the point, where, in the domain (a), that function has its maximum modulus, coincides with a point where a_x attains its upper limit value.

6. We will now say something about the dependence between the quantities a and β. The number a may vary from *zero* to an amount A, which is the upper limit of the radii of domains, in which the quantity a_x determined by (6) is a limited function. The number A cannot in any case be greater than the radius of convergence of one of the functions $a_m(x)$, but it may be less, since, even when all those functions are regular in a certain domain (a), it is possible that the upper limit (6) has not a finite value in some point of (a). It might also occur that the limit (6) did exist in all the points of (a), but was not bounded in that domain. On the other hand it may happen that the number A is infinite (e.g. if $a_m(a) = $ constant $= c^m$).

From the fact that the quantity a has been defined as the upper limit of the function a_x in the domain (a), it follows at once that a cannot decrease if a increases, in other words that a is a monotone function of a. Therefore according to (7), β is a *monotonely increasing* function of a, not smaller than a. (β may be *equal* to a, e.g. if $a_m(x) = 1 : m!$, for in that case $a_x = $ constant $= 0$).

Let b be the value of β for $a = 0$, and B the one for $a = A$; in many cases B will be infinite, but it need not be so. Every value β may assume lies, as β is a monotonely increasing function of a, in the interval (b, B), and corresponds to only *one* value of a. The number b_x which, as a β-value, belongs to $a = 0$, may be zero, if $a_{x_0} = 0$. In that ease *any* function for which x_0 is an *ordinary* point, with arbitrarily small domain of regularity, has in x_0 a transmuted determined by (1). If a, as a function of a, is in that case continuous in $a = 0$, the series (1) produces for *any* function, with arbitrarily small domain of convergence, a transmuted in a certain *domain* of x_0. The transmuting series in that case is, according to a name introduced by PINCHERLE, *of the first kind*.

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

(Communicated in the meeting of December 21, 1916).

21. *Ternary systems with two indifferent phases.*

In the previous communication we have deduced the four P, T-diagramtypes, which occur in ternary systems with two indifferent phases. Now we shall consider a case more in detail.

We take a ternary system with the components water and the two salts Z and A which are not volatile, in which of the salt Z yet also the hydrate $Z . n\, H_2O$ occurs, which we shall represent by Z_n (fig. 1).

Suppose, the invariant equilibrium

$$Z + Z_n + L_d + G$$

occurs in the binary system $W + Z$ at the temperature T_d and under the pressure P_d. The liquid L_d is represented in fig. 1 by the point d between W and Z_n; of course we might as well have taken d between Z and Z_n. When we add the salt A to this equilibrium, then the equilibrium $Z + Z_n + L + G$ arises; the liquid L proceeds then a curve $d\,h\,m$ (fig. 1). It is evident that T and P change along this curve $d\,h\,m$ from point to point.
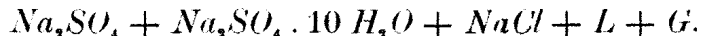
Now we assume that in the point m the added salt A dissolves no more, so that at T_m and under P_m the invariant equilibrium:

$$Z + Z_n + A + L_m + G$$
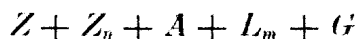
is formed. A similar case is found e. g. in the system: $water + Na_2SO_4 + NaCl$. In the binary system: $water + Na_2SO_4$ viz. at $32°.5$ the equilibrium
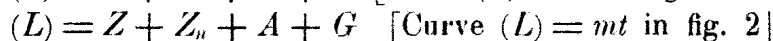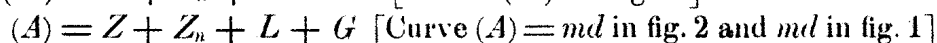
$$Na_2SO_4 + Na_2SO_4 . 10\, H_2O + L + G$$
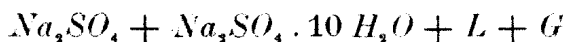
occurs. On addition of $NaCl$ at $17°.9$ arises:
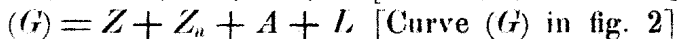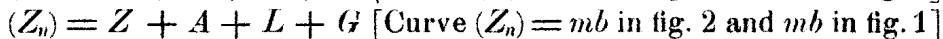
$$Na_2SO_4 + Na_2SO_4 . 10\, H_2O + NaCl + L + G.$$

As the gas-phase G is represented in fig. 1 by the point W, the phases Z, Z_n and G are situated on a straight line. Z, Z_n and G are, therefore, the singular phases, A and L_m the indifferent phases of the equilibrium:

$$Z + Z_n + A + L_m + G.$$
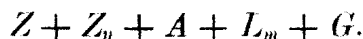
Consequently from the invariant point start the singular equilibria:

$(M) = Z + Z_n + G$ [Curve (M) in fig. 2]
$(A) = Z + Z_n + L + G$ [Curve $(A) = md$ in fig. 2 and md in fig. 1]
$(L) = Z + Z_n + A + G$ [Curve $(L) = mt$ in fig. 2]

and further the equilibria:

$(Z) = Z_n + A + L + G$ [Curve $(Z) = rm$ in fig. 2 and rm in fig. 1]
$(Z_n) = Z + A + L + G$ [Curve $(Z_n) = mb$ in fig. 2 and mb in fig. 1]
$(G) = Z + Z_n + A + L$ [Curve (G) in fig. 2]
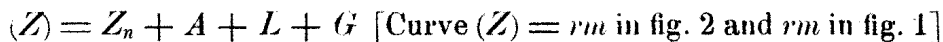
Let us first consider the binary system $W + Z$, in which at T_d and under P_d the invariant equilibrium

$$Z + Z_n + L_d + G$$

occurs. From the invariant point d (fig. 2) start the equilibria:

$Z + L + G$, represented by curve da (fig. 2)

$Z_n + L + G$, ... do (fig. 2)

$Z + Z_n + L$, ... ds (fig. 2)

$Z + Z_n + G$, ... dmt (fig. 2)

The solutions of the first equilibrium are represented in fig. 1 by points of da, those of the second equilibrium by points of do. Curve ds is drawn vertically in fig. 2; the little curve with the arrows indicates that it may proceed as well a little towards the right as to the left. [This little arc has the same meaning for the curve (G) in this and in the following figures].

It follows from the reaction: $Z_n \rightleftarrows Z + G$ which may occur between the phases of the equilibrium $Z + Z_n + G$, that curve $t\,m\,d$ is a curve ascending with the temperature. With this reaction from left to right viz. as well the volume as the entropy increases.

This curve $d\,m\,t$ is at the same time the (M)-curve of the ternary system $W + Z + A$. Consequently on this curve is situated somewhere the point m in which occurs the invariant equilibrium:

$$Z + Z_n + A + L_m + G$$

of the ternary system. The two other singular equilibria:

$$(A) = Z + Z_n + L + G \text{ and } (L) = Z + Z_n + A + G$$
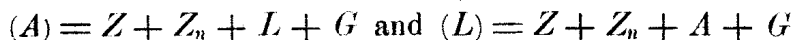
coincide with this curve $t\,m\,d$. As the equilibrium (A) exists under higher pressures and at higher temperatures than the equilibrium (L), (A) is represented by curve $m\,d$ and (L) by curve mt in fig. 2. [Further we shall show this yet in another way].

The equilibrium $(G) = Z + Z_n + A + L$ goes, starting from m towards higher pressures and it may go as well towards higher as towards lower temperatures. [We shall refer to this later].

Now we have still to draw in fig. 2 the curves (Z) and (Z_n). For this we consider the concentration-diagram of fig. 1. In this are represented the solutions of:

$$(A) = Z + Z_n + L + G \text{ by curve } m\,d$$
$$(Z) = Z_n + A + L + G \text{ ,, ,, } m\,r$$
$$(Z_n) = Z + A + L + G \text{ ,, ,, } m\,b$$
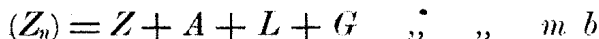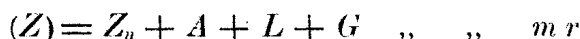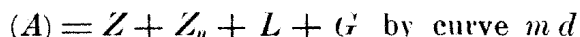
We make the obvious supposition that the curves $m\,d$ and $m\,b$ go towards higher pressures, starting from m and that curve $m\,r$ goes towards lower temperatures, starting from m. [We shall refer to this later].

The dotted curves are the saturation curves of Z_n, Z and A under their own vapour-pressure; the little arrows indicate the direction, in which the pressure increases.

The regions, in which Z_n, Z and A occur as solid phases, are indicated by circumcircled letters.
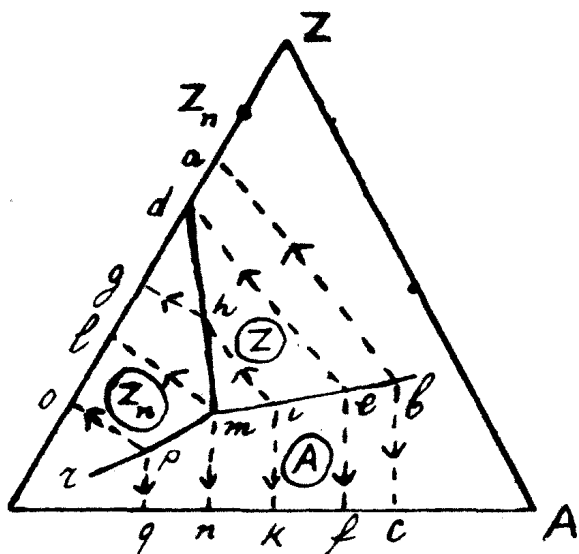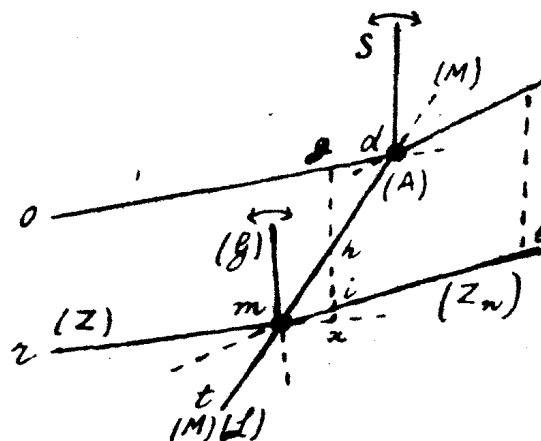

Fig. 1.

Fig. 2.

It appears from the direction of the little arrow on curve $h\,i$ (fig. 1) that the vapour-pressure is higher in h than in i. This saturation-curve $h\,i$ is represented in fig. 2 by a straight line $h\,i$ parallel to the P-axis, the point h is situated, therefore, higher than the point i, so that curve $m\,h\,d$ must be situated above curve $m\,i\,b$.

Curve $a\,b$ of fig. 1 is represented in fig. 2 by the straight line $a\,b$ parallel to the P-axis; as, in accordance with fig. 1, the pressure is higher in a than in b, in fig. 2 point a must be situated above point b and consequently curve $d\,a$ above curve $m\,b$.

We have drawn in fig. 2 curve $m\,b$ starting from m towards higher pressures, later on we shall see that this need not be always the case.

Now we have still to determine in fig. 2 the position of curve (Z) with respect to the other curves. We are able to do this in different ways, we shall show that the metastable prolongation mx of curve $r\,m$ is situated below curve $m\,b$.

For this we imagine in fig. 1 the curves $g\,h$ and $k\,i$ to be prolonged till they intersect one another in a point x. This point of intersection is a point of the metastable prolongation of curve $r\,m$. As $T_x = T_h = T_g = T_i$, the points x, h, g and i are situated in fig. 2 on a straight line parallel to the P-axis. It is apparent from fig. 1 that the vapour-pressure is smaller in point x than in h and in i; in fig. 2 the point x is situated, therefore, below point i, so that curve mx is situated below curve mb.

We could also draw in fig. 2 still the P,T-curve of the equilibrium $A + L + G$ of the binary system $W + A$; it appears from fig. 1 that this curve must be situated in fig. 2 above the curves rm and mb.

In our previous considerations we have followed for the deduction of the P,T-diagram the same way as in the deduction of the P,T-diagrams for some special cases in binary systems [Communication XI]. We have used viz. the concentration-diagrams and some of their properties. In the case which is discussed now, we used the property that the vapour-pressure increases along the saturation-curves in the direction of the little arrows. Further we have made the obvious supposition that in the concentration-diagram (fig. 1) the curves mb and md go starting from m towards higher temperatures and that curve mr goes, starting from m towards lower temperatures.

We may, however, follow also quite another way, in which we may deduce as well the P,T- as the concentration-diagram and in which we more plainly feel the suppositions which are assumed in the deductions.

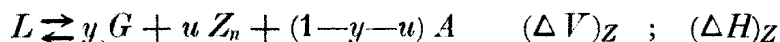For this we consider the different reactions which may occur in the invariant equilibrium:

$$Z + Z_n + A + L + G$$
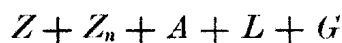
With this we shall assume that the liquid L is represented in fig. 1 by a point m within the triangle $Z_n A W$. From the position of the five phases with respect to one another follow the reactions:

1. For the singular equilibrium $(M) = Z + Z_n + G$

$$Z_n \rightleftarrows x\, G + (1-x)\, Z \qquad (\Delta V)_M \quad ; \quad (\Delta H)_M$$

2. For the equilibrium $(Z) = Z_n + A + L + G$

$$L \rightleftarrows y\, G + u\, Z_n + (1-y-u)\, A \qquad (\Delta V)_Z \quad ; \quad (\Delta H)_Z$$

Herein $x, y, u, 1-x$ and $1-x-y$ have positive values, which may be determined when the compositions of the phases are known. $(\Delta V)_M$ and $(\Delta H)_M$ are the changes in volume and entropy when reaction (1) proceeds from left to right, so that the indicated quantities participate in the reaction. The same is true for $(\Delta V)_Z$ and $(\Delta H)_Z$. At the following reactions we shall indicate in the same way the changes in volume and entropy.

Now we may deduce, as has been discussed formerly, from 1 and 2 the reactions for the other monovariant equilibria and also the isovolumetrical and isentropical reaction. We find:

3. For the equilibrium $(G) = Z + Z_n + A + L$

$(y + xu) Z_n + x (1-y-u) A \leftrightarrows x L + y (1-x) Z$ $(\Delta V)_G$; $(\Delta H)_G$.

Herein is :

$(\Delta V)_G = y (\Delta V)_M - x (\Delta V)_Z$; $(\Delta H)_G = y (\Delta H)_M - x (\Delta H)_Z$

4. For the equilibrium $(Z_n) = Z + A + L + G$

$L \leftrightarrows (y + ux) G + u (1-x) Z + (1-y-u) A$ $(\Delta V)_n$; $(\Delta H)_n$

Herein is:

$(\Delta V)_n = u (\Delta V)_M + (\Delta V)_Z$; $(\Delta H)_n = u (\Delta H)_M + (\Delta H)_Z$

5. For the isovolumetrical reaction:

$(\Delta V)_n . Z_n + (1-y-u) (\Delta V)_M . A + (\Delta V)_G . G \leftrightarrows$

$\quad (1-x) (\Delta V)_Z . Z + (\Delta V)_M . L \qquad 0$: $(\Delta H)_V$

Herein is: $(\Delta H)_V = (\Delta V)_Z . (\Delta H)_M - (\Delta V)_M . (\Delta H)_Z$

6. For the isentropical reaction:

$(\Delta H)_n . Z_n + (1-y-u) (\Delta H)_M . A + (\Delta H)_G . G \rightleftarrows$

$\quad (1-x) (\Delta H)_Z . Z + (\Delta H)_M . L \qquad (\Delta V)_H$; 0.

Herein is: $(\Delta V)_H = (\Delta V)_M . (\Delta H)_Z - (\Delta V)_Z (\Delta H)_M$

consequently $\qquad (\Delta V)_H = - (\Delta H)_V$

In order to express in another way the occurring changes in volume and entropy, we represent the volumes and entropies of the unity of quantity of the phases

$$Z \quad Z_n \quad A \quad L \quad \text{and} \quad G$$

by $\qquad\qquad V_Z \quad V_n \quad V_A \quad V_L \quad \text{and} \quad V_G$

and $\qquad\qquad H_Z \quad H_n \quad H_A \quad H_L \quad \text{and} \quad H_G$

With the aid of the reactions 1—6 we find :

$(\Delta V)_M = x V_G + (1-x) V_Z - V_L$

$(\Delta H)_M = x H_G + (1-x) H_Z - H_L$

$(\Delta V)_Z = y V_G + u V_n + (1-y-u) V_A - V_L$

$(\Delta H)_Z = y H_G + u H_n + (1-y-u) H_A - H_L$

$(\Delta V)_G = x V_L + y (1-x) V_Z - (y+xu) V_n - x (1-y-u) V_A$

$(\Delta H)_G = x H_L + y (1-x) H_Z - (y+xu) H_n - x (1-y-u) H_A$

$(\Delta V)_n = (y + ux) V_G + u (1-x) V_Z + (1-y-u) V_A - V_L$

$(\Delta H)_n = (y + ux) H_G + u (1-x) H_Z + (1-y-u) H_A - H_L$

$(\Delta H)_V = (1-x) (\Delta V)_Z H_Z + (\Delta V)_M . H_L - (\Delta V)_n . H_n$

$\qquad\qquad - (1-y-u) (\Delta V)_M . H_A - (\Delta V)_G H_G$

$(\Delta V)_H = (1-x) (\Delta H)_Z V_Z + (\Delta H)_M . V_L - (\Delta H)_n . V_n$

$\qquad\qquad - (1-y-u) (\Delta H)_M . V_A - (\Delta H)_G V_G .$

Now we have to examine whether those changes in volume and entropy are positive or negative. When we knew the values of $x, y, u, V_Z \ldots, H_Z \ldots$, then those changes would be easy to calculate. When this is not the case, then we have to try to find in another way they are positive or not.

$(\Delta V)_M$ and $(\Delta H)_M$ are the increase of volume and entropy at the reaction

$$Z_n \rightarrow x \, G + (1 - x) \, Z$$

consequently at the separation of the hydrate Z_n into anhydric salt Z and watervapour G. Consequently we are allowed to assume that $(\Delta V)_M$ and $(\Delta H)_M$ are positive.

$(\Delta V)_Z$ and $(\Delta H)_Z$. We write :

$$(\Delta V)_Z = y \, (V_G - V_A) + u V_n + (1 - u) \, V_A - V_L$$
$$(\Delta H)_Z = y \, (H_G - H_A) + u H_n + (1 - u) \, H_A - H_L.$$

Consequently both are positive for values of y which are not too small. For small values of y $(\Delta H)_Z$ becomes negative, for $y = 0$ we find viz

$$(\Delta H)_Z = u H_n + (1 - u) \, H_A - H_L$$

which is negative, when we assume that heat is wanted for the melting of solid substances.

$(\Delta V)_Z$ can become negative for very small values of y; for this is it necessary that $u \, V_n + (1 - u) \, V_A - V_L$ is negative.

$(\Delta V)_G$ and $(\Delta H)_G$. It appears from the value of $(\Delta V)_G$ that this may be as well positive as negative. $(\Delta H)_G$ is the change in entropy at reaction 3, in which only solid substances and the liquid L participate. When we assume that heat is wanted for the formation of liquid, then $(\Delta H)_G$ is positive.

$(\Delta V)_n$ and $(\Delta H)_n$. $(\Delta V)_n$ is always positive on account of the large value of V_G. For $y = 0$ becomes:

$$(\Delta V)_n = u x \, V_G + u (1 - x) \, V_Z + (1 - u) \, V_A - V_L .$$

When in fig. 1 the point m is not situated in the immediate vicinity of point A, so that u and consequently also $u x$ does not become extremely small, then $(\Delta V)_n$ is still positive, even for $y = 0$.

$(\Delta H)_n$ is positive; for small values of y it may, however, become negative, for this it is necessary that

$$u x \, H_G + u (1 - x) \, H_Z + (1 - u) \, H_A - H_L$$

is negative.

$(\Delta V)_H$ and $(\Delta H)_H$. It is apparent from the value mentioned for $(\Delta V)_H$ that this has the same sign as $- (\Delta H)_G$ on account of the large value of V_G. Hence it appears that $(\Delta V)_H < 0$ and $(\Delta H)_V > 0$.

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We have seen above that the sign of $(\Delta V)_Z$, $(\Delta H)_Z$ and $(\Delta H)_n$ depends on the value of y, consequently of the position of the point m in fig. 1. In proportion as viz. the point m is situated more closely to the line AZ_n, y becomes smaller; when m is situated on AZ_n then $y = 0$.

1. First we consider the case that the point m is situated not too closely to the line AZ_n. Then we have:

$(\Delta V)_M$, $(\Delta V)_Z$ and $(\Delta V)_n > 0$; $(\Delta V)_H < 0$; $(\Delta V)_G \gtrless 0$

$(\Delta H)_M$, $(\Delta H)_Z$, $(\Delta H)_G$, $(\Delta H)_n$ and $(\Delta H)_V > 0$.

It follows from 5, when we omit the reaction coefficients, for the isovolumetrical reaction that:

$$Z_n + A \pm G \rightleftarrows Z + L \qquad 0 \; ; \; (\Delta H)_V > 0$$

$$(Z)\,(L) \qquad (Z_n)\,(A)$$
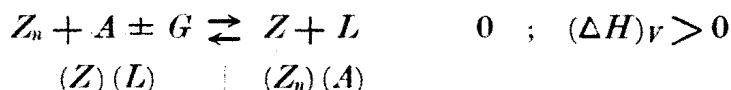
Towards lower T | Towards higher T.

As $(\Delta V)_G$ may be as well positive as negative, we give in this reaction to the phase G as well the sign $+$ as $-$

It follows from this reaction that the curves (Z) and (L) go towards lower temperatures starting from the invariant point m and the curves (Z_n) and (A) towards higher temperatures. As the phase G may have as well the positive as the negative sign, the direction of curve (G) is undefined; it may go, starting from the invariant point as well towards higher as towards lower T.

When we omit the coefficients in the isentropical reaction, then follows from 6:

$$Z_n + A + G \rightleftarrows Z + L \qquad (\Delta V)_H < 0 \; ; \; 0$$

$$(Z)\,(L) \qquad (Z_n)\,(A)\,(G)$$
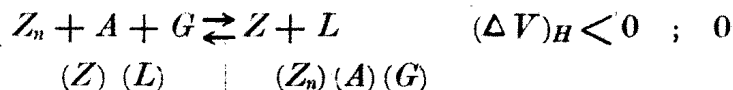
Towards lower P | Towards higher P.

Hence it appears that the curves (Z) and (L) go towards lower pressures, starting from the invariant point and the curves (Z_n), (A) and (G) go towards higher pressures.

It is apparent from both these reactions that the curves must be situated as in fig. 2 as regards their direction of pressure and temperature. The curves (Z) and (L) must go viz. starting from m towards lower P and T, the curves (Z_n) and (A) towards higher P and T. Curve (G) must go towards higher P, starting from m, but it may go as well towards lower as towards higher T.

Now we have still to determine the position of the curves with respect to one another. We have viz. still to show that in fig. 2 curve (Z_n) is situated below curve (A) and above the metastable prolongation of curve (Z), etc.

As in the three singular equilibria (M), (A) and (L) the same reaction (1) occurs:

$$\left(\frac{dP}{dT}\right)_M = \left(\frac{dP}{dT}\right)_A = \left(\frac{dP}{dT}\right)_L = \frac{(\Delta H)_M}{(\Delta V)_M}.$$

For the equilibrium (Z_n) we have

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

Hence it follows:

$$\left(\frac{dP}{dT}\right)_A - \left(\frac{dP}{dT}\right)_n = \frac{(\Delta H)_M}{(\Delta V)_M} - \frac{(\Delta H)_n}{(\Delta V)_n}.$$

As $(\Delta V)_M$ and $(\Delta V)_n$ are positive, the second side has the same sign as

$$(\Delta V)_n (\Delta H)_M - (\Delta V)_M (\Delta H)_n$$

As, in accordance with (4)

$$(\Delta V)_n = u(\Delta V)_M + (\Delta V)_Z \text{ and } (\Delta H)_n = u(\Delta H)_M + (\Delta H)_Z$$

that form passes into:

$$(\Delta V)_Z (\Delta H)_M - (\Delta V)_M (\Delta H)_Z = (\Delta H)_V > 0.$$

Consequently it is apparent from this:

$$\left(\frac{dP}{dT}\right)_A - \left(\frac{dP}{dT}\right)_n > 0 \text{ or } \left(\frac{dP}{dT}\right)_A > \left(\frac{dP}{dT}\right)_n$$

Or curve (A) must be situated in fig. 2 above curve (Z_n).
Now we take:

$$\left(\frac{dP}{dT}\right)_n - \left(\frac{dP}{dT}\right)_Z = \frac{(\Delta H)_n}{(\Delta V)_n} - \frac{(\Delta)_Z}{(\Delta V)_Z}.$$

The second part has the same sign as:

$$(\Delta V)_Z (\Delta H)_n - (\Delta V)_n (\Delta H)_Z.$$

When we substitute in this again the values of $(\Delta V)_n$ and $(\Delta H)_{jn}$ from 4, then it passes into $u(\Delta H)_V > 0$. Hence it follows:

$$\left(\frac{dP}{dT}\right)_n - \left(\frac{dP}{dT}\right)_Z > 0 \text{ or } \left(\frac{dP}{dT}\right)_n > \left(\frac{dP}{dT}\right)_Z$$

or curve (Z_n) must be situated in fig. 2 above the prolongation of curve (Z).

II. Now we let the point m in fig. 1 approach more closely to line AZ_n, so that y gets small values. As long as the changes in volume and entropy keep the same signs as in 1, we obtain a P,T-diagram as in fig. 2.

For small values of y $(\Delta V)_Z$, $(\Delta H)_Z$ and $(\Delta H)_n$ may change their

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sign and become, therefore, negative; now we shall consider those cases more in detail.

The first of those three quantities which becomes negative when y diminishes, is

$$(\Delta H)_Z = y\,(H_G - H_A) + u\,H_n + (1 - u)\,H_A - H_L.$$

When $(\Delta V)_Z = y\,(V_G - V_A) + u\,V_n + (1 - u)\,V_A - V_L$ becomes negative, then this may however, only take place, on account of the large value of V_G, for very small values of y.

$(\Delta H)_n$ can only become negative, when $(\Delta H)_Z$ is negative: this follows from:

$$(\Delta H)_n = u\,(\Delta H)_M + (\Delta H)_Z$$

in which $u\,(\Delta H)_M$ is positive.

Consequently we distinguish four cases.

a. $(\Delta H)_Z < 0$: $(\Delta V)_Z > 0$; $(\Delta H)_n > 0$

b. $(\Delta H)_Z < 0$; $(\Delta V)_Z > 0$; $(\Delta H)_n < 0$

c. $(\Delta H)_Z < 0$; $(\Delta V)_Z < 0$: $(\Delta H)_n > 0$ $(\Delta V)_G > 0$

d. $(\Delta H)_Z < 0$; $(\Delta V)_Z < 0$; $(\Delta H)_n < 0$ $(\Delta V)_G > 0.$

In c and d at the same time $(\Delta V)_G$ is taken > 0; it follows from:

$$(\Delta V)_G = y\,(\Delta V)_M - x\,(\Delta V)_Z$$
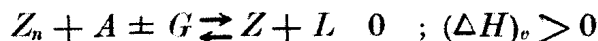
that this must be the case.

Hence it appears viz. that for extremely small values of y [and only for those $(\Delta V)_Z$ may become negative] $(\Delta V)_G$ and $(\Delta V)_Z$ have opposite signs.

a. Now we have:

$(\Delta V)_M$, $(\Delta V)_Z$ and $(\Delta V)_n > 0$; $(\Delta V)_H < 0$; $(\Delta V)_G \gtrless 0$

$(\Delta H)_M$, $(\Delta H)_G$, $(\Delta H)_n$ and $(\Delta H)_y > 0$; $(\Delta H)_Z < 0.$

When we omit the coefficients in (5), then the isovolumetrical reaction becomes:

$$Z_n + A \pm G \rightleftarrows Z + L \quad 0 \quad ; (\Delta H)_v > 0$$

$$(Z)\ (L) \mid (Z_n)\ (A)$$

Towards lower T | Towards higher T

If follows from (6) for the isentropical reaction:

$$Z + Z_n + A + G \rightleftarrows L \qquad (\Delta V)_H < 0 \quad ; \quad 0$$

$$(L) \mid (Z)\ (Z_n)\ (A)\ (G)$$

Towards lower P | Towards higher P

It follows from both these reactions that the curves must be

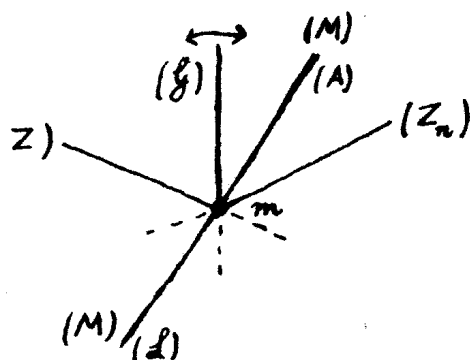situated as in fig. 3, with respect to their directions of temperature and pressure.

Fig. 3.

In the same way as in I we may show that curve Z_n must be situated below curve (A) and above the metastable part of curve (Z), etc, so that we obtain a partition of curves as in fig. 3.
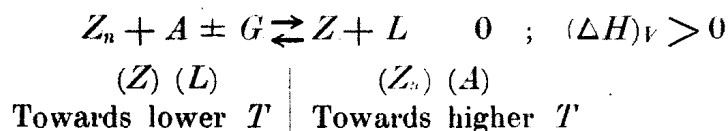
Fig. 2 and 3 differ from one another only in this respect that curve (Z) goes, starting from m in fig. 2 towards lower and in fig. 3 towards higher pressures.

b. Now we have:

$(\Delta V)_M, (\Delta V)_Z$ and $(\Delta V)_n > 0 ; (\Delta V)_H < 0 ; (\Delta V)_G \gtreqless 0$

$(\Delta H)_M, (\Delta H)_G$ and $(\Delta H)_V > 0 ; (\Delta H)_n$ and $(\Delta H)_Z < 0$

The isovolumetrical reaction becomes:

$$Z_n + A \pm G \rightleftarrows Z + L \qquad 0 \quad ; \quad (\Delta H)_V > 0$$

(Z) (L)	(Z_n) (A)
Towards lower T	Towards higher T

The isentropical reaction becomes:

$$Z + A + G \rightleftarrows Z_n + L \qquad (\Delta V)_H < 0 \quad ; \quad 0$$

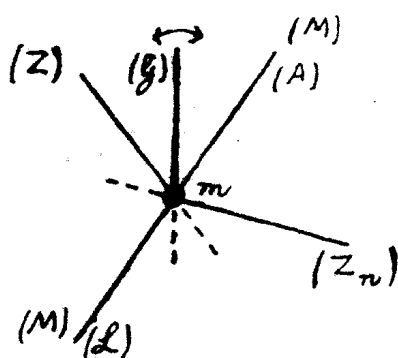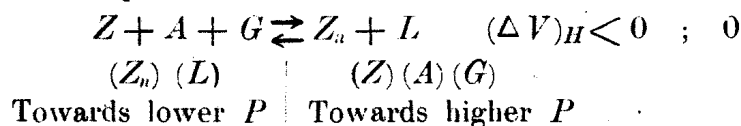| (Z_n) (L)	(Z) (A) (G)
Towards lower P	Towards higher P

Fig. 4.

From both these reactions it follows that the curves must be situated as in fig. 4 with respect to their directions of temperature and pressure. In the same way as in I we may show now again that curve (Z_n) must be situated below curve (A) and above the metastable part of curve (Z), etc. so that we obtain a partition of the curves as in fig. 4.
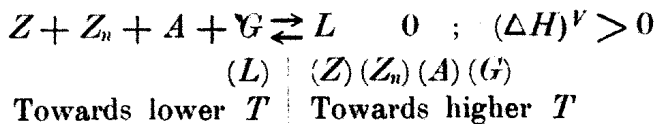
Figs. 3 and 4 differ from one another only in that respect, that curve (Z_n) goes starting from m in fig. 3 towards higher and in fig. 4 towards lower pressures.

c. Now we have

$(\Delta V)_M, (\Delta V)_n$ and $(\Delta V)_G > 0$; $(\Delta V)_Z$ and $(\Delta V)_H < 0$

$(\Delta H)_M, (\Delta H)_n, (\Delta H)_G$ and $(\Delta H)_\Gamma > 0$; $(\Delta H)_Z < 0$.

The isovolumetrical reaction becomes now:

$$Z + Z_n + A + G \rightleftarrows L \qquad 0 \quad ; \quad (\Delta H)^V > 0$$

$$(L) \quad | \quad (Z) (Z_n) (A) (G)$$

Towards lower T | Towards higher T

The isentropical reaction becomes:

$$Z + Z_n + A + G \rightleftarrows L \qquad (\Delta V)_H < 0 \quad ; \quad 0$$

$$(L) \quad | \quad (Z) (Z_n) (A) (G)$$

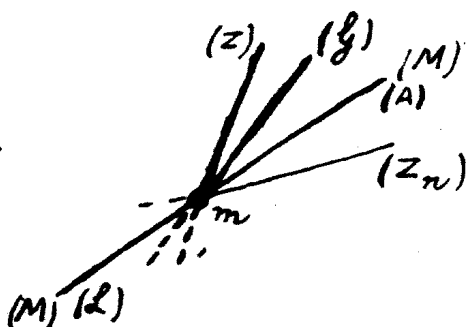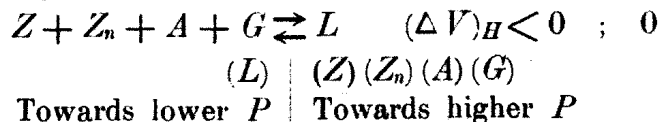Towards lower P | Towards higher P

Fig. 5.

From both these reactions it follows that the curves must be situated as in fig. 5 with respect to their direction of temperature and pressure.

Now we have still to show that curve (Z) is situated above (G), curve (G) above (A) and curve (A) above (Z_n); this latter appears again in the same way as in I.

In order to show that curve (Z) is situated above curve (G) we take:

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

As $(\Delta V)_Z$ is negative, the second part has the same sign as:

$$(\Delta V)_Z . (\Delta H)_G - (\Delta V)_G . (\Delta H)_Z.$$

When we substitute in this:

$$(\Delta V)_G = y(\Delta V)_M - x(\Delta V)_Z \text{ and } (\Delta H)_G = y(\Delta H)_M - x(\Delta H)_Z$$

then we find:

$$y[(\Delta V)_Z(\Delta H)_M - (\Delta V)_M(\Delta H)_Z] = y(\Delta H)_V > 0$$

Hence it is apparent that in fig. 5 curve (Z) must be situated above curve (G).

In order to show that curve (G) is situated above curve (A) we take:

$$\left(\frac{dP}{dT}\right)_G - \left(\frac{dP}{dT}\right)_A = \frac{(\Delta H)_G}{(\Delta V)_G} - \frac{(\Delta H)_M}{(\Delta V)_M}.$$
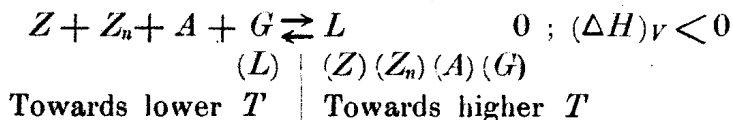
In the same way as above we find that the second part must have the same sign as $x(\Delta H)_V$, so that this is positive. In fig. 5 curve (G) must be situated, therefore, above curve (A).

d. Now we have:

$(\Delta V)_M$, $(\Delta V)_n$ and $(\Delta V)_G > 0$; $(\Delta V)_Z$ and $(\Delta V)_H < 0$
$(\Delta H)_M$, $(\Delta H)_G$ and $(\Delta H)_V > 0$; $(\Delta H)_Z$ and $(\Delta H)_n < 0$.

The isovolumetrical reaction becomes:

$$Z + Z_n + A + G \rightleftarrows L \qquad\qquad 0 \;;\; (\Delta H)_V < 0$$

$$(L) \;\mid\; (Z)\,(Z_n)\,(A)\,(G)$$

Towards lower T | Towards higher T

The isentropical reaction becomes:

$$Z + A + G \rightleftarrows Z_n + L \qquad (\Delta V)_n < 0 \;;\; 0$$

$$(Z_n)\,(L) \qquad\mid\quad (Z)\,(A)\,(G)$$
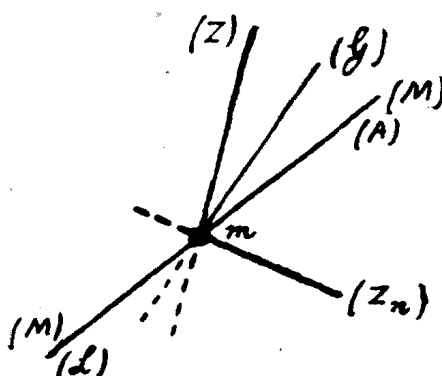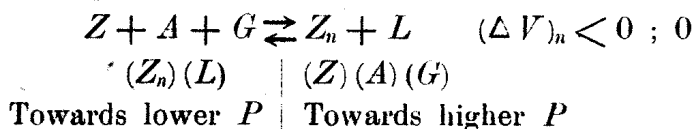
Towards lower P | Towards higher P

Fig. 6.

From both these reactions it appears that the curves must be situated as in fig. 6 with respect to their direction of temperature and pressure. It is apparent in the same way as in c, that, just as in fig. 5, also in fig. 6 curve (Z) must be situated above (G) and curve (G) above (A).

The only difference between fig. 5 and fig. 6 is this: curve (Z_n) goes, starting from m in fig. 5 towards higher, in fig. 6 towards lower pressures.

When we compare the P, T-diagrams deduced above, with one another, then we see that they belong to a same type, viz. that of fig 4 (XII). This must, of course, be the case, as the phases, G, Z_n, Z, L_m and A are situated with respect to one another in the same way as the five phases in fig. 3 (XII).

In a P, T-diagram we imagine a curve $X + Y + L + G$, to be drawn in which X and Y represent two salts. On this curve is situated a point of maximum-pressure, there may also be situated a point of maximum temperature. We call the part at the left of the point of maximum pressure the ascending branch, the part between the point of maximum pressure and the point of maximum temperature the descending branch and the other part the returning branch.

The difference between the figs 2—6 is dependent on the position of the invariant point m. In fig. 2 this point is situated on the ascending branch of each of the curves (Z) and (Z_n), in fig. 3 on the descending branch of curve (Z) and on the ascending branch of (Z_n), in fig. 4 on the descending branch of each of the curves (Z) and (Z_n) in fig. 5, on the returning branch of curve (Z) and on

the ascending branch of (Z_n) and in fig. 6 on the returning branch of curve (Z) and on the descending branch of curve (Z_n).

As we have found now the P,T-diagrams, we may easily deduce the corresponding concentration-diagrams with the aid of those.

I shall not enter into this subject any further and leave this deduction to the reader.
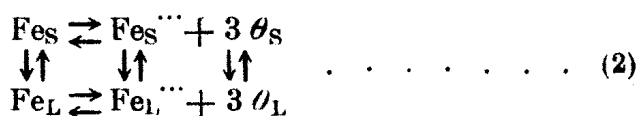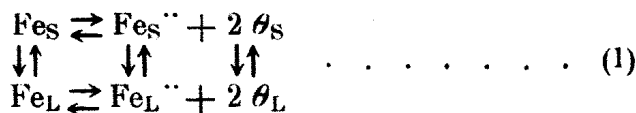
Leiden, Inorg. Chem. Lab.   *(To be continued.)*

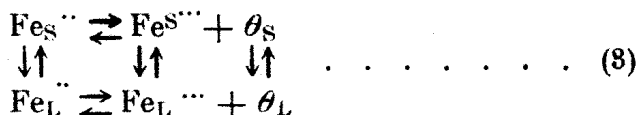**Chemistry**. — *"A New Method for the Passification of Iron."* By Prof. A. SMITS and C. A. LOBRY DE BRUYN. (Communicated by Prof. P. ZEEMAN).

(Communicated in the meeting of Dec. 21, 1916).

I. If iron is immersed in an electrolyte, we have to deal with the following complex equilibria:

$$Fe_S \rightleftarrows Fe_S\ddot{} + 2\,\theta_S$$
$$\updownarrow \qquad \updownarrow \qquad \updownarrow$$
$$Fe_L \rightleftarrows Fe_L\ddot{} + 2\,\theta_L \qquad\qquad \dots \dots \dots (1)$$

$$Fe_S \rightleftarrows Fe_S\dddot{} + 3\,\theta_S$$
$$\updownarrow \qquad \updownarrow \qquad \updownarrow$$
$$Fe_L \rightleftarrows Fe_L\dddot{} + 3\,\theta_L \qquad\qquad \dots \dots \dots (2)$$

from which follows:

$$Fe_S\ddot{} \rightleftarrows Fe^{S\dddot{}} + \theta_S$$
$$\updownarrow \qquad \updownarrow \qquad \updownarrow$$
$$Fe_L\ddot{} \rightleftarrows Fe_L\dddot{} + \theta_L \qquad\qquad \dots \dots \dots (3)$$

Those of these equilibria that are indicated by vertical arrows except the equilibrium between the uncharged ironatoms in the solid phase and the electrolyte refer to that part of the heterogeneous equilibrium that governs the potential difference.

Now it has been pointed out before that the iron, which is in internal equilibrium, can be in electromotive equilibrium only with a solution which contains almost exclusively ferro-ions, so that under these circumstances the equilibrium:

$$Fe_L\ddot{} \rightleftarrows Fe_L\dddot{} + \theta_L$$
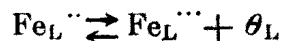
in solution lies almost entirely to the left.

If we now add ferri-ions, a consequence of this will be that ferro-ions and electrons from the iron go into solution, which disturbs the equilibrium in the iron surface.

This disturbance can now cease again, as a result of the reaction

$$Fe_S \rightarrow Fe_S\ddot{} + 2\,\theta_S$$