

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

(Communicated in the meeting of February 24, 1917).

The occurrence of two indifferent phases; the equilibrium  $M$  is variable singular.

Now we consider the case that the singular equilibrium ( $M$ ) is no more constant, but variable; one or more phases of  $M$  have, therefore, a variable composition. (Comm. X).

When ( $M$ ) is constant singular, then, as we have deduced in communication X, the following propositions hold:

1. When the two indifferent phases have the same sign, then  $M$  is transformable.

2. When the two indifferent phases have opposite sign, then  $M$  is not transformable.

It is evident that the same rules are valid also when  $M$  is a variable singular equilibrium.

In order to examine what  $P, T$ -diagrams can occur now, we take an invariant point with the phases  $F_1 \dots F_{n+2}$ , in which  $F_p$  and  $F_{p+1}$  are the indifferent — and consequently the other ones are the singular phases. Then we have the singular equilibria:

$$(M) = F_1 + \dots + F_{p-1} + F_{p+2} + \dots + F_{n+2}$$

$$(F_p) = (M) + F_{p+1} \text{ and } (F_{p+1}) = (M) - F_p$$

in which ( $M$ ) now contains one or more phases of variable composition.

When ( $M$ ) is constant singular, then curve ( $M$ ) is monodirectional [fig. 1 (X)] or bidirectional [fig. 2 (X)]; in the first case the 3 singular curves coincide in the same direction, in the second case ( $F_p$ ) and ( $F_{p+1}$ ) coincide in opposite direction.

When ( $M$ ) is however variable singular then the three singular curves can no more coincide. Let viz.  $P_0$  and  $T_0$  be the pressure and temperature of the invariant equilibrium and let us assume that in ( $M$ ) and consequently also in ( $F_p$ ) and ( $F_{p+1}$ ) the phases  $F_x, F_y$  etc. of variable composition occur. Under  $P_0$  and at  $T_0$   $F_x$  and  $F_y$  have then the same composition in ( $M$ ) and ( $F_p$ ). Now we take a temperature  $T_1$ . When we bring ( $M$ ) to the temperature  $T_1$  and under the corresponding pressure, then  $F_x$  and  $F_y$  get another composition  $F'_x$  and  $F'_y$ . Those compositions are of course such compositions that between the phases of ( $M$ ) the phases-reaction is still always possible.

When we bring ( $F_p$ ) to the temperature  $T_1$  and under the corres-

ponding pressure, then  $F_x$  and  $F_y$  do not get the composition  $F_x'$  and  $F_y'$ , but another composition  $F_x''$  and  $F_y''$ .

When we take away at  $T_1$  the phase  $F_{p+1}$ , from  $(F_p) = (M) + F_{p+1}$ , then we do not obtain the equilibrium  $(M)$ , but, as  $F_x''$  and  $F_y''$  have another composition than  $F_x'$  and  $F_y'$ , an equilibrium different from  $(M)$ . Consequently curves  $(M)$  and  $(F_p)$  do not coincide. The same is true for  $(M)$  and  $(F_{p+1})$  and for  $(F_p)$  and  $(F_{p+1})$ ; the singular curves do not coincide, therefore. They form, as is drawn in the figs. 1–5, three separate curves. Now we can show:

1. the three singular curves touch one another in the point  $i$ .
2.  $(F_p)$  and  $(F_{p+1})$  are situated on the same side of the  $(M)$ -curve.

The first follows immediately from the relation

$$T \frac{dp}{dT} = \frac{\Delta W}{\Delta V}.$$

In the point  $i$  viz. the reaction, which occurs in the three singular equilibria, is the same, so that in the point  $i$   $\frac{dF}{dT}$  is the same also for the three curves.

In order to show the second, we consider the bivariant equilibrium:

$$(F_p F_{p+1}) = F_1 + \dots + F_x + F_y + \dots + F_{p-1} + F_{p+2} \dots F_{n+2}. \quad (1)$$

This region has a turning-line  $(M)$ , which is defined by the fact that in (1) the variable phases  $F_x, F_y, \dots$  have such a composition that a phases-reaction is possible between those  $n$  phases. The singular curve  $(M)$  is, therefore, the same as the turning-line of the region  $(F_p, F_{p+1})$ ; consequently we have here the special case, which we have already mentioned in (VIII) viz. that the point  $i$  in fig. 5 (VIII) is situated on the turning-line  $xyzu$  of the region  $(F_p, F_{p+1})$ . As  $(F_p)$  and  $(F_{p+1})$  must be situated within the turning-line of this region, they are situated, therefore, on the same side of the  $(M)$ -curve.

In order to deduce the  $P, T$ -diagrams, we are able to apply again the rules of the isovolumetrical and isentropical reaction to the curves  $(M)$ ,  $(F_p)$  and  $(F_{p+1})$ . In this application with respect to the  $(M)$ -curve we have, however, to bear in mind the following.

When we have a constant singular curve  $(M)$ , then we are able to realise always a whole series of equilibria (for instance between the temperatures  $T_1$  and  $T_2$ ) of the  $(M)$ -curve with the aid of one single complex  $K$  of definite composition. When  $(M)$  is however variable singular, then this not always remains possible. Then we may have the case, that we can obtain only one single equilibrium of the  $(M)$ -curve (e.g. that of a temperature  $T$ ) with each definite

complex  $K$ ; in order to realise the equilibrium of a temperature  $T + dT$ , we have to take then a complex of another composition.

When the latter is the case and when  $T_0$  is the temperature and  $P_0$  the pressure of the invariant point, then we can not obtain with a same complex  $K$  an equilibrium of the temperature  $T_0$  and  $T_0 + dT$  or of the pressures  $P_0$  and  $P_0 + dP$ ; the rules of the isovolumetrical and of the isentropical reaction, therefore, are then not applicable.

In the first case we have:

the two indifferent phases have the same sign; the equilibrium ( $M$ ) is, therefore, transformable.

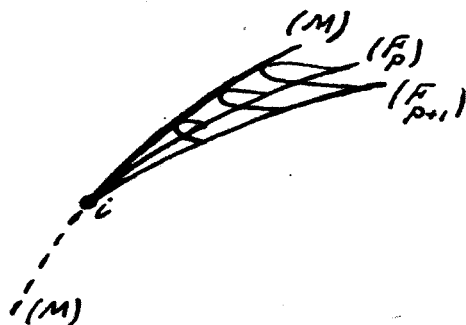


Fig. 1.

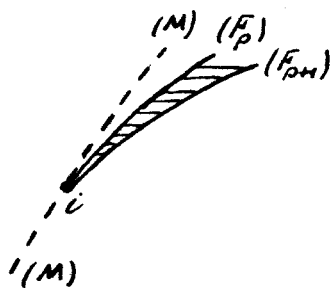


Fig. 2.

The stable parts of the curves ( $F_p$ ) and ( $F_{p+1}$ ) go in the same direction, starting from the point  $i$ ; then we obtain  $P, T$ -diagrams as in figs. 1 and 2.

[In those and the following figures only the stable part of the curves ( $F_p$ ) and ( $F_{p+1}$ ) is drawn; the metastable part of the ( $M$ )-curve is dotted.] In fig. 1 the one part of the ( $M$ )-curve is stable, the other part metastable; in fig. 2 the ( $M$ )-curve is only stable in the point  $i$ .

In the second case we have:

the two indifferent phases have opposite sign, the equilibrium ( $M$ ) is therefore, not transformable.

The stable parts of the curves ( $F_p$ ) and ( $F_{p+1}$ ) proceed in opposite direction, starting from the point  $i$ ; then we obtain  $P, T$ -diagrams as in the figs. 3, 4 and 5. In fig. 3 the ( $M$ )-curve is bidirectionable, in fig. 4 monodirectionable, in fig. 5 it is metastable, except in the point  $i$ .

[In a following communication we shall show that the ( $M$ )-curve can also have a turning-point. When this is casually situated in the point  $i$ , then the diagrams under consideration will be changed by [this in some respect.]

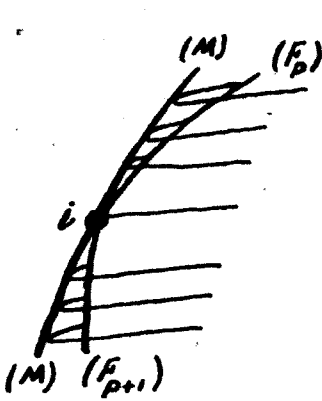


Fig. 3.

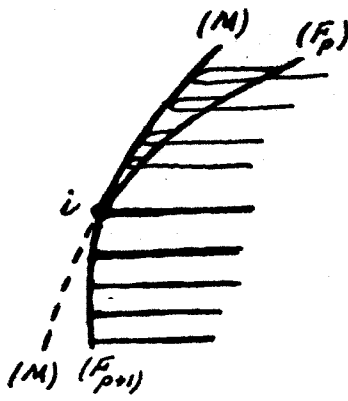


Fig. 4.

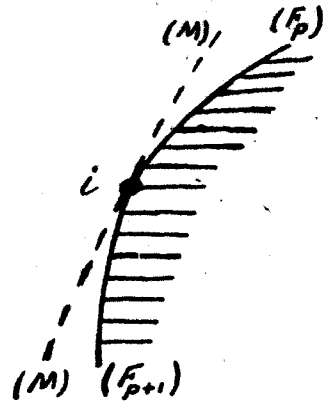


Fig. 5.

The stable part of the region  $(F_p F_{p+1})$  extends itself between the curves  $(F_p)$  and  $(F_{p+1})$ . This region is indicated in the figures by some horizontal lines and little arcs.

In fig. 1 it extends from  $(F_p)$  and  $(F_{p+1})$  up to the  $(M)$ -curve; the stable part of the region  $(F_p F_{p+1})$  consists, therefore, of two leaves, which cover one another partly.

In fig. 2 the stable part of the region  $(F_p F_{p+1})$  cannot extend as far as the part of the  $(M)$ -curve, which is situated in the vicinity of the point  $i$ . It may be situated, as is drawn in fig. 2 and then it has one leaf.

I leave to the reader the deduction of the regions in the figs. 3—5.

Now we shall consider some cases, which we can easily deduce from fig. 1 (VIII) and the corresponding fig. 2 (VIII). We imagine in fig. 1 (VIII) the liquid  $L$  on the line  $GZ_2$ , so that  $L$  and  $d$  coincide. Then we have the variable singular equilibrium:

$$(M) = Z_2 + L + G$$

which is transformable. This equilibrium  $(M)$  is represented in fig. 1 (VIII) by the line  $GdZ_2 = GLZ_2$ , the turning-line of the region  $Z_2 LG$ , the stable part of which is situated between the curves  $La$  and  $Lb$ . Now we distinguish two cases:

I. Curve  $La$  is situated at the left and curve  $Lb$  at the right side of  $GZ_2$  (viz. when we go from  $G$  towards  $Z_2$ ). The part  $dZ_2 = LZ_2$  of the equilibrium  $(M)$  is, therefore, stable, the part  $dG = LG$  is metastable.

Let us imagine in fig. 2 (VIII) the  $(M)$ -curve to be drawn also, which starts from  $i$  in accordance with fig. 1 (VIII) and which must be situated above the curves  $ia$  and  $ib$ . The three singular curves  $(M)$ ,  $(Z_1)$  and  $(Z_2)$  must then touch one another in  $i$ . The three

curves are then situated with respect to one another as in fig. 1.

We are able to deduce the position of the three curves also from fig. 3 (VIII). Curve  $(M) = dg$ , which touches  $ia$  in  $d$ , represents the turning-line of the region  $(Z_1, Z_2) = Z, LG$ . When we let coincide  $d$  with  $i$ , then  $ig$ ,  $ia$  and  $ib$  must touch one another in  $i$ . Hence we see also that the position of the three singular curves and that of the region  $(Z_1, Z_2) = Z, LG$  is in accordance with fig. 1.

As long as point  $L$  is situated in fig. 1 (VIII) at the right side of the line  $GZ_2$ , in figs. 2 (VIII) and 3 (VIII) curve  $ia$  is situated above  $ib$ . When, however, in fig. 1 (VIII)  $L$  falls on  $GZ_2$ , then in the figs. 2 (VIII) and 3 (VIII)  $ia$  and  $ib$  touch one another in  $i$ , but  $ia$  may be situated as well above as below  $ib$ . This appears at once from fig. 1 (VIII).

We may consider the position of  $L$  on the line  $GZ_2$  as a transition case viz. between the case that  $L$  is situated at the right [fig. 1 (VIII)] and that  $L$  is situated at the left of the line  $GZ_2$ . In the first case  $ia$  is situated above  $ib$  [fig. 2 (VIII)], in the second case  $ib$  must be situated above  $ia$ .

[When we wish to consider this transition more in detail, then we have to bear in mind the following. When  $L$  is situated as in fig. 1 (VIII), then in fig. 2 (VIII) curve  $(Z_1)$  must be situated above  $(Z_2)$ . This is only true, however, in so far as we consider points of those curves in the vicinity of point  $i$ . It is apparent from fig. 1 (VIII) that this is certainly true for points on  $Ld$  and  $Lm$ . At a further distance from  $i$  the curves  $(Z_1)$  and  $(Z_2)$  in fig. 2 (VIII) may, however, intersect one another. It appears viz. from the direction of the little arrows e.g. on curve  $agb$  in fig. 1 (VIII) that the pressure in  $a$  and  $b$  might be the same. When this is the case, then in fig. 2 (VIII) the points  $a$  and  $b$  must coincide and consequently the curves  $(Z_1)$  and  $(Z_2)$  have a point of intersection.]

II. Both the curves  $La$  and  $Lb$  are situated in fig. 1 (VIII) at the right side of the line  $GZ_2$ . The equilibrium  $(M)$  is, therefore, metastable, except in the point  $L$ .

Now we imagine in fig. 2 (VIII) to be also drawn the metastable  $(M)$ -curve. It appears from fig. 1 (VIII) that the  $(M)$ -curve must be situated above curve  $(Z_2)$  and this curve above curve  $(Z_1)$ . Those three curves must then touch one another in  $i$ . The position of the three singular curves and of the region  $(Z_1, Z_2) = Z, LG$  is then in accordance with fig. 2.

Now we imagine in fig. 1 (VIII) the liquid  $L$  on the line  $GZ_2$ , so that  $L$  and  $e$  coincide. Then we have the variable singular equilibrium:

$$(M) = Z_2 + L + G$$

which is, however, no more transformable now. This equilibrium ( $M$ ) is represented in fig. 1 (VIII) by the line  $GeZ_1 = GLZ_1$ , the turning-line of the region  $Z_1LG$ , the stable part of which is situated between the curves  $Lb$  and  $Lc$ . According to the position of the curves  $La$ ,  $Lb$  and  $Lc$  with respect to the line  $GLZ_1$ , in the  $P, T$ -diagram of fig. 2 (VIII) different cases follow which are in accordance with the figs. 3—5.

At the deduction of the figs. 1—5 we have assumed the following. When we bring the equilibria ( $M$ ), ( $F_p$ ) and ( $F_{p+1}$ ) from  $T_0$  and  $P_0$  to the temperature  $T_1$  and corresponding pressures, then the variable phases (e. g.  $F_x$ ) get other compositions in each of the three equilibria [e. g.  $F_x'$ ,  $F_x''$  and  $F_x'''$ ]. This is however not always the case. Let us assume viz. that in the invariant point the phases of the singular equilibrium:

$$(M) = F_1 + F_2 + \dots + F_x + \dots + F_{n+2}$$

contain together only  $n-1$  of the components, in the equilibrium ( $M$ ) then one of the  $n$  components is missing; we call this component  $K$ .

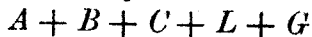
The variable phase  $F_x$  contains, therefore, also only  $n-1$  components (or less) and this is not only the case at  $T_0$  and under  $P_0$ , but also at other  $T$  and  $P$ ; this is not only the case in the equilibrium ( $M$ ), but also in the other equilibria.

This is e. g. the case when  $F_x$  is a gas and  $K$  a substance which is not volatile or when  $F_x$  is a mixed-crystal and  $K$  not miscible with this.

In the equilibrium:

$$(F, F_2) = F_1 + F_2 + \dots$$

we have now  $n-1$  components in  $n$  phases, consequently it is not bivariant, but monovariant; in the  $P, T$ -diagram it is, therefore, not represented by a region, but by a curve. The equilibria ( $M$ ), ( $F_1$ ) and ( $F_2$ ) coincide, therefore, with this curve. As the equilibrium ( $M$ ) of course is not transformable (viz. the substance  $K$  is missing), the ( $M$ )-curve is bidirectionable and the curves ( $F_1$ ) and ( $F_2$ ) coincide, therefore, in opposite direction. Then we obtain fig. 2 (X). A similar case shall occur e. g. in a ternary system with the components  $A$ ,  $B$  and  $C$ , when in the invariant point exists the equilibrium



in which the gas-phase  $G$  contains only two substances e. g.  $B$  and  $C$ .

#### Summary of the $P, T$ -diagramtypes.

When we take an invariant point with the phases  $F_1 \dots F_{n+2}$ , then different cases may occur.

I. Reactions are possible, in which all phases of the invariant point may participate. We write those reactions :

$$a_1 F_1 + a_2 F_2 + \dots + a_{n+2} F_{n+2} = 0 \quad (1)$$

and

$$\mu_1 a_1 F_1 + \mu_2 a_2 F_2 + \dots + \mu_{n+2} a_{n+2} F_{n+2} = 0 \quad (2)$$

Now we distinguish the following cases.

A.  $\mu_1, \mu_2, \dots$  are all different. Consequently there are no indifferent phases, then we obtain the general  $P, T$ -diagramtypes.

B.  $\mu_1 = \mu_2 = \mu$ . Consequently there are two indifferent phases viz.  $F_1$  and  $F_2$  and three singular curves viz.  $(M)$ ,  $(F_1)$  and  $(F_2)$ . In the equilibrium  $(F_1, F_2)$  may occur the reaction :

$$(\mu - \mu_3) a_3 F_3 + (\mu - \mu_4) a_4 F_4 + \dots = 0 \quad (3)$$

This equilibrium  $(F_1, F_2)$  may be mono- or bivariant (not invariant). When  $(F_1, F_2)$  is monovariant, then it is represented in the  $P, T$ -diagram by a curve, then the singular curves coincide [Figs. 1 (X) and 2 (X)].

When  $(F_1, F_2)$  is bivariant, then it is represented in the  $P, T$ -diagram by a region, the 3 singular curves touch one another in the invariant point [figs. 1-5 (XV)].

C.  $\mu_1 = \mu_2 = \mu_3 = \mu$ . Consequently there are three indifferent phases viz.  $F_1, F_2$  and  $F_3$  and four singular curves viz.  $(M)$ ,  $(F_1)$ ,  $(F_2)$  and  $(F_3)$ . In the equilibrium  $(F_1, F_2, F_3)$  may occur the reaction:

$$(\mu - \mu_4) a_4 F_4 + (\mu - \mu_5) a_5 F_5 + \dots = 0 \quad (4)$$

This equilibrium  $(F_1, F_2, F_3)$  is tri-, bi- or monovariant.

When it is monovariant, then the singular curves coincide. An example is discussed in Communication XIV.

D.  $\mu_1 = \mu_2 = \dots = \mu_r = \mu$ ; in which  $r \leq n$ . Consequently there are  $r$  indifferent phases and  $r + 1$  singular equilibria. In the equilibrium  $(F_1, F_2, \dots, F_r)$  may occur the reaction :

$$(\mu - \mu_{r+1}) a_{r+1} F_{r+1} + \dots = 0 \quad (5)$$

This equilibrium may be from  $r$ - to monovariant.

E.  $\mu_1 = \dots = \mu_k = \mu$  and  $\mu_{l+1} = \dots = \mu_{l+m} = \mu'$ , in which  $K < l$ . Consequently there are two groups of indifferent phases. To the first group belong  $K + 1$ , to the second group  $m + 1$  singular curves.

For  $K = l$  E passes into D.

Also three and more groups of indifferent phases may occur. We find an example in the system water + a salt A + a salt B, when in the invariant point occur the phases  $G + A + B + A_m + B_n$ , in which  $A_m$  and  $B_n$  represent hydrates.

II. No reaction is possible, in which all phases of the invariant point may participate.

When e.g. the phase  $F_1$  cannot take part into one single reaction, then in (1) and (2)  $a_1$  becomes  $= 0$ . Then we have an invariant point with  $n + 1$  phases, for which the considerations sub I are true.

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(To be continued).

**Physics.** — “*Experimental Inquiry into the Laws of the Brownian Movement in a Gas.*” By Miss A. SNETHLAGE. (Communicated by Prof. P. ZIEEMAN).

(Communicated in the meeting of Feb. 24, 1917).

1. In a former paper<sup>1)</sup> some objections have been advanced to EINSTEIN'S formula for the Brownian movement by Prof. VAN DER WAALS JR. and me. According to this formula:

$$\overline{\Delta^2} = \frac{2RT}{N} B \dots \dots \dots (1)$$

in which  $\overline{\Delta^2}$  represents the mean square of the displacement which a “Brownian particle” obtains per second in a definite direction. Equation (1) has been derived on the supposition that the particle meets in its movement with a resistance of friction. Accordingly  $B$  is the inverse value of the factor of resistance which is found when the particle travels with constant velocity under influence of an external force. Statistical mechanics, however, teaches that a particle, in equilibrium with the surrounding molecules, does not experience a force dependent on its velocity, hence no ordinary friction. We have written the equation of motion in the form:

$$\ddot{u} = -pu + q \dots \dots \dots (2)$$

and derived a value for  $\overline{\Delta^2}$ , which does not lay claim to great accuracy, but leads, at least for the Brownian movement in a gas, to  $\overline{\Delta^2}$  being proportional with  $\frac{1}{a^2}$ , when  $a$  represents the radius of the particle.

According to STOKES' formula with CUNNINGHAM'S correction:

$$\frac{1}{B} = 6\pi\zeta ak \dots \dots \dots (3)$$

in which  $\zeta$  represents the coefficient of friction of the medium and

$$k = \left(1 + A \frac{\lambda}{a}\right)^{-1}$$

<sup>1)</sup> These Proc. 18, 1916, p. 1322.