Huygens Institute - Royal Netherlands Academy of Arts and Sciences (KNAW)

Chemistry. — *"In-, mono- and divariant equilibria"*. XX. By Prof. Schreinemakers.

Equilibria of n components in n phases, in which the quantity of one of the components approaches to zero; the influence of a new substance on an invariant (P or T) equilibrium.

In the communications XVI, XVII and XVIII we have seen that a region is two-leafed in the vicinity of a turning-line and one-leafed in the vicinity of a limit-line [e.g. curve ab or cd in fig. 1 (XVI)]. We shall consider the latter case more in detail.

We take the equilibrium $E = F_1 + F_2 \ldots + F_n$ of n components in n phases under constant pressure. This equilibrium is (Comm. XVII) monovariant (P); viz. it has one freedom under constant pressure.

The equations (2) and (3) (XVII) are true for this equilibrium; on change of one of the variables e.g. of x_1 this equilibrium traces in the P,T-diagram a straight line parallel to the T-axis.

In the vicinity of a limit-line of a region e.g. in the vicinity of curve ab or cd in fig. 1 (XVI), the quantity of one of the components approaches to zero. When this is the case with the component X, viz. with that component, the quantities of which are indicated in the different phases by $x_1 x_2 \ldots x_n$, then in (2) and (3) (XVII):

$$\frac{\partial Z_1}{\partial x_1} \ , \ \frac{\partial Z_2}{\partial x_2} \ . \quad . \ . \ \frac{\partial Z_n}{\partial x_n}$$

become infinitely large, viz in Z_1 the term $x_1 \, log \, x_1$ is found, in Z_2 the term $x_2 \, log \, x_2$ etc.

Now we write:

$$Z_1 = Z_1' + RT \, x_1 \, log \, x_1 \qquad Z_2 = Z_2' + RT \, x_2 \, log \, x_2 \quad . \quad ., \quad (1)$$

Herein $Z_1' \ Z_2' \ldots$ and their differential quotients remain always finite also for $x_1 = 0$, $x_2 = 0 \ldots$ It follows from (1):

$$\left. \begin{array}{l} \dfrac{\partial Z_1}{\partial x_1} = \dfrac{\partial Z_1'}{\partial x_1} + RT \, (1 + log \, x_1) \\[2ex] \dfrac{\partial Z_2}{\partial x_2} = \dfrac{\partial Z_2'}{\partial x_2} + RT \, (1 + log \, x_2) \end{array} \right\} \quad . \quad . \quad . \quad . \quad (2)$$

etc. The n equations (2) (XVII) now pass into:

$$Z_1' - RT\,x_1 - x_1\frac{\partial Z_1'}{\partial x_1} - y_1\frac{\partial Z_1'}{\partial y_1}\ \ldots\ldots = K$$

$$Z_2' - RT\,x_2 - x_2\frac{\partial Z_2'}{\partial x_2} - y_2\frac{\partial Z_2'}{\partial y_2}\ \ldots\ldots = K$$

$$\ldots\ (3)$$

etc. The first series of the equations (3) (XVII) passes into:

$$\frac{\partial Z_1'}{\partial x_1} + RT\,log\,x_1 = \frac{\partial Z_2'}{\partial x_2} + RT\,log\,x_2 = \ldots\ldots = K_x - RT \quad . \ (4)$$

The following series of the equations (3) (XVII) become:

$$\frac{\partial Z_1'}{\partial y_1} = \frac{\partial Z_2'}{\partial y_2} = \ldots\ldots = \frac{\partial Z_n'}{\partial y_n} = K_y \quad \ldots\ldots \ (5)$$

etc. It follows from (4):

$$RT\,log\,\frac{x_2}{x_1} = \frac{\partial Z_1'}{\partial x_1} - \frac{\partial Z_2'}{\partial x_2}$$

$$RT\,log\,\frac{x_3}{x_1} = \frac{\partial Z_1'}{\partial x_1} - \frac{\partial Z_3'}{\partial x_3}$$

$$\ldots\ldots\ (6)$$

or

$$x_2 = \mu_2\,x_1 \qquad x_3 = \mu_3\,x_1\ \ldots\ldots x_n = \mu_n\,x_1 \ . \quad . \quad . \ (7)$$

in which $\mu_2\,\mu_3\ldots$ are defined by (6).

For values infinitely small of $x_1\,x_2\ldots$ the ratios between $x_1\,x_2\ldots x_n$ are consequently defined by (7).

Now we give the increments: $dT.x_1\,x_2\ldots dy_1\ldots dy_2$ etc., to the variables $T\,x_1\,x_2\ldots y_1\,y_2\ldots$ etc., in which we put $x_1 = 0$ $x_2 = 0\ldots$

Now it follows from (3):

$$H_1\,dT + RT\,x_1 + y_1\,d\frac{\partial Z_1'}{\partial y_1} + \ldots\ldots = -\,dK$$

$$H_2\,dT + RT\,x_2 + y_2\,d\frac{\partial Z_2'}{\partial y_2} + \ldots\ldots = -\,dK$$

$$\ldots\ (8)$$

etc. in which the sign d indicates that we have to differentiate according to all variables.

Now we add the n equations (8) after having multiplied the first by λ_1, the second by λ_2 etc. Then we obtain, when we use the relations which follow from (5):

$$\Sigma\,(\lambda\,H)\ dT + RT\,\Sigma\,(\lambda\,x) + \Sigma\,(\lambda\,y)\,d\left(\frac{\partial Z_1'}{\partial y_1}\right) + \ldots = -\,\Sigma\,(\lambda)\ dK \ (9)$$

Now we define $\lambda_1\,\lambda_2\ldots$ in such a way that they satisfy the $n-1$ equations (10)

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$$\Sigma(\lambda) = \lambda_1 + \lambda_2 + \ldots \ldots + \lambda_n = 0$$
$$\Sigma(\lambda y) = \lambda_1 y_1 + \lambda_2 y_2 + \ldots \ldots + \lambda_n y_n = 0 \quad \Big\} \quad . \quad . \quad (10)$$
$$\Sigma(\lambda z) = \lambda_1 z_1 + \lambda_2 z_2 + \ldots \ldots + \lambda_n z_n = 0$$

etc. By this the $n-1$ ratios between the coefficients $\lambda_1 \lambda_2 \ldots$ are defined. As

$$\Sigma(\lambda x) = \lambda_1 x_1 + \lambda_2 x_2 + \ldots \ldots + \lambda_n x_n \quad \Big\} \quad . \quad . \quad (11)$$
$$\Sigma(\lambda H) = \lambda_1 H_1 + \lambda_2 H_2 + \ldots \ldots + \lambda_n H_n$$

the ratio $\Sigma(\lambda x) : \Sigma(\lambda H)$ is also defined. Now it follows from (9)[1]:

$$(dT)_P = -\frac{RT \, \Sigma(\lambda x)}{\Sigma(\lambda H)} \quad \ldots \ldots \quad (12)$$

The value of dT in (12) depends on $\Sigma(\lambda x)$, consequently on the n increments $x_1 x_2 \ldots x_n$. We may express them, however, in one of those increments e.g. in x_1. With the aid of (7) we obtain then:

$$(dT)_P = -\frac{RT x_1 \, \Sigma(\lambda \mu)}{\Sigma(\lambda H)} \quad . \quad \ldots \quad (13)$$

wherein:

$$\Sigma(\lambda \mu) = \lambda_1 \mu_1 + \lambda_2 \mu_2 + \ldots \ldots \lambda_n \mu_n \quad \ldots \ldots \quad (14)$$

When we take the equilibrium $E = F_1 + F_2 + \ldots + F_n$ of n components in n phases at constant temperature, then it is monovariant (T). In the same way as above we find now:

$$(dP)_T = \frac{RT \, \Sigma(\lambda x)}{\Sigma(\lambda V)} = \frac{RT x_1 \, \Sigma(\lambda \mu)}{\Sigma(\lambda V)} \quad \ldots \quad (15)$$

Herein $\lambda_1 \lambda_2 \ldots$ have again the values, which are defined by (10) $\Sigma(\lambda x)$ has also the same value of (11) viz.:

$$\Sigma(\lambda x) = \lambda_1 x_1 + \lambda_2 x_2 + \ldots \ldots + \lambda_n x_n \quad \Big\}$$
while
$$\Sigma(\lambda V) = \lambda_1 V_1 + \lambda_2 V_2 + \ldots \ldots + \lambda_n V_n \quad \Big\} \quad . \quad . \quad (16)$$

$\Sigma(\lambda\mu)$ has again the same value as in (14).

In the previous considerations it is assumed that the quantity of the component X in the equilibrium $E = F_1 + F_2 + \ldots + F_n$ of n components in n phases is very small. When, however, this quantity becomes zero, then E passes into an equilibrium of $n-1$ components in n phases. This is monovariant and is represented in the P,T-diagram by a curve. Under constant pressure it is invariant (P), at constant temperature invariant (T). In this invariant $(P$ or $T)$ equilibrium between the phases $F_1 \ldots F_n$ may occur a

[1] For another deduction see F. A. H. SCHREINEMAKERS, Die heterogenen Gleich gewichte von H. W. BAKHUIS ROOZEBOOM. III. 289.

reaction; the quantities $\lambda_1 \ldots \lambda_n$ of the phases participating in this reaction are defined by (10). The change in entropy occurring with this reaction $\Sigma(\lambda H)$ is defined by (11), the change in volume $\Sigma(\lambda V)$ is defined by (16).

Some of the coefficients $\lambda_1 \ldots \lambda_n$ are positive, other ones are negative. As long as we do not assume for this a definite rule, we may arbitrarily interchange positive and negative. We assume the following: The coefficients of the phases, which occur with a reaction, are taken positive; the coefficients of the phases which disappear with the reaction, are taken negative.

Now $\Sigma(\lambda)$ is the algebraical sum of the quantities of the phases which participate in the reaction, of course this is zero.

$\Sigma(\lambda y)$ is the algebraical sum of the quantity of the component Y which participates in the reaction; this is also zero. The same is true for the other components.

As the component X does not occur in the invariant (P or T) equilibrium, $\Sigma(\lambda x)$ has, therefore, another meaning. When we add, however, a little of the component X to this equilibrium, then it is divided between the n phases; this division is defined by (7), so that $x_1 \ldots x_n$ and consequently also $\Sigma(\lambda x)$ are defined.

Now we imagine a reaction in the invariant (P or T) equilibrium; $\lambda_1 \ldots \lambda_n$ represent, therefore, the quantities of the phases participating in the reaction. When those phases would contain the quantities $x_1 \ldots x_n$ of the new component, then $\Sigma(\lambda x)$ would be the algebraical sum of the quantity of the component X, which participates in this reaction. For this reason we shall call $\Sigma(\lambda x)$ "the fictitious quantity of reaction of the component X".

Now we take a point on the limit-curve of a region, e.g. point h on the limit-curve $a\,b$ in fig. 1. (XVI). This limit-curve represents an equilibrium of $n-1$ components (viz. the components $Y, Z, U ..$) in n phases, consequently a monovariant equilibrium. In the point h itself $PT y_1 y_2 \ldots z_1 z_2 \ldots$ etc. have definite values; the same is true for the ratios of $\lambda_1 \ldots \lambda_n$ which are defined by (10) Now we add a little of the component X, this is divided over the n phases; this division is defined by (7). For a definite value of e.g. x_1 the ratios $\Sigma(\lambda x) : \Sigma(\lambda H)$ and $\Sigma(\lambda x) : \Sigma(\lambda V)$ are also defined. In accordance with (12) and (15) we know consequently also $(dT)_P$ and $(dP)_T$.

When $(dT)_P$ is positive, then the region E is situated at the right of the point h; we enter then the region, just as in fig. 1 (XVI) starting from h in the direction hl.

When $(dP)_T$ is negative, then the region E is situated below

point h; then we enter the region, just as in fig. 1 (XVI) starting from h in the direction hm.

Consequently the region E is situated at the right and below the point h.

The direction of curve ab itself is defined in every point by:

$$\frac{dP}{dT} = \frac{\Sigma\,(\prime\,H)}{\Sigma\,(\lambda V)} \quad \cdots \quad \cdots \quad (17)$$

It follows from our assumption over the sign of $(dT)_P$ and $(dP)_T$ that we have assumed $\Sigma(\lambda x) : \Sigma(\lambda H)$ to be negative and $\Sigma(\lambda x) : \Sigma(\lambda V)$ also to be negative. Then it follows from (17) that curve ab must be a curve, rising with the temperature, in the vicinity of point h, as is also drawn in fig. 1 (XVI).

In fig. 3 (XVI) $abchd$ represents a limit-curve which has a maximum of pressure in b and a maximum of temperature in c. It follows with the aid of (17) from the direction of branch ab that $\Sigma(\lambda H)$ and $\Sigma(\lambda V)$ have the same sign; we now choose the signs of $\lambda_1 \ldots \lambda_n$ in such a way that both are positive. Then it follows from the direction of the branches bc and cd with the aid of (17), which signs $\Sigma(\lambda H)$ and $\Sigma(\lambda V)$ must have on those branches. Then we have:

on branch ab	$\Sigma(\lambda H) > 0$	$\Sigma(\lambda V) > 0$
in b	$\Sigma(\lambda H) = 0$	$\Sigma(\lambda V) > 0$
on branch bc	$\Sigma(\lambda H) < 0$	$\Sigma(\lambda V) > 0$
in c	$\Sigma(\lambda H) < 0$	$\Sigma(\lambda V) = 0$
on branch cd	$\Sigma(\lambda H) < 0$	$\Sigma(\lambda V) < 0$

In each point of curve $abchd$ $\Sigma(\lambda x)$ has a definite sign; we are able to find this with the aid of (7) and (10).

When we assume that $\Sigma(\lambda x)$ is negative in each point of the curve, then it follows from (12) and (15) that the region E must be situated entirely within the limit-curve $abcd$ and consequently not, as in fig. 3 (XVI), where the part afe is situated outside.

When in each point of the curve $abcd$ $\Sigma(\lambda x) > 0$, then it follows from (12) and (15) that the region must be situated at the left of and above branch ab, at the right of and above branch bc, at the right of and below branch cd. Then we have fig. 5 (XVI). [As it is apparent from the position of the letters, the printer has turned this figure; for this reason the reader has to place it in such a way that the tangent is horizontal in b and vertical again in c].

We may assume also that $\Sigma(\lambda x)$ is positive in the one part of the curve, negative in another part. We assume that $\Sigma(\lambda x)$ is

positive in part abf of curve $abcd$ fig. 3 (XVI) and negative in the part fcd. Then it follows from (12) and (15) that the region must be situated as is drawn in fig. 3 (XVI) viz. that a part afe of this region must be situated outside the limit-line and that this region must have a turning line ef.

It appears from the following that this point f must be a point of the turning-line. In this point $\Sigma(\lambda x) = 0$. As in this point also the equations (10) are valid, a phase reaction $\lambda_1 F_1 + ... + \lambda_n F_n = 0$ may occur between the n phases of the equilibrium $E = F_1 + ... + F_n$, in which an infinitely small quantity of the component X occurs now also.

Consequently when in a definite point f of curve $abcd$ $\Sigma(\lambda x) = 0$, then f is a common point of turning- and limit-line; later we shall see that f is a point of contact. When $\Sigma(\lambda x)$ changes in sign in f, then f is a terminating point of the turning-line as in fig. 3 (XVI); when however $\Sigma(\lambda x)$ does not change its sign in f, then f is not a terminating point, but the curve proceeds further.

From (12), (15) and (17) follows the relation:

$$(dP)_T : (dT)_P = -\left(\frac{dP}{dT}\right)_{x=0} \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (18)$$

The index $x = 0$ in the second part of (18) indicates that $\dfrac{dP}{dT}$ is true for the limit-curve, in which the component X is missing.

In order to comprehend the meaning of (18), we imagine the P, T-curve of the limit-equilibrium, to be drawn in which the component X does not occur, therefore. For this we take the curves ab and cd in the figures 1, 2 and 4 (XVI) and curve $abcd$ in the figures 3 and 5 (XVI). [We have to place again the latter figure in the right position].

We shall call the branches on which the pressure increases with increase of T the "ascending" branches, e.g. the branches ab and cd in the figures 1, 2, 3, 4 and 5 (XVI). A branch like e.g. bc in figs. 3 and 5 (XVI), on which the pressure decreases at increase of T, is called a "descending" branch.

On an ascending branch $\left(\dfrac{dP}{dT}\right)_{x=0}$ is positive, then it follows from (18) that $(dP)_T$ and $(dT)_P$ have opposite signs. When $(dT)_P$ is positive and consequently $(dP)_T$ negative, then the region is situated at the right and below the branch; this is the case with respect to branch ab in the figs. 1, 2 and 4 (XVI) and with respect to branch cd in the

figs. 2, 4 and 5 (XVI). When $(dT)_P$ is negative and $(dP)_T$ consequently positive, then the region is situated at the left and above the branch; this is the case with respect to branch $a\,b$ in figs. 3 and 5 (XVI), and with respect to branch $c\,d$ in the figs. 1 and 3 (XVI).

Consequently we find: A region is situated always at the right and below or at the left and above the ascending branch of its limit-curve.

On the descending branch of a limit-curve $\left(\dfrac{dP}{dT}\right)_{x=0}$ is negative. It follows from (18) that then $(dP)_T$ and $(dT)_P$ have the same sign. When both are positive, then the region is situated, therefore, at the right and above the branch. When both are negative, then it is situated at the left and below the branch. In fig. 5 (XVI) the region is situated at the right and above branch bc; in fig. 3 (XVI) the region is situated at the right and above the part $b\,f$, and at the left and below the part $f\,c$ of branch $b\,c$.

Consequently we find: .

a region is situated at the right and below, or at the left and above the ascending branch of its limit-curve; it is situated at the right and above, or at the left and below the descending branch of its limit-curve.

In Communication XI on: Equilibria in ternary systems, we have already deduced this same property for a special case viz. for the ternary region $F + L + G$, in which F represents a binary compound, with respect to its binary limit curve $F+L+G$.

Now it appears that this is true in general for each arbitrary region with respect to all its limit-curves.

We may express the results obtained above also in another way. The equilibrium $E = F_1 + \ldots + F_n$ of $n-1$ components in n phases is monovariant or invariant (P or T). When we add a little of a new substance X, then a new equilibrium $E' = F'_1 + \ldots + F'_n$ may arise. Herein the invariable phases have the same composition as in E; the variable phases (which of course not all need to contain the new substance X) differ still only very little from those in E.

We now may put the question:

how must the temperature change under constant P or: how must the pressure change at constant T in order that in both cases the equilibrium E passes into E'.

It is clear that both questions are only another form of the questions, treated above: how must the temperature be changed

under constant P and the pressure at constant T in order to pass from a limit-curve into the corresponding region.

We take the equilibrium $E = L + F_2 + F_3 + \ldots$ of $n-1$ components in n phases (or of n components in $n + 1$ phases). Herein $F_2 F_3 \ldots$ represent solid substances of invariable composition and L a liquid. On addition of a new substance X this occurs then only in the liquid.

When in this equilibrium E at constant T and under constant P there occurs the reaction:

$$\lambda_1 L + \lambda_2 F_2 + \lambda_3 F_3 + \ldots\ldots = 0 \ldots \ldots (19)$$

then $\Sigma(\lambda x) = \lambda_1 x$, when viz. x represents the concentration of the new substance in the liquid.

When we put $\lambda_1 = 1$, then $\Sigma(\lambda H)$ and $\Sigma(\lambda V)$ are the increases of entropy and volume, when one quantity of liquid is formed at the phase-reaction. We represent them by ΔH and ΔV.

(12) and (15) pass now into:

$$(dT)_P = -\frac{RT x}{\Delta H} \quad \text{and} \quad (\Delta P)_T = \frac{RT x}{\Delta V}. \quad \ldots \quad (20)$$

When we represent by ΔW the quantity of heat which is to be added in order to form with the reaction one quantity of liquid, then (20) passes into:
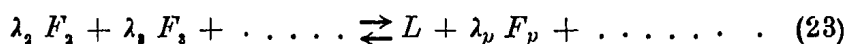
$$(dT)_P = -\frac{RT^2 x}{\Delta W} \quad \text{and} \quad (\Delta P)_T = \frac{RT x}{\Delta V} \quad \ldots \quad (21)$$

Reaction (19) may represent the common melting of the solid substances $F_2 F_3 \ldots$; this is the case when the reaction is of the form:

$$\lambda_2 F_2 + \lambda_3 F_3 + \ldots\ldots \rightleftarrows L \ldots \ldots (22)$$

and when $\lambda_2 \lambda_3$ are positive.

When the reaction is of the form:

$$\lambda_2 F_2 + \lambda_3 F_3 + \ldots\ldots \rightleftarrows L + \lambda_p F_p + \ldots\ldots \ldots (23)$$

in which we take also positive all coefficients, then it represents the conversion of the liquids $F_2 F_3 \ldots$ into $F_p \ldots$ when simultaneously liquid is formed.

Now we assume that heat is to be added at the formation of liquid from solid substances, consequently at melting in accordance with (22) and at conversion in accordance with (23); then ΔW is positive; the change in volume at melting or conversion may be as well positive as negative. Now it follows from (21):

The common melting- or conversion temperature of one or more substances is lowered by addition of a new substance;

the common melting- or conversion-pressure of one or more substances is;

raised by a new substance, when the volume increases on melting or conversion;

lowered, when the volume decreases on melting or conversion.
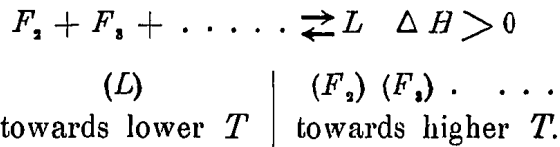
This increase and decrease are at first approximation proportional to the quantity of the new substance.

When we apply those rules to the melting of a simple substance, then follows the known rule of the decrease of melting or freezing point; the first formula (21) is then the known formula of RAOULT-VAN 'T HOFF.

We may apply the previous deductions also when we substitute in (19) the liquid L by a gas G. In general ΔV is then positive and approximately equal to the volume V of the gas; by this we may give another form to the second formula (21) viz.

$$(dP)_T = Px \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (24)$$

We may deduce the previous rules also in the following way. We take the equilibrium $E = L + F_2 + F_3 + \ldots$, in which the new substance X is not yet present under constant pressure; then it is invariant (P) and it consists at a definite temperature, which we shall call T_0. When we assume that reaction (22) takes place from left to right at addition of heat, then it follows:
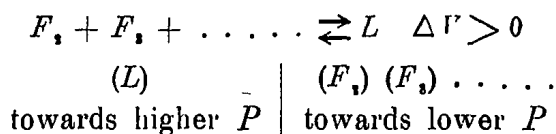
$$F_2 + F_3 + \ldots \ldots \rightleftarrows L \quad \Delta H > 0$$

(L) | $(F_2) \, (F_3) \cdot \ldots$

towards lower T | towards higher T.

Consequently the equilibrium $(L) = F_2 + F_3 + \ldots$ consists at temperatures lower than T_0. When we add the new substance X, then E passes into $E' = L' + F_2 + F_3 + \ldots$, in which L_1 differs from L; this equilibrium E' exists at a temperature T'' which differs from T_0.

When we take away the liquid L' from E', then it passes into $F_2 + F_3 + \ldots$, consequently in the equilibrium (L) discussed above; as this exists at lower temperatures than T_0, it follows $T'' < T_0$. On addition of the new substance the common melting-point must fall, therefore.

From reaction (23) we find the same for the common point of conversion. When we take at constant temperature the equilibrium $E = L + F_2 + F_3 + \ldots$, in which the new substance is not yet present, it is invariant (T); then it exists under a definite pressure P_0.

When reaction (22) takes place with increase of volume from left to right, then follows:

$$F_2 + F_3 + \ldots \ldots \rightleftarrows L \quad \Delta r > 0$$

$$(L) \quad \underline{\quad} \quad \bigg| \quad (F_2)\ (F_3) \ldots \ldots$$

towards higher P | towards lower P

The equilibrium $(L) = F_2 + F_3 + \ldots$ exists, therefore, under pressures, larger than P_0. Hence is follows that the equilibrium E' occurs also under a pressure higher than P_0. Consequently when at common melting increase of volume takes place, then the melting pressure rises.

From reaction (23) the same follows for the common point of conversion.

When we assume that $\Delta V < 0$, then it follows that on addition of the new substance the pressure of melting or conversion falls.
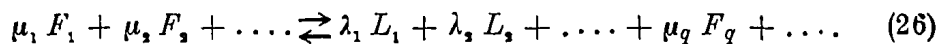
Now we take the equilibrium:

$$E = L_1 + L_2 + \ldots \ldots + F_1 + F_2 + \ldots \ldots$$
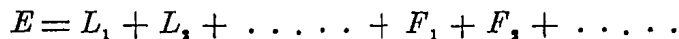
of $n - 1$ (or n) components in n (or $n + 1$) phases. Again L_1 L_2 represent liquids, F_1 F_2 solid phases of constant composition. Formerly[1]) we have called the temperature at which this equilibrium occurs under constant pressure the "Schichtungstemperatur"; we may call it also the stratification-temperature. We write the reaction occurring in this equilibrium:

$$\lambda_1 L_1 + \lambda_2 L_2 + \ldots \ldots + \mu_1 F_1 + \mu_2 F_2 + \ldots \ldots = 0. \quad (25)$$
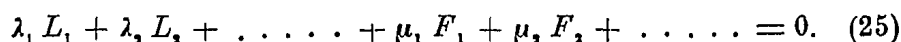
We may distinguish at this reaction the 2 main types:

$$\mu_1 F_1 + \mu_2 F_2 + \ldots \rightleftarrows \lambda_1 L_1 + \lambda_2 L_2 + \ldots + \mu_q F_q + \ldots \quad (26)$$

$$\lambda_1 L_1 + \ldots + \mu_1 F_1 + \mu_2 F_2 + \ldots \rightleftarrows \lambda_p L_p + \ldots + \mu_q F_q \ldots \quad (27)$$

in which we take all coefficients positive. In (26) the solid substances may be wanting on the right side, in (27) on the right or on the left side. Experimental examples of both types are known[2]). In order to express the difference between the two reactions we shall say: in (26) all liquids are situated in reaction-conjunction, in (27) two or more are situated in reaction-opposition[3]).

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[1]) F. A. H. SCHREINEMAKERS, die heterogenen Gleichgewichte von H. W. BAKHUIS ROOZEBOOM III[2] 108.

[2]) F. A. H. SCHREINEMAKERS ibid. III[2] 106 – 113, 193—203.

[3]) In order to prevent confusion, see the following. In the books III[1] and III[2] mentioned above phases are many times spoken of which are situated in the diagram in conjunction or opposition. When we call this situation diagram conjunction and diagram opposition, then it appears that reaction-conjunction corresponds with diagram opposition and reaction-opposition with diagram-conjunction.

When we add a new substance, then this divides itself between the liquids; its concentrations $x_1 x_2 \ldots$ are defined by (7). [It is apparent that the μ's in (7) have quite another meaning as in (25), (26) and (27)].

For reaction (26) $\Sigma(\lambda x) = \lambda_1 x_1 + \lambda_2 x_2 + \ldots$, in which occur only the λ's, not the μ's. As the λ's are all positive, $\Sigma(\lambda x)$ is also positive. With this we assume that heat must be added, in order that reaction (26) takes place from left to right, so that also $\Sigma(\lambda H)$ is positive. The sign of $\Sigma(\lambda V)$, however, is indefinite. [It is apparent that in $\Sigma(\lambda H)$ and $\Sigma(\lambda V)$ the μ's of (26) occur also].

Now it follows from (12) and (15)

$$(dT_P < 0 \text{ and } (dP)_T \gtrless 0 \quad . \quad . \quad . \quad . \quad . \quad (28)$$

Hence it follows: when we have an invariant (P or T) equilibrium with 2 or more liquids, which are situated all in reaction-conjunction and when we add a new substance, then:

under constant P the stratification temperature is lowered; ·

at constant T the stratification-pressure is raised when the volume increases at the formation of the liquids;

lowered when the volume decreases at the formation of liquids.

For reaction (27) is

$$\Sigma(\lambda x) = \lambda_p x_p + \ldots \ldots - \lambda_1 x_1 - \lambda_2 x_2 - \ldots$$

so that $\Sigma(\lambda x)$ may be as well positive as negative. This depends on the partition of the new substance X between the different liquids.

In order to illustrate this further we consider a definite case, viz. the equilibrium

$$E = L_1 + L_2 + Z + U + \ldots \ldots + N. \quad . \quad . \quad (29)$$

between the n components $Y Z \ldots N$. Consequently in this equilibrium, all components, excepted Y, occur as solid phases. As there are, therefore, $n-1$ solid and 2 liquid phases, it is invariant (P or T). Now we represent the reaction by:

$$\lambda_1 L_1 + \lambda_2 L_2 + \lambda_3 Z + \lambda_4 U + \ldots \ldots + \lambda_{n+1} N = 0 \quad . \quad (30)$$

so that $\Sigma(\lambda x) = \lambda_1 x_1 + \lambda_2 x_2$. For the definition of the relation between λ_1 and λ_2 we take from (10) the equation $\Sigma(\lambda y) = 0$. As the substance Y occurs only in the two liquids, it follows:

$$\Sigma(\lambda y) = \lambda_1 y_1 + \lambda_2 y_2 = 0 \quad . \quad . \quad . \quad . \quad . \quad (31)$$

Hence it appears that λ_1 and λ_2 have opposite signs, so that reaction (30) belongs to type (27). We write it in the form:

$$\lambda_1 L_1 + \lambda_3 Z + \lambda_4 U + \ldots \ldots \rightleftarrows L_2 \quad . \quad . \quad . \quad (32)$$

We have put, therefore $\lambda_2 = 1$, consequently λ_1 is positive; of course one or more of the coefficients $\lambda_3 \ldots$ may be negative.

Further we assume that L_2 is the liquid, which is formed on addition of heat. [When this should be the case with L_1, then we should have placed L_1 in the left part of (32)]. Now we have:

$$\Sigma (\lambda y) = y_2 - \lambda_1 y_1 \text{ and } \Sigma (\lambda x) = x_2 - \lambda_1 x_1.$$

Hence it follows:

$$\Sigma (\lambda x) = x_1 \left(\frac{x_2}{x_1} - \frac{y_2}{y_1} \right). \quad \ldots \ldots \quad (33)$$

Now it follows from (12) and (15):

$$(dT)_P = - \frac{RT^2 x_1 \left(\frac{x_2}{x_1} - \frac{y_2}{y_1} \right)}{\Delta W} \quad \ldots \ldots \quad (34)$$

and

$$(dP)_T = \frac{RT x_1 \left(\frac{x_2}{x_1} - \frac{y_2}{y_1} \right)}{\Delta V} \quad \ldots \ldots \quad (35)$$

Herein ΔW is the heat, wanted for forming one quantity of the liquid L_2; ΔV is the increase of volume occurring at this formation, which can be as well positive as negative.

Now we shall mean by partition-coefficient of a substance: the concentration of that substance in the liquid, which is formed on addition of heat, divided by the concentration of that substance in the other liquid. $x_2 : x_1$ is consequently the partition-coefficient of the new substance, $y_2 : y_1$ that of the component, which does not occur as solid phase.

Consequently we find:

when in an invariant (P or T) equilibrium with 2 liquids only components occur as solid phases, then both liquids are situated in reaction-opposition. The stratification-temperature under constant P by addition of a new substance:

is elevated (lowered) when the partition-coefficient of the new substance is smaller (larger) than that of the component which does not occur as solid phase [1]).

We may deduce from (35) similar rules for the influence of a new substance on the change in pressure at constant temperature.

We may also give a more simple form to (34) and (35). We have viz. expressed the concentrations of the components in the liquids in such a way that each liquid contains in all one molecule. We may, however, also mean by concentration the quantity of the

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· [1]) For some examples of the influence of a third substance on binary equilibria see F. A. H. SCHREINEMAKERS, Die heterogenen Gleichgewichte von H. W. BAKHUIS ROOZEBOOM III[2] 160.

components when the liquid contains one molecule of the component which does not occur as solid phase, consequently in our case of the component Y. As, therefore, y_1 and y_2 become $= 1$, (34) and (35) pass into:

$$(dT)_P = -\frac{RT^2\,(r_2-x_1)}{\Delta W} \quad \text{and} \quad (dP)_T = \frac{RT\,(x_2-x_1)}{\Delta V}. \quad (36)$$

Now we find:

the stratification-temperature is raised (lowered) under constant P on addition of a new substance, when the concentration of the new substance in the liquid, which is formed on addition of heat, is smaller (larger) than its concentration in the other liquid.

The first formula (36) has been deduced formerly for equilibria with two[1]) and more[2]) components.

To be continued.

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[1]) F. A. H. SCHREINEMAKERS. Zeitschr. f Phys. Chem. 25, 320 (1898).
[2]) H. A. LORENTZ ibid. 25. 332 (1898).