case } a \text{ is } (dP)_x \gtrless 0$$
$$\text{,, ,, } b \text{ ,, } (dP)_x < 0$$
$$\text{,, ,, } c \text{ ,, } (dP)_x < 0$$

as is also indicated in fig. 1.

In fig. 2 is:

$$\frac{x_2}{y - y_2} < \frac{x_1}{y - y_1} \quad \text{or} \quad \frac{x_2}{x_1} < \frac{y - y_2}{y - y_1} \quad . \quad . \quad . \quad . \quad (35)$$

It follows from (28): $(dT')_x < 0$. From (31)—(33) it follows:

$$\text{in case} \quad a \text{ is } (dP)_x < 0$$
$$\text{,, \quad ,, } \quad b \text{ ,, } (dP)_x < 0$$
$$\text{,, \quad ,, } \quad c \text{ ,, } (dP)_x \gtrless 0$$

as is indicated also in fig. 2.

In fig. 1 the pressure may as well increase as decrease in the case a; it is apparent from (31) that $(dP)_x$ shall be positieve for large values of $x_2 : x_1$. As L_1 (and consequently also q_1) is the liquid which contains the most of the solid substance F we shall call L_1 (and consequently also q_1) the concentrated and L_2 the diluted solution.

We, therefore, find the following:

when the threephases-triangle solid-liquid-liquid turns its concentrated solution towards the side of the components-triangle (fig. 1) then the temperature increases and the pressure generally decreases; only when the concentration of the new substance in the diluted liquid (consequently x_2) is much larger than in the concentrated liquid consequently x_1), then in the case a the pressure may increase also.

In fig. 2 in the case c the pressure may as well increase as decrease; it appears from (33) that $(dP)_x$ shall be positive for small values of $x_2 : x_1$.

Consequently we find the following:

when the threephases-triangle solid-liquid-liquid turns its concentrated solution away from the side of the components-triangle (fig. 2) then the temperature decreases and generally the pressure also.

Only when the concentration of the new substance is much larger in the concentrated solution (x_1) than in the diluted solution (x_2), then in the case c the pressure may also increase.

We may obtain the previous results also by using the P, T-diagram of the equilibrium $E(x = 0)$. We may deduce this in the following way.

The direction of temperature of the equilibrium $(G) = F + L_1 + L_2$ is defined by the sign of the coefficient of the phase G in the isovolumetrical reaction (19). As $b \Delta V$ may be as well positive as negative, curve (G) may go, starting from the invariant point i, as well towards higher as towards lower temperatures.

The direction of pressure of the equilibrium (G) is defined by the sign of the coefficient of G in the isentropical reaction (20). As $-b \Delta H$ is negative in each of the cases a, b and c, curve (G) proceeds, starting from the invariant point i, towards higher pressures.

As further, in accordance with (17):

$$\left(\frac{dP}{dT}\right)_G = \frac{\Delta H}{\Delta V}$$

and ΔV is very small, curve (G) is ascending, starting from point i fast vertically. In figs 3 and 4 this curve is drawn vertically upwards; the double arrow indicates that starting from i, it may run either towards the right or to the left.

As the coefficient $-(1 + a) \Delta V'$ of the phase L_1 is negative in each of the cases a, b and c, in accordance with (19) curve $(L_1) = F + L_2 + G$ is going starting from point i towards lower pressures (figs 3 and 4).

In the cases a and b the coefficient $(1 + a) \Delta H'$ of phase L_1 is positive in equation (20) so that curve (L_1) is going, starting from i, towards lower pressures (fig. 3). In the case c is $(1 + a) \Delta H^1$ negative and curve (L_1) is going, therefore, starting from i, towards higher pressures (fig. 4). This is in accordance also with that which follows from (18) viz.

$$\left(\frac{dP}{dT}\right)_{L_1} = \frac{\Delta H'}{\Delta V'}.$$

Consequently we have defined the direction of the curves (G) and (L_1); fig. 3 is true for the cases a and b, fig. 4 for the case c.

With the aid of (19) and (20) we should be able to determine also the position of the curves (F) and (L_2) and then we could prove that the four curves are situated with respect to one another as in figs 3 and 4. [Compare f. i. Communication XIII]. As we know, however, the situation of the curves (G) and (L_1) we can find the position of curves (F) and (L_2) much more easily by using the rule for the position of the four monovariant curves of a binary equilibrium [Compare Communication I fig. 2].

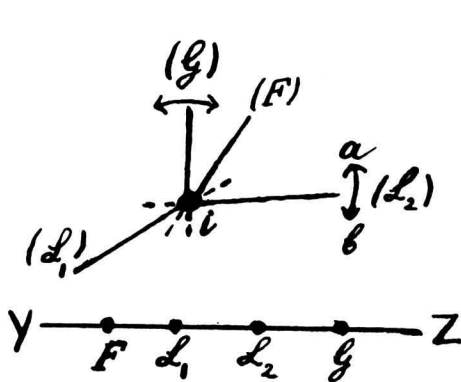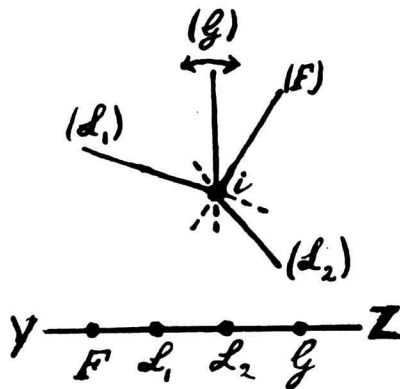In accordance with this rule we must meet, when we go, starting

Fig. 3.

Fig. 4.

from curve (G) in the direction of the hands of a clock towards curve (L_1) firstly curve (F) and afterwards curve (L_2). As further (G) and (F) must form a bundle and their prolongations must be situated between (L_1) and (L_2) and as the angle between two succeeding curves, must be always smaller than 180°, hence follows for the curves (F) and (L_2) a situation as in the figures 3 and 4.

In fig. 3 curve (L_2) is drawn horizontally; starting from i it may run either upwards or downwards; this has been indicated by the double little arrow. When it goes upwards, starting from i, then its prolongation must yet always be situated above curve (L_1). It appears from the coefficient of the phase L_2 in reaction (20) that curve (L_2) must go in case a starting from i upwards and in case b, starting from i downwards. This has also been indicated in fig. 3.

As we know the P,T-diagram of the equilibrium $E(x=0)$ we can easily determine the situation of curve E. It follows viz. from our general considerations in the beginning of this communication, that curve E must be situated between the curves (L_1) and (L_2). For $x_2 : x_1 = \infty$ curve E coincides with (L_2) for $x_2 : x_1 = 0$ with curve (L_1). When $x_2 : x_1$ changes from ∞ towards 0 than curve E moves in the direction of the hands of a clock from (L_2) towards (L_1).

Firstly we now take the case a, so that we must imagine in fig. 3 curve (L_2) to be drawn upwards starting from i. When we do change now $x_2 : x_1$ from ∞ to 0, then it follows from the different positions which curve E may obtain, that the following cases may occur:

$$(dT)_x > 0 \quad \text{and} \quad (dP)_x > 0$$
$$(dT)_x > 0 \quad \text{and} \quad (dP)_x < 0$$
$$(dT)_x < 0 \quad \text{and} \quad (dP)_x < 0$$

In case b we must image in fig. 3 curve (L_2) to be drawn downwards starting from i. When we do change $x_2 : x_1$ from ∞ to 0, then it follows from the situation of curve E:

$$(dT)_x > 0 \quad \text{and} \quad (dP)_x < 0$$
$$(dT)_x < 0 \quad \text{and} \quad (dP)_x < 0$$

In case c fig. 4 is true. When $x_2 : x_1$ changes again from ∞ to 0, then it follows from the position of curve E:

$$(dT)_x > 0 \quad \text{and} \quad (dP)_x < 0$$
$$(dT)_x < 0 \quad \text{and} \quad (dP)_x < 0$$
$$(dT)_x < 0 \quad \text{and} \quad (dP)_x > 0$$

We see that those deductions are in accordance with the previous ones and with the figs 1 and 2.

Our previous considerations are all valid in the supposition that the four phases $F L_1 L_2$ and G are situated with respect to one another as is indicated in the figs 1—4. When the four phases are situated otherwise with respect to one another, the reader my deduce all in similar way.

We now shall assume that the new substance is volatile, so that it occurs in the phases $L_1 L_2$ and G with the concentrations $x_1 x_2$ and x_3.

We find with the aid of (7) and (19):

$$M (dT)_x = - (1 + a) \triangle V' x_1 + [a \triangle V_1 - (1 + b) \triangle V] x_2 + b \triangle V . x_3 \quad (36)$$

and with the aid of (8) and (20):

$$M . (dP)_x = - (1 + a) \triangle H' x_1 + [a \triangle H' - (1 + b) \triangle H] x_2 + b \triangle H \cdot x_3 \quad (37)$$

wherein

$$M = (\triangle H . \triangle V' - \triangle H' . \triangle V) : RT$$

so that the direction of temperature and pressure of curve E are defined by (36) and (37).

As $\triangle V$ is very small in comparison with $\triangle V'$ we may neglect in (36) the terms with $\triangle V$ as long as x_3 is not very large, then it follows with approximation:

$$(dT)_x \gtrless 0 \quad \text{voor} \quad \frac{x_2}{x_1} \gtrless \frac{y - y_3}{y - y_1} . \quad . \quad . \quad . \quad . \quad (38)$$

Only for very great values of x_3 in comparison with x_1 and x_2 the term $b \triangle V . x_3$ in (36) will be of great importance and will be approximately

$$(dT)_x = \frac{RT \triangle V}{\triangle H . \triangle V'} b x_3 = \frac{RT}{\triangle V'} . \left(\frac{dT}{dP} \right)_G b x_3 \quad . \quad . \quad (39)$$

In (37) $\triangle H$ is not small in comparison with $\triangle H'$ and the term $b \triangle H . x_3$ will assert its influence already with values of x_3 which are not too small.

Consequently, in general the influence of the new substance on $(dT)_x$ and $(dP)_x$ will be larger in proportion as the new substance is more volatile and it will assert its influence sooner on $(dP)_x$ than on $(dT)_x$.

We may also deduce anything about the position of curve E with the aid of the general considerations at the beginning of this communication. Hence it follows viz that curve E must be situated either between the curves (L_1) and (L_2) or between (L_1) and (G) or between (L_2) and (G). As in the figs 3 and 4 the prolongation of each of those curves is situated between both the other curves, curve E may go, therefore, starting from point i in every direction.

Consequently the temperature may as well increase as decrease, and the pressure may increase or decrease as well at rising as at falling temperature, dependent on the position of curve E.

It follows from (12):

when x_1 is extremely small with respect to x_2 and x_3 then curve E is situated between (G) and (L_2);

when x_2 is extremely small with respect to x_1 and x_3 then curve E is situated between (G) and (L_1);

when x_3 is extremely small with respect to x_1 and x_2 then curve E is situated between (L_1) and (L_2);

when x_1 is extremely large with respect to x_2 and x_3 then curve E is situated in the vicinity of $L_1)$;

when x_2 is extremely large with respect to x_1 and x_3 then curve E is situated in the vicinity of (L_2);

when x_3 is extremely large with respect to x_1 and x_2 then curve E is situated in the vicinity of (G).

In each of those cases we can see at once from the figs 3 and 4 which signs $(dT)_x$ and $(dP)_x$ may have.

When f.i. x_2 is very small with respect to x_1 and x_3 then curve E is situated between (L_1) and (G); when now fig. 4 is valid then the pressure shall, therefore, always increase and the temperature shall decrease. In the special case only, when x_3 is still also extremely large with respect to x_1 and when at the same time $\Delta V > 0$ [then curve (G) proceeds, starting from i, a little to the left] then the temperature may fall a little.

When we add a new substance which is not volatile, but which forms mixed crystals with the solid substance F, then we have in figs. 3 and 4 the curves (F) (L_1) and (L_2). It appears from the position of those curves with respect to one another that the previous considerations are also valid in this case.

When we wish to calculate $(dT)_x$ then, as is apparent from (19) we have to substitute in (36) $b \Delta V x_3$ by $(\Delta V + \Delta V') x$. When we neglect again the terms with ΔV then we find:

$$M(dT)_x = [x - (1+a) x_1 + ax_2] \Delta V'$$

or:

$$(dT)_x = \frac{RT}{\Delta H} \cdot \frac{x (y_1 - y_2) - (y - y_2) x_1 + (y - y_1) x_2}{y_1 - y_2} \quad . \quad . \quad (40)$$

In the figs 5 and 6 YZ represents a side of the components-triangle, $F L_1 L_2$ and G the four phases of the invariant binary equilibrium $E(x=0)$. When we add a new substance then the ternary equilibrium $E = F + L_1 + L_2 + G$ arises. The solid sub-

stance F and the liquids L_1 and L_2 then proceed along the curves $F q r$, $L_1 q_1 r_1$ and $L_2 q_2 r_2$. When we add only little of the new substance, then the 3 phases are represented by the points $q\ q_1$ and q_2 which we must imagine in the immediate vicinity of the side YZ.

When we put $t = x(y_1-y_2)-(y-y_2)x_1 + (y-y_1)x_2$ and when we consider x and y as running coordinates, then $t = 0$ represents the equation of the straight line which goes in fig. 5 and 6 through q_1 and q_2.

When the point q is situated on the line q_1q_2 then $t = 0$; the sign of $(dT)_x$ is then determined by the terms which have been neglected in (40).

When q is situated at the right side of the line q_2q_1 (viz. when we go from q_2 towards q_1) as in fig. 5, then $t > 0$; when q is situated at the left side of the line $q_2 q_1$, as in fig. 6, then $t < 0$. Hence it follows, therefore, that in fig. 5 the temperature increases and in fig. 6 the temperature decreases, as is also indicated in both figures.
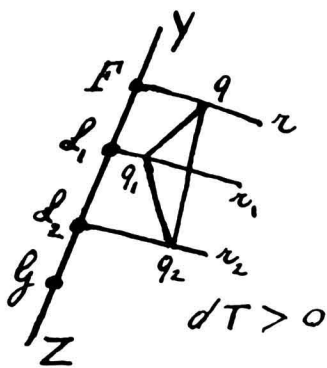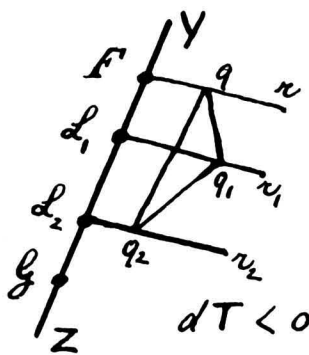

Fig. 5.   Fig. 6.

Consequently we find the following:

when we add to the invariant binary equilibrium $E\ (x = 0) = = F + L_1 + L_2 + G$ a substance which is not volatile and which forms mixed crystals with the solid substance F, then

the temperature rises, when the threephases-triangle solid-liquid liquid turns its concentrated liquid towards the side of the components-triangle (fig. 5)

the temperature falls when the threephases-triangle turns its concentrated solution away from this side (fig. 6).

Comparing fig. 1 with fig. 5 and fig. 2 with fig. 6, the reader will see that for the change of temperature the same rules are true, independent of the fact whether the new substance forms mixed crystals with F or not.

Finally we could still treat the general case that the new substance forms not only mixed crystals with F but that it is volatile also.

It follows from figs. **3** and 4, in connection with the theories discussed in the beginning of this communication that curve E can go in all directions, starting from point i.

In order to define $(dT')_x$ we must still include in (36) the term $(\Delta V + \Delta V')_x$; then we get again (40) approximately unless x_s is extremely large.

Consequently in this case also the figs. 5 and 6 remain valid, unless the threephases-triangle $q\,q_1\,q_2$ becomes very narrow and the concentration of the new substance in the vapour is extremely large.

<p align="right">(To be continued).</p>

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