

**Chemistry.** — “Equilibria in systems, in which phases, separated by a semipermeable membrane. VI. By F. A. H. SCHREINEMAKERS.

(Communicated at the meeting of February 28, 1925).

In the previous communications we have discussed some simple cases of osmose in binary and ternary systems. We now shall deduce some general properties.

*The osmotic water-attraction of a system of phases.*

In our previous considerations we have discussed already the O.W.A. of a liquid and in some simple cases also that of one or more solid substances; now we shall consider more general cases. We take the osmotic equilibrium:

$$E = [E_1(n_1 r_1) | E_2(n_2 r_2) \dots \dots \dots] \quad (1)$$

in which  $E_1$  is a system of  $n_1$  components in  $r_1$  phases under the pressure  $P_1$  and  $E_2$  a system of  $n_2$  components in  $r_2$  phases under the pressure  $P_2$ .

We now imagine that a small quantity of water (in general: of the diffusing substance) passes from the system  $E_2$  into the system  $E_1$ ; then the thermodynamical potential of the system  $E_1$  will change with  $\delta Z_1$ , that of the system  $E_2$  with  $\delta Z_2$ . When  $\delta Z_1 + \delta Z_2 \cong 0$ , then system (1) is in equilibrium, when  $\delta Z_1 + \delta Z_2 < 0$ , then water will diffuse through the membrane. In order to define the direction, in which the water will diffuse through the membrane, we have to know  $\delta Z_1$  and  $\delta Z_2$ . Firstly we shall define  $\delta Z_1$  for the system  $E_1$ ; for this we distinguish different cases.

*I. The system  $E_1$  consists of a liquid only.*

We call the  $n_1$  components, of which the liquid  $L_1$  consists,  $XY\dots W$ ; we represent the composition of the liquid by:

$$x_1 \text{ Mol } X + y_1 \text{ Mol } Y \dots + (1 - x_1 - y_1 \dots) \text{ Mol } W.$$

We assume that there are  $q_1$  quantities of this liquid  $L_1$ , each with the thermodynamical potential  $\zeta_1$ . When a small quantity  $\mu$  of the diffusing substance  $W$  passes from the system  $E_2$  into those  $q_1$  quantities of the liquid  $L_1$ , then follows:

$$\delta Z_1 = (q_1 + \mu) \left( \zeta_1 + \frac{\partial \zeta_1}{\partial x_1} dx_1 + \frac{\partial \zeta_1}{\partial y_1} dy_1 \dots \right) - q_1 \zeta_1.$$

As, when  $\mu$  is infinitely small with respect to  $q$ ,

$$dx_1 = \frac{q_1 x_1}{q_1 + \mu} - x_1 = -\frac{\mu}{q_1} x_1 \quad dy_1 = \frac{q_1 y_1}{q_1 + \mu} - y_1 = -\frac{\mu}{q_1} y_1$$

etc. we may write also:

$$\delta Z_1 = \left( \zeta_1 - x_1 \frac{\partial \zeta_1}{\partial x_1} - y_1 \frac{\partial \zeta_1}{\partial y_1} - \dots \right) \mu = \varphi_1 \mu \quad \dots \quad (2)$$

Previously we have seen that the value of  $\varphi_1$  in connection with a corresponding value of the system  $E_2$  decides whether the substance  $W$  will diffuse from the liquid  $L_1$  towards the system  $E_2$  or reversally; for the sake of abbreviation we shall say therefore that  $\varphi_1$  defines the O.W.A. of the liquid  $L_1$ .

II. *The system  $E_1$  consists of two or more liquids.*

When two or more liquids are in equilibrium with one another, then they are isotonic with respect to all components; consequently they also have the same O.W.A. It is obvious, therefore, also that the O.W.A. of a complex of liquids is equal to the O.W.A. of each of them, separately. We are able to prove this still also in the following way. For the sake of simplicity we take a system of two liquids viz.

$$E_1 = L_1 + L_2 \quad \dots \quad (3)$$

We represent the composition of

$$L_1 \text{ by } x_1 \text{ Mol } X + y_1 \text{ Mol } Y \dots + (1-x_1-y_1 \dots) \text{ Mol } W$$

$$L_2 \text{ by } x_2 \text{ Mol } X + y_2 \text{ Mol } Y \dots + (1-x_2-y_2 \dots) \text{ Mol } W.$$

We take  $q_1$  quantities of  $L_1$  and  $q_2$  quantities of  $L_2$ , each with the thermodynamical potential  $\zeta_1$  and  $\zeta_2$ . We now imagine that a small quantity  $\mu$  of the diffusing substance  $W$  passes from the system  $E_2$  into the system  $E_1$ . When  $a_1$  quantities of  $W$  go towards the  $q_1$  quantities of  $L_1$  and  $a_2$  quantities of  $W$  towards the  $q_2$  quantities of  $L_2$ , then is, therefore  $a_1 + a_2 = \mu$ . Further we assume that at the same time  $\delta n_x \delta n_y \dots \delta n_w$  quantities of the substances  $XY \dots W$  pass from the  $q_2$  quantities of  $L_2$  into the  $q_1$  quantities of  $L_1$ . We now have:

$$\delta Z_1 = (q_1 + \Delta + a_1) \left( \zeta + \frac{\partial \zeta}{\partial x} dx + \frac{\partial \zeta}{\partial y} dy \dots \right)_1 \quad \dots \quad (4)$$

$$+ (q_2 - \Delta + a_2) \left( \zeta + \frac{\partial \zeta}{\partial x} dx + \frac{\partial \zeta}{\partial y} dy \dots \right)_2 - q_1 \zeta_1 - q_2 \zeta_2$$

in which  $\Delta = \delta n_x + \delta n_y \dots + \delta n_w$ .

Further we find:

$$q_1 dx_1 = \delta n_x - x_1 (\Delta + a_1) \quad q_2 dx_2 = -\delta n_x + x_2 (\Delta - a_2)$$

$$q_1 dy_1 = \delta n_y - y_1 (\Delta + a_1) \quad q_2 dy_2 = -\delta n_y + y_2 (\Delta - a_2)$$

etc. With the aid of this (3) passes into:

$$\delta Z_1 = (\varphi_1 - \varphi_2) \Delta + \left( \frac{\partial \zeta_1}{\partial x_1} - \frac{\partial \zeta_2}{\partial x_2} \right) \delta n_x + \left( \frac{\partial \zeta_1}{\partial y_1} - \frac{\partial \zeta_2}{\partial y_2} \right) \delta n_y + \varphi_1 a_1 + \varphi_2 a_2 \quad (5)$$

in which :

$$\begin{aligned} \varphi_1 &= \zeta_1 - x_1 \frac{\partial \zeta_1}{\partial x_1} - y_1 \frac{\partial \zeta_1}{\partial y_1} \dots \\ \varphi_2 &= \zeta_2 - x_2 \frac{\partial \zeta_2}{\partial x_2} - y_2 \frac{\partial \zeta_2}{\partial y_2} \dots \end{aligned}$$

We now imagine firstly the system (3) by itself so that  $a_1 = 0$  and  $a_2 = 0$ . Then follow from (5) the known equations for equilibrium :

$$\varphi_1 = \varphi_2 \quad \frac{\partial \zeta_1}{\partial x_1} = \frac{\partial \zeta_2}{\partial x_2} \quad \frac{\partial \zeta_1}{\partial y_1} = \frac{\partial \zeta_2}{\partial y_2} \text{ etc. } \dots \dots \quad (6)$$

When now, as is assumed above,  $\mu = a_1 + a_2$  quantities of  $W$  diffuse from  $E_2$  towards the two liquids and when we assume that both these liquids are in equilibrium with one another, then (5) passes, therefore, into :

$$\delta Z_1 = \varphi_1 a_1 + \varphi_2 a_2 = \varphi_1 \mu = \varphi_2 \mu. \quad \dots \dots \quad (7)$$

Consequently it is apparent from this, as is already said above, that the O.W.A. of liquid  $L_1$  is equal to that of  $L_2$  and equal to that of the complex  $L_1 + L_2$ .

III. *The system  $E_1$  contains, besides one or more liquids, still other phases.*

In the examples, discussed already formerly, we have seen that the O.W.A. of a binary or ternary liquid, which is saturated with a solid substance, is equal to the O.W.A. of the liquid only. Consequently the O.W.A. of a liquid does not change by the presence of a solid substance, with which it is in equilibrium. Generally this is the case. Let us take f. i. the system :

$$E_1 = L_1 + L_2 \dots + F_1 + F_2 + \dots$$

in which  $L_1, L_2$  etc. represent liquids and  $F_1, F_2 \dots$  other phases. Then the O.W.A. of  $L_1$  is equal to that of  $L_2$  etc. and equal to that of the total system  $E_1$ .

In order to show this for a system

$$E_1 = L + F_1 + F_2 \dots + F_{r-1} \dots \dots \quad (8)$$

we represent the composition of

$$\begin{aligned} L &\text{ by } x \text{ Mol } X + y \text{ Mol } Y \dots + (1 - x - y \dots) \text{ Mol } W \\ F_1 &\text{ ,, } a_1 \text{ Mol } X + \beta_1 \text{ Mol } Y \dots + (1 - a_1 - \beta_1 \dots) \text{ Mol } W \\ F_2 &\text{ ,, } a_2 \text{ Mol } X + \beta_2 \text{ Mol } Y \dots + (1 - a_2 - \beta_2 \dots) \text{ Mol } W \end{aligned}$$

etc.; we call the thermodynamical potentials  $\zeta, \zeta_1, \zeta_2$  etc.

We now imagine that a small quantity  $\mu$  of the diffusing substance

$W$  passes from a system  $E_2$  into the system  $E_1$ ; this will cause also that  $\delta n_1 \delta n_2 \dots$  quantities of the phases  $F_1 F_2 \dots$  pass into the liquid  $L$ . The change of the thermodynamical potential of the system  $E$  then is:

$$\delta Z_1 = (q + \Delta + \mu) \left( \zeta + \frac{\partial \zeta}{\partial x} dx + \frac{\partial \zeta}{\partial y} dy \dots \right) - q\zeta - \zeta_1 \delta n_1 - \zeta_2 \delta n_2 \dots \quad (9)$$

in which:  $\Delta = \delta n_1 + \delta n_2 \dots + \delta n_{r-1}$ . Further is assumed that in the equilibrium (8)  $q$  quantities of liquid occur. When we represent the quantities of the components  $X Y \dots W$ , which pass into the liquid, by  $\delta n_x \delta n_y \dots \delta n_w$ , then they are defined by:

$$\left. \begin{aligned} \delta n_x &= a_1 \delta n_1 + a_2 \delta n_2 + a_3 \delta n_3 \dots \\ \delta n_y &= \beta_1 \delta n_1 + \beta_2 \delta n_2 + \beta_3 \delta n_3 \dots \end{aligned} \right\} \dots \dots \quad (10)$$

etc. Hence follows the relation:

$$\delta n_x + \delta n_y \dots + \delta n_w = \Delta + \mu.$$

Now we find for the values, which we have to give to  $dx dy \dots$  in (9):

$$q \cdot dx = \delta n_x - x(\Delta + \mu)$$

$$q \cdot dy = \delta n_y - y(\Delta + \mu)$$

etc. With the aid of this (9) passes into:

$$\delta Z_1 = \left( \zeta - x \frac{\partial \zeta}{\partial x} - y \frac{\partial \zeta}{\partial y} \dots \right) (\Delta + \mu) - \zeta_1 \delta n_1 - \zeta_2 \delta n_2 \dots + \frac{\partial \zeta}{\partial x} \cdot \delta n_x + \frac{\partial \zeta}{\partial y} \cdot \delta n_y \dots \quad (11)$$

If we imagine in (11) the values of  $\delta n_x \delta n_y \dots$  from (10), to be substituted then it appears that (11) contains besides  $\mu$  still the  $r-1$  variations  $\delta n_1 \delta n_2 \dots$

Firstly we take the system (8) by itself, so that  $\mu = 0$ . Then follow from (11) the known  $r-1$  equations for equilibrium

$$\zeta - \zeta_i + (a_i - x) \frac{\partial \zeta}{\partial x} + (\beta_i - y) \frac{\partial \zeta}{\partial y} + \dots = 0 \quad (12)$$

$$i = 1, 2, \dots (r-1)$$

When, as is assumed above,  $\mu$  quantities of the substance  $W$  diffuse towards the system  $E_1$  and when we assume that this system is in equilibrium, then (11) passes into:

$$\delta Z_1 = \left( \zeta - x \frac{\partial \zeta}{\partial x} - y \frac{\partial \zeta}{\partial y} \dots \right) \mu \quad (13)$$

The O.W.A. of the whole system (8) is the same, therefore, as that of the liquid.

Of course the considerations above are also true, when one of the solid phases is the diffusing substance  $W$ .

IV. *The system  $E_1$  consists of solid substances only.*

We take a system:

$$E_1(n, r) = F_1 + F_2 \dots + F_r \dots \dots \dots (14)$$

of  $n$  components in  $r$  phases, we represent the composition of a phase  $F_i$  by:

$$a_i \text{ Mol } X + \beta_i \text{ Mol } Y \dots + (1 - a_i - \beta_i \dots) \text{ Mol } W$$

$$i = 1, 2, \dots, r$$

We assume that those solid phases have a constant composition. We now may distinguish several cases, according to the fact whether from system (14) by acceptance or loss of a small quantity of the diffusing substance  $W$  a liquid arises or not.

1°. *A liquid arises.*

When we take a system as f. i.



of course this cannot lose water but it can take in water.

In the latter case it passes into:



in which  $L$  is a liquid saturated with the solid substances. However, there are also systems which can form a liquid, also with loss of water.

A simple example is a. o. the hydrate  $Fe_2Cl_6 \cdot 12H_2O$  f. i. at  $30^\circ$ ; this passes, when we withdraw from it a little water, into the equilibrium  $L + Fe_2Cl_6 \cdot 12H_2O$ , in which the liquid  $L$  contains more  $Fe_2Cl_6$  than the hydrate. Consequently we distinguish two cases.

a. *The liquid is formed, when the system takes the diffusing substance.*

In the previous communication we have put in some simple cases of ternary systems the O.W.A. of one or two solid substances equal to that of the liquid, which arises at the acceptance of a small quantity of water. That this is generally the case, appears a. o. in the following way. We assume that system (14) by acceptance of a small quantity of the diffusing substance  $W$  passes into the system:

$$L + F_1 + F_2 \dots + F_r \dots \dots \dots (15)$$

We give to  $L$  the composition:

$$x \text{ Mol } X + y \text{ Mol } Y \dots + (1 - x - y \dots) \text{ Mol } W.$$

When this liquid arises by the liquefaction of  $\delta n_1$  quantities of  $F_1 + \delta n_2$  quantities of  $F_2$  etc., with  $\mu$  quantities of  $W$ , then we have:

$$x = \frac{a_1 \delta n_1 + a_2 \delta n_2 \dots}{\Delta + \mu} \quad ; \quad y = \frac{\beta_1 \delta n_1 + \beta_2 \delta n_2 \dots}{\Delta + \mu} \quad ; \quad \dots \quad (16)$$

etc. in which

$$\Delta = \delta n_1 + \delta n_2 \dots + \delta n_r .$$

The change of the thermodynamical potential then is:

$$\delta Z_1 = \zeta (\Delta + \mu) - \zeta_1 \delta n_1 - \zeta_2 \delta n_2 \dots \dots \dots (17)$$

When we assume that system (15) is in equilibrium, then  $r$  equations of the form (12) are valid for this. With the aid of those and of (16) we find:

$$\zeta \cdot \Delta + \left( x \frac{\partial \zeta}{\partial x} + y \frac{\partial \zeta}{\partial y} + \dots \right) \mu - \zeta_1 \delta n_1 - \zeta_2 \delta n_2 \dots = 0$$

so that (17) passes into:

$$\delta Z_1 = \left( \zeta - x \frac{\partial \zeta}{\partial x} - y \frac{\partial \zeta}{\partial y} - \dots \right) \cdot \mu \dots \dots \dots (18)$$

Hence follows that the O.W.A. of a system of solid phases is equal to the O.W.A. of the liquid, which arises when the system takes a little of the diffusing substance.

*b. The liquid is formed, when the system loses the diffusing substance.*

We now find the same as in case a. By recapitulation of both cases, it follows:

when in a system of solid substances a liquid  $L_1$  is formed with acceptance of the diffusing substance  $W$  and a liquid  $L_2$  is formed with loss of this substance  $W$ , then the O.W.A. of this system has two values; the one is equal to that of liquid  $L_1$  and is valid for the acceptance, the other to that of liquid  $L_2$  and is valid for the loss of the diffusing substance.

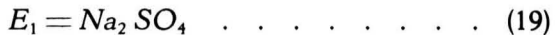
In the previous communications we have discussed already some simple examples.

*2. Two or more liquids arise,*

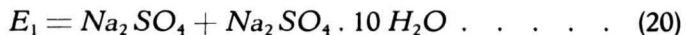
After the former considerations it is not necessary to discuss this case more in detail.

*3. No liquid arises.*

When a system  $E_1$  of solid substances takes a little of the diffusing substance  $W$  f.i. water and no liquid is formed, then this taken water must be held in any way by the solid substances, or it must be deposited like ice or it must occur as watervapour. Let us take f.i. the system:



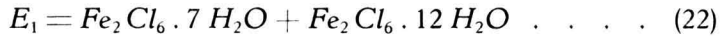
which consists of one substance only; this may pass by acceptance of water into the system:



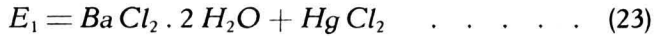
The system



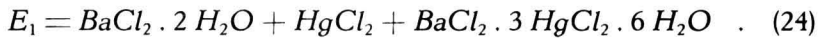
may pass into:



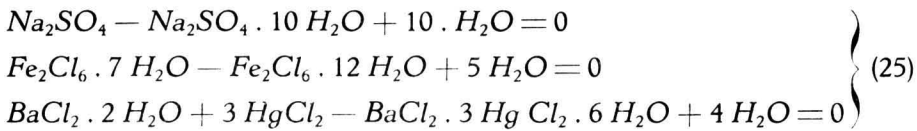
and the system:



below 17°.2 into the system:



We represent the reactions occurring in those systems by



From the systems 19, 21 and 23 a new phase arises, therefore, by acceptance of water; this is no more the case in the systems 20, 22 and 24 which have originated from those; only the quantities of the phases, which are present already, change in them. The same is true also, when we withdraw a little water from those systems 20, 22 and 24. Consequently we may say that in those systems at acceptance or loss of water a phases-reaction occurs, as is represented in (25), viz. a reaction, at which not the composition but only the quantity of the phases changes. As the systems 19, 21 and 23 by acceptance of a very small quantity of water pass at once already into 20, 22 and 24, we shall consider the latter only, consequently systems, in which at acceptance or loss of the diffusing substance a phases-reaction occurs.

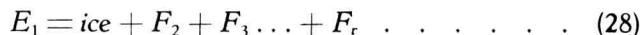
We now take a similar system:



we represent the reaction, when  $\mu$  quantities of the diffusing substance  $W$  are taken in by:



In this [compare the reactions 25] some of the reaction-coefficients are positive, and other ones negative. Of course it may be also the case that one or more of the phases of (26) do not participate in the reaction<sup>1)</sup>, the corresponding reaction-coefficients in 27 are zero then. A simple case we have f.i. in the system:



<sup>1)</sup> Then we have a singular equilibrium. Compare for this: F. A. H. SCHREINEMAKERS: In-, mono- and plurivariants equilibria. XXVII and XXVIII.

when water is the diffusing substance. Reaction (27) then becomes:

$$-\mu \text{ quantities of ice} + \mu \text{ quantities of water} = 0. \quad \dots \quad (29)$$

or in the ordinary form: water  $\rightleftharpoons$  ice.

When system 26 takes in  $\mu$  quantities of the diffusing substance  $W$ , then is the change of the thermodynamical potential:

$$\delta Z_1 = -\lambda_1 \zeta_1 - \lambda_2 \zeta_2 \dots - \lambda_r \zeta_r. \quad \dots \quad (30)$$

As viz. the quantity of a phase decreases when this is negative [compare f. i. the reactions 25], we must give in 30 the negative sign to  $\lambda_1 \lambda_2 \dots$

We now take a liquid  $L$  which is in equilibrium with the system 26. This is always possible. Let us take f. i. the system  $Na_2SO_4 + Na_2SO_4 \cdot 10H_2O$  at a definite temperature  $T_1$  and under a definite pressure  $P_1$  and let us consider the system:



at the same  $T_1$  and  $P_1$ . Then we have three phases, while  $T_1$  and  $P_1$  are given; consequently the liquid must contain three components at least. When it contains three components, then its composition is completely defined; when it contains four components, then it is represented by the points of a curve in space; etc.

When we take the system with the two ternary double-salts.  $D \cdot a H_2O + D \cdot \beta \cdot H_2O$ , so that in this a phases-reaction may occur by acceptance or loss of water. Then the liquid of the equilibrium  $D \cdot a H_2O + D \cdot \beta H_2O + L$  must contain also three components at least. As the solid phases are ternary compounds, the liquid, however, contains already from itself the three components. Consequently we need not add one or more new components, as in the previous system. The composition of the ternary liquid  $L$  is completely defined; in general there are two different ternary liquids, which may be in equilibrium with  $D \cdot a H_2O + D \cdot \beta H_2O$ .

We now consider the equilibrium;

$$F_1 + F_2 + F_3 \dots + F_r + L \quad \dots \quad (31)$$

The compositions of the solid phases are represented by:

$$a_i \text{ Mol } X + \beta_i \text{ Mol } Y \dots + (1 - a_i - \beta_i \dots) \text{ Mol } W$$

$$i = 1, 2 \dots r$$

that of the liquid  $L$ , which contains, besides the components  $XY \dots W$  yet also one or more other components  $MN \dots$  by

$$m \text{ Mol } M + n \text{ Mol } n \dots + x \text{ Mol } X + y \text{ Mol } Y \dots$$

$$+ (1 - m - n \dots - x - y \dots) \text{ Mol } W.$$

We now take in system 31  $q$  quantities of liquid. When the solid



substances take  $\delta w$  quantities of the substance  $W$  from those  $q$  quantities of liquid, then phases-reaction 27 occurs; however, the quantities which participate in this reaction are  $\delta w : \mu$  times as large now. The thermodynamical potential of the solid phases changes by this with :

$$-(\lambda_1 \zeta_1 + \lambda_2 \zeta_2 \dots \lambda_r \zeta_r) \frac{\delta w}{\mu} \dots \dots \dots (32)$$

that of the total liquid  $L$  with

$$\left( -\zeta + m \frac{\partial \zeta}{\partial m} + n \frac{\partial \zeta}{\partial n} \dots + x \frac{\partial \zeta}{\partial x} + y \frac{\partial \zeta}{\partial y} \dots \right) \delta w \dots \dots (33)$$

The total thermodynamical potential of the system 31 changes, therefore, with the sum 32 and 33. As at the equilibrium this change must be zero at constant  $T$  and  $P$  for each reaction possible in the system, the sum of 32 and 33 is zero, therefore, consequently also their sum when the factor  $\delta w$  is omitted. Hence follows that for 30 we may write also :

$$\delta Z_1 = \left( \zeta - m \frac{\partial \zeta}{\partial m} + n \frac{\partial \zeta}{\partial n} \dots - x \frac{\partial \zeta}{\partial x} - y \frac{\partial \zeta}{\partial y} \dots \right) \mu \dots \dots (34)$$

This means :

the O.W.A. of a system of solid phases between which a phases-reaction may occur by acceptance or loss of the diffusing substance  $W$ , is equal to the O.W.A. of each liquid, with which that system of solid phases can be in equilibrium.

Consequently it follows also from this :

all solutions, which can be in equilibrium with a system of solid substances in which a phases-reaction can occur by acceptance or loss of the diffusing substance  $W$ , have the same O.W.A. and are isotonic, therefore.

The O.W.A. of the system  $Na_2 SO_4 + Na_2 SO_4 \cdot 10 H_2O$  is equal, therefore, to that of each arbitrary liquid  $L$  of the equilibrium :

$$Na_2SO_4 + Na_2SO_4 \cdot 10 H_2O + L \dots \dots \dots (35)$$

Above we have seen that this liquid must contain besides the components  $H_2O$  and  $Na_2 SO_4$  yet at least one other substance. It is indifferent which are those substances or substance f.i. alcohol, acetone,  $KCl$ , sugar etc., provided that only the liquid is in equilibrium with the two solid substances. Consequently an infinite number of liquids exists which may be in equilibrium with  $Na_2 SO_4 + Na_2 SO_4 \cdot 10 H_2O$ ; they are all isotonic.

The same is true also for systems as f.i.  $Na Cl + ice$ ,  $Na_2 SO_4 + ice$  etc. and in general for a system;  $ice + F_2 + F_3 \dots$ ; the phases-reaction which takes place at acceptance or loss of water is then;  $water \rightleftharpoons ice$ .

The preceding properties are deduced in supposition that the phases of system 26 have a constant composition; however, they are valid also for solid substances with a variable composition (f.i. mixed-crystals) and also when one of the phases is gaseous. Consequently they are true also for a system:  $water\text{-vapour} + F_2 + F_3 \dots$

From the preceding considerations follow at once the results, which we have deduced in the previous communications for simple cases in ternary systems. Let us take f.i. fig. 2 (Communication V); with the aid of the rule, deduced above sub IV. 1. a, we find: the O.W.A. of the solid substance  $X$  is equal to that of liquid  $b$ ; that of the hydrate  $H$  is equal to that of liquid  $a$  and that of the solid mixture  $X + Y$  is equal to that of liquid  $c$  (and of course equal also to that of the liquids of the isotonic curves, which go through the points  $b, a$  and  $c$ ).

In fig. 3 (Comm. V) the O.W.A. of the ternary compound  $D$  is equal to that of liquid  $s$ , in fig. 4 it is equal to that of the liquid  $d$ . The O.W.A. of the complex  $X + D$  is in both figures equal to that of the liquid  $d$  and that of  $Y + D$  equal to that of liquid  $c$ .

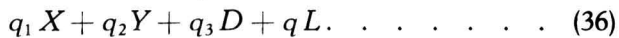
A phases-reaction can occur between the phases  $Y + H$  in fig. 2 by acceptance and loss of water; with the aid of the rule, deduced sub IV. 3 it follows, that the O. W. A. of  $Y + H$  is equal to that of liquid  $d$ .

In the equilibria represented by figs. 3 and 4 (Comm. V) also the complex  $X + Y + D$  can exist. According to IV. 8 this complex has the same O.W.A. as the liquid in each arbitrary equilibrium:



Of course an infinite number of those equilibria exists, but then the liquid must contain, besides the components  $X Y$  and  $W$ , still one or more other components.

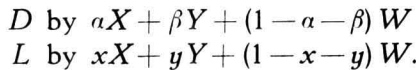
This follows also at once from the figs. 3 and 4; herein viz. no liquid exists, which can be in equilibrium with the three solid substances  $X Y$  and  $D$ . Yet in the ternary system itself also liquids exist, which have the same O.W.A. as the complex  $X + Y + D$ . In order to show this we take an arbitrary system:



in which  $q_1$  etc. represent the quantities of the different phases. We take  $q$  positive and very small with respect to  $q_1 q_2$  and  $q_3$ . As, however, this system (36) is not stable, it passes into the complex:



We now represent the thermodynamical potentials by  $\zeta_x \zeta_y \zeta_D$  and  $\zeta$ , the composition of



With the transition of system (36) into (37) the total thermodynamical potential must decrease; hence follows:

$$\zeta - x \zeta_x - y \zeta_y > (1 - x - y) K . . . . . (38)$$

in which

$$K = \frac{\zeta_D - a \zeta_x - \beta \zeta_y}{1 - a - \beta} . . . . . (39)$$

(38) is valid for every arbitrary liquid, therefore, for each value of  $x$  and  $y$ . If we put  $x=0$  and  $y=0$  than (38) passes into  $\zeta_w > K$ , in which  $\zeta_w$  is the thermodynamical potential of water.

We now imagine a liquid  $L$ , which has the same O.W.A. as the complex  $X + Y + D$ ; consequently we have the osmotic equilibrium:

$$\left( X + Y + D \mid L \right) . . . . . (40)$$

in which the reaction:

$$aX + \beta y - D + (1 - a - \beta) W = 0$$

occurs. The composition  $x y$  of this liquid  $L$  of equilibrium (40) is defined by:

$$\zeta - x \frac{\partial \zeta}{\partial x} - y \frac{\partial \zeta}{\partial y} = K . . . . . (41)$$

in which  $K$  has the value, indicated in (39). Now we may always satisfy (41). For  $x=0$  and  $y=0$  the first part of (41) becomes  $\zeta_w$  and, therefore, greater than  $K$ . Let we change  $x$  and  $y$ , then the first part can obtain, therefore, all values between  $\zeta_w$  and  $-\infty$ ; consequently there are also values of  $x$  and  $y$ , for which the first part becomes equal to  $K$ ; consequently we can always satisfy (41). Hence follows, therefore:

in figs. 3 and 4 (Comm. V) is situated anywhere a curve, which represents the solutions, which have the same O.W.A. as the solid complex  $X + Y + D$ .

We are able to deduce something about the position of this isotonic curve. We imagine in those figs. 3 and 4 each of the three saturation-curves to be drawn totally. That of  $D$  then forms a closed curve;  $a c$  then terminates in a point, which we shall call  $c'$ , and  $b d$  in a point which we shall call  $d'$ ; those points  $c'$  and  $d'$  are situated on the side  $X Y$ . As the system  $X + Y$  is stable, those curves  $a c c'$  and  $b d d'$  intersect one another in a point  $s'$  within the triangle.

We now can show that the point of intersection of the isotonic curve with the saturation-curve  $a c c' s'$  is situated on the part  $c' s'$ . For this it is sufficient to show that the solution, which is represented by this point of intersection is supersaturated with respect to the solid substance  $X$ .

This solution is defined by the equations:

$$\zeta - x \frac{\partial \zeta}{\partial x} - y \frac{\partial \zeta}{\partial y} = K . . . . . (42)$$

$$\zeta - x \frac{\partial \zeta}{\partial x} + (1 - y) \frac{\partial \zeta}{\partial y} = \zeta_y . . . . . (43)$$

the first of which represents the isotonic curve and the second one the saturation-curve of the solid substance  $Y$ . We find from this:

$$\zeta + (1 - x) \frac{\partial \zeta}{\partial x} - y \frac{\partial \zeta}{\partial y} - \zeta_x = \frac{\zeta - x \zeta_x - y \zeta_y - (1 - x - y) K}{x} . . . . . (44)$$

We find this by substituting in the first part of (44) f.i. the values of  $\frac{\partial \zeta}{\partial x}$  and  $\frac{\partial \zeta}{\partial y}$ , which follow from (42) and (43). When the first part should be zero, then this meant that the liquid was in equilibrium with the solid substance  $X$ . According to (38) the second part of (44) is positive, however; this means that the liquid is supersaturated with respect to the solid substance  $X$ .

Generally we are able to prove now that all liquids of the isotonic curve are supersaturated; consequently this curve is situated totally within the supersaturated region.

The O.W.A. of the solid complex  $X + Y + D$  is, therefore, greater than those of the liquids  $c$  and  $d$  (figs. 3 and 4 comm. V) and those of all other saturated and unsaturated liquids. When we bring the solid complex in osmotic contact with one of those saturated or unsaturated liquids, then it takes water in and passes into one of the equilibria  $X + D + \text{liquid } d$  or  $Y + D + \text{liquid } c$ .

*(To be continued).*

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