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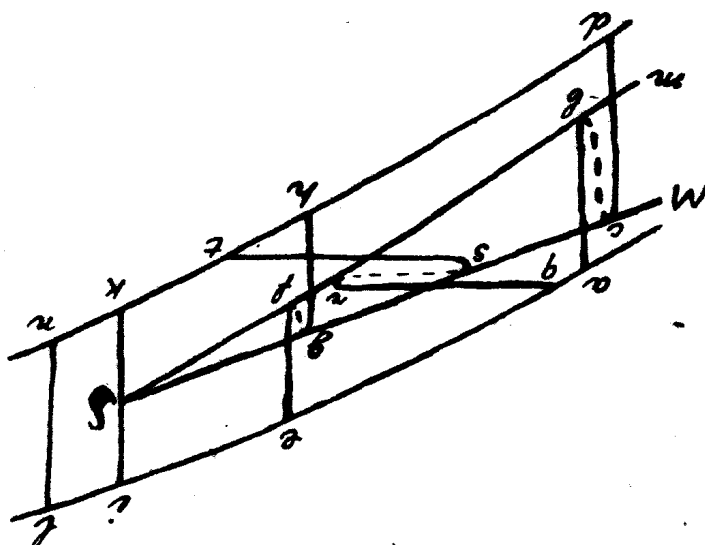


Fig. 7.

its own vapour-pressure have no more a point of minimum- or maximum-pressure, the pressure increases from  $n$  towards  $l$  (figs. 6 and 7).

The point of minimum pressure follows therefore, in figs. 6 and 7 a curve  $mS$ , the point of maximum-pressure follows a curve  $MS$ . The equilibrium  $E_R$  consists, therefore, of two branches, which meet in  $S$ ; we may, however, also say that only one single turning-line exists  $E_R = mSM$ , which has a singular point in  $S$ .

Later we shall show in general that the two branches  $mS$  and  $MS$  of a turning-line  $E_R$  touch one another in the singular point  $S$  and that the tangent in  $S$  is situated between the two branches.

The region  $E$  in fig. 7 is now one-leafed, except in the part, situated within the turning-line, which is three-leafed. Of course this is only true in so far as this part is situated between the limit-lines.

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(*To be continued.*)

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

(Communicated in the meeting of April 28, 1917).

*Equilibria of  $n$  components in  $n$  phases.*

Now we shall consider more in detail the equilibrium:

$$E = F_1 + F_2 + \dots + F_n \dots \dots \dots (1)$$

which we have already discussed in the previous communication.

We represent the composition of:

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$$F_1 \text{ by } x_1, y_1, z_1, \dots, 1 - x_1 - y_1 - z_1, \dots$$

$$F_2 \text{ ,, } x_2, y_2, z_2, \dots, 1 - x_2 - y_2 - z_2, \dots$$

The  $\xi$ , the entropy and the volume of  $F_1$ , we call  $Z_1, H_1$ , and  $V_1$ ; those of  $F_2$ , we call  $Z_2, H_2$  and  $V_2$ ; etc.

Then we may write the conditions for equilibrium:

$$\left. \begin{aligned} Z_1 - x_1 \frac{\partial Z_1}{\partial x_1} - y_1 \frac{\partial Z_1}{\partial y_1} \dots &= K \\ Z_2 - x_2 \frac{\partial Z_2}{\partial x_2} - y_2 \frac{\partial Z_2}{\partial y_2} \dots &= K \end{aligned} \right\} \dots \dots \dots (2)$$

viz.  $n$  equations (2) of which we only have written two. Further we have:

$$\left. \begin{aligned} \frac{\partial Z_1}{\partial x_1} = \frac{\partial Z_2}{\partial x_2} = \dots = \frac{\partial Z_n}{\partial x_n} &= K_x \\ \frac{\partial Z_1}{\partial y_1} = \frac{\partial Z_2}{\partial y_2} = \dots = \frac{\partial Z_n}{\partial y_n} &= K_y \end{aligned} \right\} \dots \dots \dots (3)$$

The corresponding equations for the variables  $z_1, z_2, \dots, u_1, u_2, \dots$  etc. have still to be added to (3).

We find in (2)  $n$ , in (3)  $n(n-1)$ , consequently in total  $n^2$  equations. Besides the  $n(n-1)$  variables  $x_1, y_1, \dots, x_n, y_n, \dots$  etc. we have still the  $n+2$  variables  $T, P, K, K_x, K_y, \dots$  consequently in total  $n^2 + 2$  variables. The equilibrium  $E$  has, therefore, two degrees of freedom and consequently it is bivariant.

We have assumed in (2) and (3) the general case that all phases have a variable composition and that each phase contains all components. When this is not the case, then we are able to make at once the necessary alterations in (2) and (3). When e.g.  $F_1$  has a constant composition  $x_1 = \alpha, y_1 = \beta$ , etc., then the first equation (2) passes into:

$$Z_1 - \alpha \frac{\partial Z_1}{\partial x_1} - \beta \frac{\partial Z_1}{\partial y_1} \dots = K \dots \dots \dots (4)$$

in which the index  $i$  relates then to a phase  $F_i$  of variable composition. Then  $Z_1$  is only still a function of  $P$  and  $T$ ; in (3) then  $\frac{\partial Z_1}{\partial x_1}, \frac{\partial Z_1}{\partial y_1}$  etc. .... disappear.

When we give to  $P, T, x, y, \dots$  the differentials  $\Delta P, \Delta T, \Delta x, \Delta y, \dots$  then we have:

$$\Delta Z = V \Delta P - H \Delta T + \frac{\partial Z}{\partial x} \Delta x + \frac{\partial Z}{\partial y} \Delta y + \dots + \frac{1}{2} d^2 Z + \frac{1}{6} d^3 Z + \dots$$

$$\Delta \left( x \frac{\partial Z}{\partial x} \right) = \frac{\partial Z}{\partial x} \Delta x + (x + \Delta x) \left[ d \frac{\partial Z}{\partial x} + \frac{1}{2} d^2 \frac{\partial Z}{\partial x} + \dots \right]$$

$$\Delta \left( y \frac{\partial Z}{\partial y} \right) = \frac{\partial Z}{\partial y} \Delta y + (y + \Delta y) \left[ d \frac{\partial Z}{\partial y} + \frac{1}{2} d^2 \frac{\partial Z}{\partial y} + \dots \right]$$

Herein the sign  $d$  indicates that we have to differentiate according to all variables, which the function contains. Further is:

$$d^2 Z = d \frac{\partial Z}{\partial P} \cdot \Delta P + d \frac{\partial Z}{\partial T} \cdot \Delta T + d \frac{\partial Z}{\partial x} \cdot \Delta x + d \frac{\partial Z}{\partial y} \cdot \Delta y + \dots$$

$$d^3 Z = d^2 \frac{\partial Z}{\partial P} \cdot \Delta P + d^2 \frac{\partial Z}{\partial T} \cdot \Delta T + d^2 \frac{\partial Z}{\partial x} \cdot \Delta x + d^2 \frac{\partial Z}{\partial y} \cdot \Delta y + \dots$$

When we neglect in  $d^2 Z$  and  $d^3 Z$  the terms which are infinitely small with respect to  $\Delta P$  and  $\Delta T$ , then we may write:

$$d^2 Z = d \frac{\partial Z}{\partial x} \cdot \Delta x + d \frac{\partial Z}{\partial y} \cdot \Delta y + \dots$$

$$d^3 Z = d^2 \frac{\partial Z}{\partial x} \cdot \Delta x + d^2 \frac{\partial Z}{\partial y} \cdot \Delta y + \dots$$

From a form:

$$Z - x \frac{\partial Z}{\partial x} - y \frac{\partial Z}{\partial y} - \dots = K$$

it follows, therefore:

$$\begin{aligned} -V\Delta P + H\Delta T + (x + \Delta x) \left( d \frac{\partial Z}{\partial x} + \dots \right) + (y + \Delta y) \left( d \frac{\partial Z}{\partial y} + \dots \right) - \left\{ \right. \\ \left. - \frac{1}{2} d^2 Z - \frac{1}{6} d^3 Z - \dots = -\Delta K \right. \end{aligned} \quad (5)$$

Now is

$$\Delta x \left[ d \frac{\partial Z}{\partial x} + \frac{1}{2} d^2 \frac{\partial Z}{\partial x} + \dots \right] + \Delta y \left[ d \frac{\partial Z}{\partial y} + \frac{1}{2} d^2 \frac{\partial Z}{\partial y} + \dots \right] = d^2 Z + \frac{1}{2} d^3 Z + \dots$$

so that we may write for (5)

$$\begin{aligned} -VdP + HdT + x \left[ d \frac{\partial Z}{\partial x} + \dots \right] + y \left[ d \frac{\partial Z}{\partial y} + \dots \right] + \dots \left\{ \right. \\ \left. + \frac{1}{2} d^2 Z + \frac{1}{6} d^3 Z + \dots = -\Delta K \right. \end{aligned} \quad (6)$$

Now we apply this to the  $n$  equations (2) and we differentiate further also the  $n(n-1)$  equations (3). First, however, we shall introduce the following notation; we put viz:

$$\frac{\partial Z_1}{\partial x_1} = (x)_1; \quad \frac{\partial Z_2}{\partial y_2} = (y)_2; \quad \frac{\partial^2 Z_3}{\partial x_3^2} = (x^2)_3; \quad \frac{\partial^3 Z_4}{\partial x_4^2 \partial y_4} = (x^2 y)_4 \text{ enz.}$$

The index outside the parentheses indicates, therefore, which of the functions  $Z_1 \dots Z_n$  has to be differentiated; the letters within the parentheses indicate according to which variables we have to differentiate.

Then it follows from the  $n$  equations (2):

$$\left. \begin{aligned} -V_1 \Delta P + H_1 \Delta T + x_1 [d(x)_1 + \dots] + y_1 [d(y)_1 + \dots] + \dots \\ \quad + \frac{1}{2} d^2 Z_1 + \frac{1}{3} d^3 Z_1 + \dots = -\Delta K \\ -V_2 \Delta P + H_2 \Delta T + x_2 [d(x)_2 + \dots] + y_2 [d(y)_2 + \dots] + \dots \\ \quad + \frac{1}{2} d^2 Z_2 + \frac{1}{3} d^3 Z_2 + \dots = -\Delta K \end{aligned} \right\} \cdot (7)$$

and still  $n-2$  other equations. It follows from (3)

$$\left. \begin{aligned} d(x)_1 + \frac{1}{2} d^2(x)_1 + \dots = d(x)_2 + \frac{1}{2} d^2(x)_2 + \dots = \Delta K_x \\ d(y)_1 + \frac{1}{2} d^2(y)_1 + \dots = d(y)_2 + \frac{1}{2} d^2(y)_2 + \dots = \Delta K_y \end{aligned} \right\} \cdot (8)$$

etc. In accordance with our notation is e.g.

$$d(x)_1 = (Px)_1 \Delta P + (Tx)_1 \Delta T + (x^2)_1 \Delta x_1 + (xy)_1 \Delta y_1 + \dots$$

or

$$\frac{\partial V_1}{\partial x_1} \Delta P - \frac{\partial H_1}{\partial x_1} \Delta T + \frac{\partial^2 Z_1}{\partial x_1^2} \Delta x_1 + \frac{\partial^2 Z_1}{\partial x_1 \partial y_1} \Delta y_1 + \dots$$

$$d(y)_1 = (Py)_1 \Delta P + (Ty)_1 \Delta T + (xy)_1 \Delta x_1 + (y^2)_1 \Delta y_1 + \dots$$

or

$$\frac{\partial V_1}{\partial y_1} \Delta P - \frac{\partial H_1}{\partial y_1} \Delta T + \frac{\partial^2 Z_1}{\partial x_1 \partial y_1} \Delta x_1 + \frac{\partial^2 Z_1}{\partial y_1^2} \Delta y_1 + \dots$$

When a phase e.g.  $F_1$  has a constant composition, then for this (4) is true; instead of the first equation (7) we find then:

$$-V_1 \Delta P + H_1 \Delta T + \alpha [d(x)_i + \dots] + \beta [d(y)_i + \dots] = -\Delta K.$$

Consequently in the first equation (7) are missing then the terms  $d^2 Z_1, d^3 Z_1$  etc.

*Equilibria of n components in n phases under constant pressure.*

When we keep the pressure constant, then we have to omit in (7) and (8) all the terms with  $\Delta P$ ; the sign  $d$  indicates then that we have to differentiate according to all variables, except  $P$ .

Now we have in (7) and (8)  $n^2$  equations and  $n^2+1$  differentials  $\Delta T, \Delta x_1, \dots$ , so that their relations are defined. Consequently to each definite differential of one of the variables e.g.  $\Delta x_1$  belongs a definite differential of each of the other variables, therefore, e.g. also of  $\Delta T$ . On change of  $x_1$  (or one of the other variables) the equilibrium  $E$  follows, therefore, in the  $P, T$ -diagram a straight line, parallel to the  $T$ -axis.

Now we shall put the question: when will the temperature be maximum or minimum?

For this it is necessary that  $\Delta T$  is of the second order; then it follows from (7) and (8) that it must be possible to satisfy:

$$\left. \begin{aligned} x_1 d(x)_1 + y_1 d(y)_1 + \dots = \Delta K \\ x_2 d(x)_2 + y_2 d(y)_2 + \dots = \Delta K \\ \dots \dots \dots \end{aligned} \right\} \dots \dots \dots (9)$$

and

$$\left. \begin{aligned} d(x)_1 = d(x)_2 = \dots = d(x)_n = \Delta K_x \\ d(y)_1 = d(y)_2 = \dots = d(y)_n = \Delta K_y \\ \dots \end{aligned} \right\} \dots \dots \dots (10)$$

in which  $d$  indicates now that we have to differentiate according to all variables except  $P$  and  $T$ .

It must be possible to solve the ratios between the  $n^2$  differentials  $\Delta x_1, \Delta x_2, \dots, \Delta y_1, \Delta y_2, \dots, \Delta K, \Delta K_x, \dots$  from the  $n^2$  equations (9) and (10); this is only then possible, when a relation exists between the coefficients. With the aid of (10) we write for (9):

$$\left. \begin{aligned} x_1 \Delta K_x + y_1 \Delta K_y + \dots = \Delta K \\ x_2 \Delta K_x + y_2 \Delta K_y + \dots = \Delta K \\ \dots \end{aligned} \right\} \dots \dots \dots (11)$$

so that we must be able to satisfy (10) and (11). Here this is the case when we are able to satisfy (11).

When we add the  $n$  equations (11) after having multiplied the first one by  $\lambda_1$ , the second one by  $\lambda_2$ , etc., then we obtain:

$$\Sigma (\lambda x) \Delta K_x + \Sigma (\lambda y) \Delta K_y + \Sigma (\lambda) \Delta K \dots \dots \dots (12)$$

Hence it is apparent that we are able to solve the ratios between  $\Delta x_1, \Delta x_2, \dots$  from (9) and (10), when

$$\left. \begin{aligned} \Sigma (\lambda) = \lambda_1 + \lambda_2 + \dots + \lambda_n = 0 \\ \Sigma (\lambda x) = \lambda_1 x_1 + \lambda_2 x_2 + \dots + \lambda_n x_n = 0 \\ \Sigma (\lambda y) = \lambda_1 y_1 + \lambda_2 y_2 + \dots + \lambda_n y_n = 0 \\ \dots \end{aligned} \right\} \dots \dots \dots (13)$$

can be satisfied.

We might also satisfy (12) by putting equal to zero  $\Delta K_x, \Delta K_y, \dots$ ; now, however, we leave this case out of consideration and we shall refer to this later; then we shall see that the equilibrium is situated on the limit of its stability.

[Mr. W. VAN DER WOUDE has drawn my attention to the fact that we can easily express the condition that (9) and (10) can be satisfied in a determinant. It appears that this can be written like the product of different other determinants, so that we know at once all the conditions looked for.

We have in (13)  $n$  equations between the  $n-1$  ratios of  $\lambda_1, \lambda_2, \dots, \lambda_n$ ; consequently (13) can only be satisfied when a ratio exists between the variables. We may find it by eliminating from the equations (13)  $\lambda_1, \dots, \lambda_n$ ; we may also write this equation in the form of the following determinant;

$$\begin{vmatrix} 1 & 1 & 1 & 1 & \dots \\ x_1 & x_2 & x_3 & x_4 & \dots \\ y_1 & y_2 & y_3 & y_4 & \dots \\ z_1 & z_2 & z_3 & z_4 & \dots \\ \dots & \dots & \dots & \dots & \dots \end{vmatrix} = 0$$

When we bear in mind, however, the compositions of the phases  $F_1 \dots F_n$  then it appears that (13) expresses, that it must be possible that between the phases a reaction of the form:

$$\lambda_1 F_1 + \lambda_2 F_2 + \dots + \lambda_n F_n = 0$$

consequently a phase-reaction occurs. Then the equilibrium is an equilibrium  $E_R$  and consequently it is situated in the  $P, T$ -diagram on a curve  $E_R$ , viz. on a turning-line of the region  $E$ .

Therefore we find:

"in an equilibrium of  $n$  components in  $n$  phases under constant  $P$  the temperature is maximum or minimum, when between the phases a phase-reaction can occur".

Consequently in a binary system  $T$  is maximum or minimum when the two phases have the same composition; in a ternary system when the 3 points which represent the phases, are situated on a straight line; in a quaternary system when the 4 phases may be represented by 4 points of a plane; etc.

Now we have still to examine when  $T$  is a maximum and when it is a minimum. For this we have to determine  $\Delta T$ . We take the equations (7) in which all the terms with  $\Delta P$  must be omitted now. When we add the equations after having multiplied the first by  $\lambda_1$ , the second by  $\lambda_2$ , etc., then we find with the aid of (8) and (13):

$$\Sigma(\lambda H) \cdot \Delta T + \frac{1}{2} \Sigma(\lambda d^2 Z) + \frac{1}{3} \Sigma(\lambda d^3 Z) + \dots = 0 \quad (14)$$

or at first approximation:

$$\Sigma(\lambda H) \cdot \Delta T = -\frac{1}{2} \Sigma(\lambda d^2 Z) \quad (15)$$

Herein is:

$$\Sigma(\lambda H) = \lambda_1 H_1 + \lambda_2 H_2 + \dots + \lambda_n H_n$$

consequently the increase of entropy which occurs at the reaction:

$$\lambda_1 F_1 + \lambda_2 F_2 + \dots + \lambda_n F_n = 0$$

Further is:

$$\Sigma(\lambda d^2 Z) = \lambda_1 d^2 Z_1 + \lambda_2 d^2 Z_2 + \dots + \lambda_n d^2 Z_n \quad (16)$$

or, as it follows from the values of  $d^2 Z_i$  etc.:

$$\Sigma (\lambda d^2 Z) = \left. \begin{aligned} & \lambda_1 [d(x)_1 \Delta x_1 + d(y)_1 \Delta y_1 + \dots] \\ & + \lambda_2 [d(x)_2 \Delta x_2 + d(y)_2 \Delta y_2 + \dots] \\ & \dots \\ & + \lambda_n [d(x)_n \Delta x_n + d(y)_n \Delta y_n + \dots] \end{aligned} \right\} \dots \quad (17)$$

or also:

$$\Sigma (\lambda d^2 Z) = \left. \begin{aligned} & \lambda_1 [(x^2)_1 \Delta x_1^2 + (y^2)_1 \Delta y_1^2 + \dots + 2 (xy)_1 \Delta x_1 \Delta y_1] \\ & \dots \\ & + \lambda_n [(x^2)_n \Delta x_n^2 + (y^2)_n \Delta y_n^2 + \dots + 2 (xy)_n \Delta x_n \Delta y_n] \end{aligned} \right\} \dots \quad (18)$$

When one of the phases e.g.  $F_1$ , has a constant composition, then in (16)  $d^2 Z_1$  disappears when there are more phases with constant composition, then in (16) and consequently also in (17) and (18) the corresponding terms disappear.

When the equilibrium  $E$  is stable (or, which comes to the same for our considerations "metastable") then  $d^2 Z_1, d^2 Z_2, \dots$  are positive; when however the equilibrium is unstable, then one or more of the forms  $d^2 Z_1, \dots$  may be negative.

Now it follows from (15) when the temperature is a maximum and when it is a minimum.

When  $\Sigma(\lambda H)$  and  $\Sigma(\lambda d^2 Z)$  have the same sign, then  $\Delta T < 0$  and consequently  $T$  is a maximum

When  $\Sigma(\lambda H)$  and  $\Sigma(\lambda d^2 Z)$  have opposite sign, then  $\Delta T > 0$  and consequently  $T$  is a minimum.

When  $\Sigma(\lambda d^2 Z) = 0$ , then  $T$  is neither maximum nor minimum.

In some cases it is easy to define this. Let us take e.g. an equilibrium

$$E = L_1 + F_2 + F_3 + \dots + F_n$$

in which  $L_1$  is a liquid and  $F_2, \dots, F_n$  phases of invariable composition e.g. solids.

We cause the phase-reaction

$$\lambda_1 L_1 + \lambda_2 F_2 + \dots + \lambda_n F_n = 0$$

to proceed in such a way that  $\lambda_1$  quantities of  $L_1$  must be formed and we take  $\lambda_1$  positive. In the equilibrium  $E$  therefore, a reaction occurs [melting or conversion of solid substances] at which liquid is formed. As, in general, heat is to be added at this reaction,  $\Sigma(\lambda H) > 0$ .

As  $F_2, \dots, F_n$  are phases with invariable composition  $\Sigma(\lambda d^2 Z) = \lambda_1 d^2 Z_1$ .

Consequently we have:

$$\Sigma (\lambda H) \Delta T = -\frac{1}{2} \lambda_1 d^2 Z_1 \quad \dots \quad (19)$$

in which  $\Sigma(\lambda H) > 0$  and  $\lambda_1 > 0$ .  $d^2 Z_1$  is positive when the equilibrium



is stable, but it may be negative when the equilibrium is unstable. Consequently  $T$  is a maximum when the equilibrium is stable, but it may be a minimum when the equilibrium is unstable.

When we summarize the previous considerations, then we find the following:

In an equilibrium of  $n$  components in  $n$  phases under constant  $P$  the temperature is maximum or minimum when a phase-reaction can occur between the phases.

When one of the phases is a liquid and when the  $n-1$  other phases are solids with invariable composition, then  $T$  is a maximum when the equilibrium is stable (or metastable);  $T$  can be a minimum when the equilibrium is unstable.

We may apply those general considerations to special cases; with this we assume that the equilibrium is stable (or metastable).

In the binary equilibrium  $E = L_1 + F_2 \dots L_1$  represents the liquid, saturated with solid  $F_2$ . In a  $T$ -concentration-diagram  $L_1$  follows, therefore, the saturation-curve under its own vapour pressure. Consequently this curve must have its maximum-temperature in the point, in which  $L_1$  has the same composition as  $F_2$ ; this is, therefore, in the melting-point of  $F_2$ .

In the ternary equilibrium  $E = L_1 + F_2 + F_3 \dots L_1$  is a liquid, saturated with  $F_2 + F_3$ . In the concentration-diagram  $L_1$  follows, therefore, the saturation-curve of  $F_2 + F_3$ , under its own vapour-pressure.  $T$  changes along this curve from point to point. It will be necessary that  $T$  is a maximum in the point of intersection of this curve with the line  $F_2, F_3$ .

Similar considerations are true for systems with 4 and more components.

In a following communication we shall refer to unstable conditions.

*Equilibria of  $n$  components in  $n$  phases under constant pressure and at a temperature which differs little from the maximum- or minimum temperature.*

As between the  $n$  phases of an equilibrium  $E_R$  a phase-reaction may occur, (13) may be satisfied. The ratios between  $\Delta x_1, \Delta y_1, \dots, \Delta x_2, \Delta y_2, \dots$  are then defined by (9) and (10). When we imagine  $\Delta x_2, \dots, \Delta y_1, \Delta y_2, \dots$  to be expressed in  $\Delta x_1$ , and this to be substituted in (18) then it appears that we may write for  $\Sigma(\lambda d^2 Z)$  a form like  $A \Delta x_1^2$ . Herein  $A$  has a definite positive or negative value. Then follows from (15):

$$\Delta x_1 = \pm \sqrt{\frac{2\Sigma(\lambda H)}{-A}} \Delta T. \quad \dots \quad (20)$$

Hence it appears that to each definite value of  $\Delta T$  two values of  $\Delta x_1$  (and consequently also of  $\Delta x_2, \dots, \Delta y_1, \Delta y_2, \dots$ ) belong, which differ from one another in sign only. When the form under the root in (20) is positive, then  $\Delta x_1, \Delta x_2, \dots, \Delta y_1, \Delta y_2, \dots$  have, therefore, each two real values; when this form is negative, then  $\Delta x_1, \dots$  are imaginary.

Consequently we distinguish two cases.

When  $\Sigma(\lambda H)$  and  $A$  have the same sign, then we must take  $\Delta T$  negative in order to obtain real values for  $\Delta x_1, \dots$ ; the temperature  $T_R$  is, therefore, a maximum. At  $T_R$  there exists therefore one single equilibrium  $E_R$ ; at  $T_R + \Delta T$  (we take  $\Delta T > 0$ ) no equilibrium  $E$  exists; at  $T_R - \Delta T$ , however, two different equilibria exist, which we shall call  $E'$  and  $E''$ .

When  $\Sigma(\lambda H)$  and  $A$  have the same sign, then we have to take  $\Delta T$  positive, in order to obtain real values for  $\Delta x_1, \dots$ . Consequently  $T_R$  is a minimum. Then at  $T_R + \Delta T$  two different equilibria  $E'$  and  $E''$  exist, at  $T_R - \Delta T$  no equilibrium  $E$  exists.

We may also express the previous in the following way.

When under constant  $P$  the temperature is a maximum on the turning-line  $E_R$ , then two leaves of the region go, starting from this turning-line, towards lower  $T$  and not a single leaf towards higher  $T$ .

When under constant  $P$  the temperature is a minimum on the turning-line  $E_R$ , then two leaves of the region go towards higher  $T$  starting from this turning-line, and no single leaf towards lower  $T$ .

With our considerations on the region  $E$  in the previous communication XVI, we have already applied these results. The figs. 2 (XVI) and 4 (XVI) in which  $ef$  represents a turning-line, are in accordance with this. In fig. 7 (XVI)  $ql$  and  $dm$  are the limit-lines,  $MSm$  a turning-line. In order to show that also this diagram is in accordance with those results, we consider the horizontal line  $qrst$ ; in order to show more distinctly the situation of those leaves, it is partly dotted and curved in  $r$  and  $s$ . In  $r$   $T$  is a maximum, this corresponds to the fact that two leaves go, starting from curve  $mS$  towards lower and no leaf towards higher  $T$ . In  $s$   $T$  is a minimum, two leaves go towards higher- and no leaf towards lower temperatures.

We have seen that at the temperature  $T_R$  only one single equilibrium  $E_R = F_1 + F_2 + \dots$  exists and that a phase-reaction may occur between the phases of this equilibrium. At  $T_R + \Delta T$  [ $\Delta T < 0$ ]

when  $T_R$  is a maximum;  $\Delta T > 0$  when  $T_R$  is a minimum] two equilibria exist, viz.

$$E' = F_1' + F_2' + \dots \text{ and } E'' = F_1'' + F_2'' + \dots$$

No phase-reaction can occur between the phases of  $E'$ ; no more between those of  $E''$ . The invariable phases have of course the same composition in the three equilibria; the compositions of the variable phases differ only little from one another in the three equilibria. Now we shall show:

a. The concentration-regions of  $E_R$ ,  $E'$  and  $E''$  are situated in the concentration-diagram outside one another.

The three equilibria have, therefore, such compositions that none of them can be converted into one of the two other equilibria.

b. The concentration-region of  $E_R$  is situated between those of  $E'$  and  $E''$ .

c. The corresponding phases of the three equilibria (e. g.  $F_1$ ,  $F_1'$  and  $F_1''$ ;  $F_2$ ,  $F_2'$  and  $F_2''$ ; etc.) are situated on a straight line; this is divided into equal parts by the phase of the equilibrium  $E_R$ .

Before showing this, we shall first elucidate the meaning by some examples.

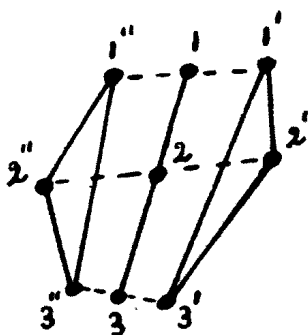


Fig. 1.

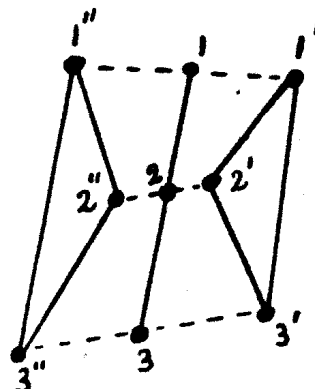


Fig. 2.

For this we choose the ternary equilibrium

$$E = F_1 + F_2 + F_3.$$

When we represent those phases in the concentration-diagram by the points 1, 2 and 3, then at  $T_R$  those three points are situated on a straight line (line 123 in figs. 1 and 2). The concentration-region of  $E_R$  is, therefore, the line 123.

At the temperature  $T_R + \Delta T$  exist the equilibria:

$$E' = F_1' + F_2' + F_3' \text{ and } E'' = F_1'' + F_2'' + F_3''$$

First we shall assume that each of the phases of the equilibrium  $E$  has a variable composition; the phases of  $E'$  are then represented

in figs. 1 and 2 by the points  $1'$ ,  $2'$  and  $3'$ ; those of  $E''$  by  $1''$ ,  $2''$  and  $3''$ . The points  $1'$ ,  $2'$  and  $3'$  are situated in the immediate vicinity of the points 1, 2 and 3; they form the anglepoints of a triangle  $1' 2' 3'$ , which represents the concentration-region of the equilibrium  $E'$ . Triangle  $1'' 2'' 3''$  represents the concentration-region of  $E''$ .

In accordance with *a* the line 123 and the triangles  $1'2'3'$  and  $1''2''3''$  must not have one single point in common, in accordance with *b* the line 123 must be situated between the two triangles; in accordance with *c*  $1'1''$ ,  $2'2''$  and  $3'3''$  are straight lines and is  $11' = 11''$ ,  $22' = 22''$  and  $33' = 33''$ . Consequently we obtain a diagram as in figs. 1 and 2.

Consequently at  $T_R + \Delta T$  two triangles arise from the straight line which occurs at the temperature  $T_R$ ; reversally the two triangles, which occur at  $T_R + \Delta T$  coincide at  $T_R$  into a straight line.

The transitions, discussed for figs 1 and 2 will occur when the ternary equilibrium  $E$  consists of 3 liquids or of 2 liquids and vapour, or of 3 kinds of mixed crystals, or of a mixed crystal + liquid + vapour etc.

When one of the phases e.g.  $F_1$  has an invariable composition, then we obtain figs 3 or 4; when two phases e.g.  $F_1$  and  $F_2$  have an invariable composition, then we obtain fig 5.

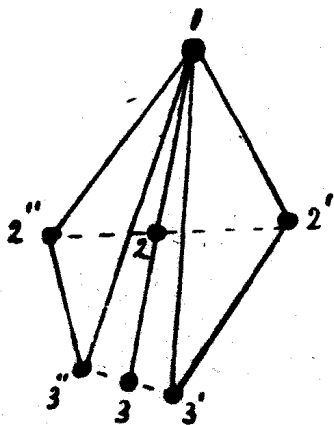


Fig. 3.

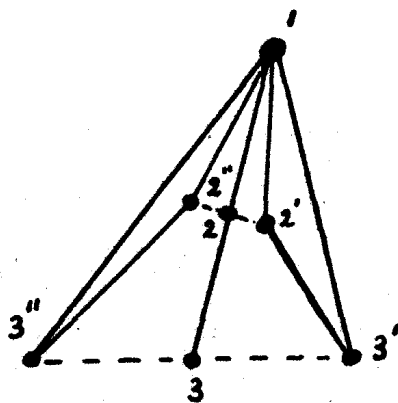


Fig. 4.

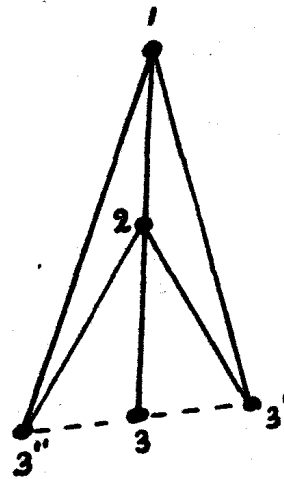


Fig. 5.

In order to show the rules, mentioned above, we represent of the equilibrium  $E_R$  the composition

of  $F_1$  by  $x_1, y_1, z_1, \dots$

„  $F_2$  „  $x_2, y_2, z_2, \dots$

etc.

Then the composition of the equilibrium  $E$  is:

$$\begin{aligned} \text{of } F_1' & x_1 + \Delta x_1, y_1 + \Delta y_1, z_1 + \Delta z_1 \\ \text{,, } F_2' & x_2 + \Delta x_2, y_2 + \Delta y_2, z_2 + \Delta z_2 \\ & \dots \dots \dots \end{aligned}$$

and the composition of the equilibrium  $E''$  is:

$$\begin{aligned} \text{of } F_1'' & x_1 - \Delta x_1, y_1 - \Delta y_1, z_1 - \Delta z_1 \\ \text{,, } F_2'' & x_2 - \Delta x_2, y_2 - \Delta y_2, z_2 - \Delta z_2 \\ & \dots \dots \dots \end{aligned}$$

Herein  $\Delta x_1, \Delta x_2, \dots$  are defined by (9) and (10); it is apparent that they may be as well positive as negative,

In order to be able to convert the equilibrium  $E_R$  into  $E'$ , it must be possible to satisfy

$$a_1 F_1 + a_2 F_2 + \dots = b_1 F_1' + b_2 F_2' + \dots \quad (21)$$

in which all coefficients must be positive.

It follows from (21):

$$\begin{aligned} a_1 + a_2 + \dots &= b_1 + b_2 + \dots \\ a_1 x_1 + a_2 x_2 + \dots &= b_1 (x_1 + \Delta x_1) + b_2 (x_2 + \Delta x_2) + \dots \\ a_1 y_1 + a_2 y_2 + \dots &= b_1 (y_1 + \Delta y_1) + b_2 (y_2 + \Delta y_2) + \dots \end{aligned}$$

etc. When we put  $a_1 - b_1 = c_1; a_2 - b_2 = c_2; \dots$  etc. then the previous equations pass into:

$$\left. \begin{aligned} c_1 + c_2 + \dots + c_n &= 0 \\ c_1 x_1 + c_2 x_2 + \dots &= b_1 \Delta x_1 + b_2 \Delta x_2 + \dots \\ c_1 y_1 + c_2 y_2 + \dots &= b_1 \Delta y_1 + b_2 \Delta y_2 + \dots \end{aligned} \right\} \dots \quad (22)$$

etc. We can eliminate  $c_1 \dots c_n$  from the  $n$  equations (22). We add them viz. after having multiplied the 1<sup>st</sup> by  $\mu_1$ , the 2<sup>nd</sup> by  $\mu_2$ , etc. As  $x_1, y_1, \dots$  viz. satisfy (9), they also satisfy:

$$\left. \begin{aligned} \mu_1 + \mu_2 x_1 + \mu_3 y_1 + \dots &= 0 \\ \mu_1 + \mu_2 x_2 + \mu_3 y_2 + \dots &= 0 \end{aligned} \right\} \dots \quad (23)$$

etc. (22) passes then into:

$$0 = b_1 [\mu_2 \Delta x_1 + \mu_3 \Delta y_1 + \dots] + b_2 [\mu_2 \Delta x_2 + \mu_3 \Delta y_2 + \dots] + \dots + b_n [\mu_2 \Delta x_n + \mu_3 \Delta y_n + \dots] \quad (24)$$

Also it appears from (9) that we may satisfy (23) by taking  $\mu_2 = a d(x)_1 = a d(x)_2 = \dots, \mu_3 = a d(y)_1 = a d(y)_2 = \dots$ , etc. Therefore (24) passes into:

$$0 = b_1 [d(x)_1 \Delta x_1 + d(y)_1 \Delta y_1 + \dots] + b_2 [d(x)_2 \Delta x_2 + d(y)_2 \Delta y_2 + \dots] + \dots$$

for which we may also write:

$$0 = b_1 d^2 Z_1 + b_2 d^2 Z_2 + \dots + b_n d^2 Z_n \quad (25)$$

It must be possible to satisfy (25) by giving positive values to  $b_1, b_2, \dots$ . When we consider only equilibria in stable (or metastable) condition, then  $d^2 Z_1, d^2 Z_2, \dots$  are positive; it is, therefore, not possible to satisfy (25) and consequently also not (21).

Hence it follows, therefore, that  $E_R$  and  $E'$  cannot be converted into one another; as we are able to deduce this in the same way for  $E_R$  and  $E''$  and also for  $E'$  and  $E''$ , the property mentioned sub  $a$  is proved. At the same time it appears from the deduction that it need not be true for equilibria in unstable condition.

For the equilibria  $E'$  and  $E''$  this property follows also at once without calculation viz. from the condition that under constant  $P$  and at constant  $T$   $\xi$  must be a minimum.

The properties, mentioned sub  $b$  and  $c$  follow now at once from property  $a$  and formula (20).

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*(To be continued).*

**Mechanics.** — “*On the relativity of inertia. Remarks concerning EINSTEIN'S latest hypothesis*”<sup>1)</sup> By Prof. W. DE SITTER.

(Communicated in the meeting of March 31, 1917).

If we neglect the gravitational action of all ordinary matter (sun, stars, etc.), and if we use as a system of reference three rectangular cartesian space-coordinates and the time multiplied by  $c$ , then in that part of the four-dimensional time-space which is accessible to our observations, the  $g_{\mu\nu}$  are very approximately those of the old theory of relativity, viz.:

$$\left. \begin{array}{cccc} -1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & +1 \end{array} \right\} \dots \dots \dots (1)$$

The part of the time-space where this is so, I shall call “our neighbourhood”. In space this extends at least to the farthest star, nebula or cluster in whose spectrum we can identify definite lines<sup>2)</sup>.

How the  $g_{\mu\nu}$  are outside our neighbourhood we do not know, and any assumption regarding their values is an extrapolation, whose uncertainty increases with the distance (in space, or in time, or in both) from the origin. How the  $g_{\mu\nu}$  are at infinity of space or of time, we will never know. Nevertheless the need has been felt to

<sup>1)</sup> A. EINSTEIN, *Kosmologische Betrachtungen zur allgemeinen Relativitätstheorie*, Sitzungsber. Berlin, 8 Febr. 1917, page 142.

<sup>2)</sup> W. DE SITTER, *On EINSTEIN'S theory of gravitation and its astronomical consequences (second paper)*, Monthly Notices R.A.S. Dec. 1916, Vol. LXXVII, p. 182. This limit refers to  $g_{44}$  only.