

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

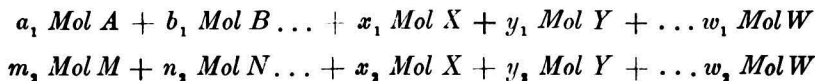
(Communicated at the meeting of October 25, 1924).

*Isotonic liquids.*

We take two liquids  $L_1$  and  $L_2$ , which are separated from one another at a definite temperature  $T$  and pressure  $P$  by a semipermeable membrane, which permits to diffuse one or more of the substances.

We shall say now that both liquids are isotonic with respect to those diffusing substances, at that  $T$  and  $P$ , at which they are in osmotic equilibrium with one another. The total thermodynamical potential is not allowed to change, therefore, when small quantities of the diffusing substances pass from the one liquid towards the other.

We give to  $L_1$  and  $L_2$ , the composition:



in which

$$w_1 = 1 - a_1 - b_1 \dots - x_1 - y_1 \dots$$

$$w_2 = 1 - m_2 - n_2 \dots - x_2 - y_2 \dots$$

Consequently we have the general case that both liquids contain, besides the common substances  $X Y \dots W$ , also not-common substances;  $A B \dots$  appear viz. in  $L_1$  only,  $M N \dots$  in  $L_2$  only.

When there is only one diffusing substance f.i.  $W$  then the equation of equilibrium is:

$$\varphi_1 = \varphi_2 \quad \dots \quad (1)$$

in which

$$\varphi_1 = \zeta_1 - a_1 \frac{\partial \zeta_1}{\partial a_1} - b_1 \frac{\partial \zeta_1}{\partial b_1} \dots - x_1 \frac{\partial \zeta_1}{\partial x_1} - y_1 \frac{\partial \zeta_1}{\partial y_1} \dots$$

$$\varphi_2 = \zeta_2 - m_2 \frac{\partial \zeta_2}{\partial m_2} - n_2 \frac{\partial \zeta_2}{\partial n_2} \dots - x_2 \frac{\partial \zeta_2}{\partial x_2} - y_2 \frac{\partial \zeta_2}{\partial y_2} \dots$$

Consequently (1) is a function of  $TP$  and all variables of both the liquids.

Is  $X$  the diffusing substance, then we find:

$$\varphi_1 + \frac{\partial \zeta_1}{\partial x_1} = \varphi_2 + \frac{\partial \zeta_2}{\partial x_2} \dots \dots \dots (2)$$

Is  $Y$  the diffusing substance, then is true:

$$\varphi_1 + \frac{\partial \zeta_1}{\partial y_1} = \varphi_2 + \frac{\partial \zeta_2}{\partial y_2} \dots \dots \dots (3)$$

etc. When all common substances  $WXY\dots$  can diffuse, then the equations (1) (2) (3)  $\dots$  are valid at the same time.

We now shall deduce some properties, and imagine  $T$  and  $P$  to be constant.

When we assume that the liquid  $L_1$  is saturated with the solid substance  $W$ , then is valid for this equilibrium  $L_1 + W$  the equation:

$$\varphi_1 = \zeta_W \dots \dots \dots (4)$$

in which the  $\zeta$  of the solid substance  $W$  is indicated by  $\zeta_W$ . When the liquid  $L_2$  is also saturated with  $W$ , then is true for this the relation  $\varphi_2 = \zeta_W$ . As from both those equations the relation (1) follows, both liquids are, therefore, isotonic with respect to the substance  $W$ .

When both liquids are saturated with the solid substance  $X$ , then are valid the two equations:

$$\varphi_1 + \frac{\partial \zeta_1}{\partial x_1} = \zeta_X \text{ and } \varphi_2 + \frac{\partial \zeta_2}{\partial x_2} = \zeta_X \dots \dots \dots (5)$$

in which  $\zeta_X$  represents the  $\zeta$  of the solid substance  $X$ . From both those equations (2) follows, so that the two liquids are isotonic with respect to the substance  $X$ . Consequently we find:

two liquids, both saturated with a same solid substance, are isotonic with respect to this substance.

All liquids, in equilibrium with ice, are, therefore, isotonic with respect to water, whatever substances are occurring in each of those liquids.

All liquids, saturated with sugar or urea etc. or with sugar + urea etc. are, therefore, isotonic with respect to sugar or urea etc. or to sugar + urea etc., whatever substances each of those substances still contains.

In the same way we can deduce also:

when a liquid is saturated with  $X + Y + Z$  and another liquid with  $X + Y + U$ , then they are isotonic with respect to  $X$  and  $Y$ , but not with respect to  $U$  and  $Z$ ;

when a liquid  $L$  is in equilibrium with a solid substance  $W$ , then all liquids which are isotonic with  $L$  with respect to this substance  $W$ , may be in equilibrium also with the solid substance  $W$ ; when two liquids  $L_1$  and  $L_2$  are isotonic with respect to  $X Y$  and  $Z$  and  $L_1$  and  $L_2$  are isotonic with respect to  $X Y$  and  $U$ , then  $L_1$  and  $L_2$  are isotonic with respect to  $X$  and  $Y$ .

We now assume that the liquids  $L_1$  and  $L_2$  are both in equilibrium with a vapour, which contains only one substance f.i.  $W$ . We then have the equations for equilibrium:

$$\varphi_1 = \zeta_W \quad \text{and} \quad \varphi_2 = \zeta_W \dots \dots \dots (6)$$

in which  $\zeta_W$  represents the  $\zeta$  of the substance  $W$  in vapour-form. As from both those equations the relation (1) follows again, both liquids are isotonic, therefore, with respect to the substance  $W$ . Consequently follows from this:

two liquids, both in equilibrium with a single vapour, are isotonic with respect to the substance of which this vapour consists.

All liquids in equilibrium with water-vapour are, therefore, isotonic with respect to water, whatever substances each of those liquids still contains.

Of course the same is true for liquids, in equilibrium with alcohol-vapour or benzene-vapour etc.

We find also:

when a liquid  $L$  is in equilibrium with a vapour  $W$ , then all liquids which are isotonic with  $L$  and contain no other volatile substances than  $W$ , may also be in equilibrium with the vapour  $W$ .

We don't consider it necessary to draw once more the attention to the fact that the deductions mentioned above are only valid for constant  $T$  and  $P$ .

We now take in a system of  $n$  components at a definite  $T$  and  $P$  a liquid  $L_1$  with the definite composition:

$$x_1 \text{ Mol } X + y_1 \text{ Mol } Y + z_1 \text{ Mol } Z \dots + (1 - x_1 - y_1 - z_1 \dots) \text{ Mol } W.$$

We now put the question: which other liquids  $L$  are isotonic with  $L_1$  at the same  $T$  and  $P$  when  $W$  is the diffusing substance.

When we represent the composition of  $L$  by:

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

then must, therefore, be satisfied:

$$\zeta - x \frac{\partial \zeta}{\partial x} - y \frac{\partial \zeta}{\partial y} - z \frac{\partial \zeta}{\partial z} \dots = \zeta_1 - x_1 \frac{\partial \zeta_1}{\partial x_1} - y_1 \frac{\partial \zeta_1}{\partial y_1} - z_1 \frac{\partial \zeta_1}{\partial z_1} \dots (7)$$

As  $x_1, y_1, z_1, \dots$  have a definite value, the second part of (7) has, therefore, a definite value also; when we represent this by  $\zeta_{(W)}$  then  $x y z \dots$  must satisfy:

$$\zeta - x \frac{\partial \zeta}{\partial x} - y \frac{\partial \zeta}{\partial y} - z \frac{\partial \zeta}{\partial z} \dots = \zeta_{(W)} \dots \dots \dots (8)$$

Consequently at constant  $T$  and  $P$  in a system of  $n$  components an infinite number of liquids exists, which are mutually isotonic with respect to a definite substance. We shall refer later to the special case that  $n = 2$ .

We may still give to (8) a meaning, by which the mutually isotonic liquids may be brought into combination with other equilibria.

We imagine for this the diffusing substance  $W$  in an imaginary solid state which we shall call  $(W)$ . We define this imaginary state in such a way that the thermodynamical potential of this substance  $(W)$  is equal to  $\zeta_{(W)}$ .

When we consider the equilibrium  $L + (W)$ , we see that equation (8) is also valid for this. Hence follows:

all liquids which are isotonic with respect to the substance  $W$ , are saturated with the imaginary solid substance  $(W)$ ;

and reversally: all liquids which are saturated with the imaginary solid substance  $(W)$  are isotonic with respect to the substance  $W$ .

By giving other values to  $x_1, y_1, z_1, \dots$  in (7) we can change the value of  $\zeta_{(W)}$  in (8). It is evident that  $\zeta_{(W)}$  may get an infinite number of values so that we must distinguish also an infinite number of modifications of the imaginary substance  $(W)$  which pass into one another without interruption. Let us consider some of those modifications, which we shall represent by  $(W_1), (W_2), (W_3)$  etc. with thermodynamical potentials  $\zeta_{(W_1)}, \zeta_{(W_2)}, \zeta_{(W_3)}$  etc.

We now take the equations:

$$\varphi = \zeta_{(W_1)} \quad \varphi = \zeta_{(W_2)} \quad \varphi = \zeta_{(W_3)} \dots \dots \dots (9)$$

in which  $\varphi$  represents the first part of equation (8). The first one of those equations represents all liquids which are mutually isotonic with respect to the substance  $W$ , or the liquids which are saturated with the modification  $(W_1)$ . We shall say that all those liquids belong to the „isotonic group  $(W_1)$ “. The second equation also represents a group of liquids which are mutually isotonic with respect to the substance  $W$ ; however they are saturated with the modification  $(W_2)$ . Those liquids form the „isotonic group  $(W_2)$ “. The third equation represents the liquids of the isotonic group  $(W_3)$  etc.

Consequently all liquids of the isotonic group ( $W_1$ ) are mutually isotonic; also all liquids of the isotonic group ( $W_2$ ); etc. Liquids of two different isotonic groups, however, are not isotonic with one another.

We find, therefore:

in a system of  $n$  components at constant  $T$  and  $P$  exists an infinite number of isotonic groups, each of which consists of an infinite number of liquids. All liquids of a same isotonic group are mutually isotonic, but liquids of different isotonic groups are not isotonic with one another.

In order to show the latter we take two liquids  $L_1$  and  $L_2$  of the composition:

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

and

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

We assume that  $L_1$  belongs to the isotonic group ( $W_1$ ) and  $L_2$  to the isotonic group ( $W_2$ ). We then have the two relations:

$$\zeta_1 - x_1 \frac{\partial \zeta_1}{\partial x_1} - y_1 \frac{\partial \zeta_1}{\partial y_1} \dots = \zeta_{(W_1)} \dots \dots \dots (10)$$

$$\zeta_2 - x_2 \frac{\partial \zeta_2}{\partial x_2} - y_2 \frac{\partial \zeta_2}{\partial y_2} \dots = \zeta_{(W_2)} \dots \dots \dots (11)$$

When we take  $n_1$  quantities  $L_1$  and  $n_2$  quantities  $L_2$ , then is the total thermodynamical potential

$$Z = n_1 \zeta_1 + n_2 \zeta_2.$$

When  $\Delta n_1$  quantities of the substance  $W$  diffuse from  $L_1$  to  $L_2$ , then we find:

$$\Delta Z = \left( -\zeta_1 + x_1 \frac{\partial \zeta_1}{\partial x_1} + y_1 \frac{\partial \zeta_1}{\partial y_1} \dots + \zeta_2 - x_2 \frac{\partial \zeta_2}{\partial x_2} - y_2 \frac{\partial \zeta_2}{\partial y_2} \dots \right) \Delta n$$

or

$$\Delta Z = [\zeta_{(W_2)} - \zeta_{(W_1)}] \Delta n \dots \dots \dots (12)$$

As the second part of (12) is not zero, the two liquids are not in osmotic equilibrium, therefore, but the substance  $W$  diffuses.

The direction of the diffusion must now be in such a way that  $\Delta Z$  is negative. When we take  $\zeta_{(W_1)} > \zeta_{(W_2)}$  then  $\Delta n$  must be positive, therefore; consequently the substance  $W$  diffuses from  $L_1$  to  $L_2$ . Consequently we may say:

the substance  $W$  diffuses from the liquid in which  $\zeta_{(W)}$  has the largest value, to a liquid with smaller value of  $\zeta_{(W)}$ .

As in the case above-discussed the substance  $W$  diffuses from  $L_1$  to  $L_2$ , we shall say that the „membrane-diffusion-pressure” or shortly the “diffusion-pressure” of the substance  $W$  is larger in  $L_1$  than in  $L_2$ . Consequently we may say also: the greater  $\zeta_{(W)}$  is in a liquid, the greater the diffusion-pressure of substance  $W$  in that liquid is.

We shall refer later to some other general properties of isotonic groups.

*Isotonic liquids in binary systems.*

Above we have seen already that the general considerations are not valid in every respect for binary systems. When we take viz. a binary system with the components  $X$  and  $W$  then (8) passes into:

$$\zeta - x \frac{\partial \zeta}{\partial x} = \zeta_{(W)} \dots \dots \dots (13)$$

which defines at constant  $T$ ,  $P$  and  $\zeta_{(W)}$  an isotonic group of liquids. But as in (13)  $x$  is no more variable, we can only satisfy (13) by one or by some definite values of  $x$ . Consequently the isotonic group consists also of only one or of some definite liquids and not, as in the general case, of an infinite number.

We imagine to be drawn on an horizontal axis the composition and on a vertical axis the  $\zeta$ 's of the binary liquids. When in the binary system dimixtion occurs, then the  $\zeta$  curve has a form like curve  $l_1s_1$  in fig. 2 of the previous communication; when all liquids rest homogeneous, then it is convex downward in each point. We now take on the axis  $W\zeta$  (fig. 2 l.c.) a part  $W\zeta_0 = \zeta_{(W)}$ . The points of contact of the tangents drawn from the point  $\zeta_0$  indicate then isotonic liquids, consequently liquids of a same isotonic group ( $W$ ).

When the  $\zeta$  curve is convex downward then only one tangent to the curve can be drawn at each position of  $\zeta_0$ ; each isotonic group consists, therefore, of one liquid only; consequently at constant  $T$  and  $P$  there are no isotonic liquids.

When the  $\zeta$  curve has a form like curve  $l_1s_1$  in fig. 2 (l.c.) then at definite situations of the point  $\zeta_0$  three tangents may be drawn. The corresponding isotonic groups then consist each of 3 liquids, of which, however, only one is stable. However, there is one isotonic group, which contains two stable (and one unstable) liquids viz. when the point  $\zeta_0$  coincides with the point of intersection of the axis  $W\zeta$  and the double-tangent  $m_1q_1$ . Limiting ourselves to stable states only, then follows, therefore:

in a binary equilibrium in which dimixtion may occur, at given  $T$  and  $P$  only two isotonic liquids exist. They are viz. the two

liquids which can be in equilibrium with one another at that  $T$  and  $P$ ; consequently they are isotonic with respect to both the components.

We shall refer to some properties when discussing the ternary systems.

*Isotonic liquids in ternary systems.*

*Isotonic curves.*

For ternary liquids with the components  $X$   $Y$  and  $W$  (8) passes into:

$$\zeta - x \frac{\partial \zeta}{\partial x} - y \frac{\partial \zeta}{\partial y} = \zeta_{(W)} \quad \dots \quad (14)$$

which defines at constant  $T$ ,  $P$  and  $\zeta_{(W)}$  the liquids of an isotonic group ( $W$ ). As (14) represents a curve, it follows, therefore:

the liquids of an isotonic group ( $W$ ) are represented in a concentration diagram by a curve; we call this the „isotonic  $W$ -curve”.

As  $\zeta_{(W)}$  may have an infinite number of values, consequently there exists at constant  $T$  and  $P$  an infinite number of those curves; they are differing by the diffusion-pressure of the substance  $W$ , which grows with the increase of  $\zeta_W$ .

In fig. 1, in which  $X$   $Y$  and  $W$  represent the three components, some isotonic  $W$ -curves are drawn a.o. the curves  $ad$ ,  $eh$  and  $im$ . Consequently all liquids of curve  $ad$  are mutually isotonic with respect to the substance  $W$ ; the same is true for all liquids of  $eh$ ,  $im$  etc. Liquids of different curves are not isotonic, however, f.i. liquid  $b$  not with  $e$  or  $g$  or  $l$  etc.

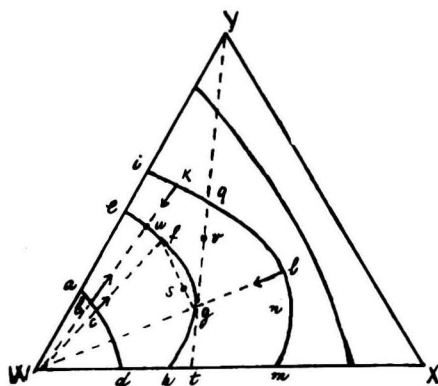


Fig. 1.

$W$   $X$   $Y$  in liquid state. We now take on the axis  $W$   $W'$  a point  $w$  in such a condition that  $Ww = \zeta_{(W)}$ ; we draw a cone which has its top in  $w$  and which touches the  $\zeta$ -surface. The projection of the tangent-curve on the plane  $X$   $Y$   $W$  is then the isotonic  $W$ -curve, belonging to this definite  $\zeta_{(W)}$ . When we change  $\zeta_{(W)}$  then we get also another isotonic curve.

We may deduce the isotonic  $W$ -curves also in the following way. We imagine in fig. 1 the  $\zeta$ 's of all liquids at constant  $T$  and  $P$  to be drawn perpendicular to the plane of design. We then get a  $\zeta$  surface  $W'X'Y'$ ; the lines  $WW'$ ,  $XX'$  and  $YY'$  represent then the  $\zeta$ 's of the substances

Following this way we can deduce easily different properties; firstly we shall assume herewith, that no dimixtion into two or more liquids can occur, so that the  $\zeta$  surface is in each point convex downward. We find a.o.:

1. Each isotonic  $W$ -curve has two terminating-points; the one is situated on the line  $WX$ , the other on  $WY$  of the triangle (fig. 1).

2. Each straight line, drawn through the point  $W$ , intersects the isotonic  $W$ -curve in one point only.

3. Two different isotonic curves can never touch or intersect one another.

4. The isotonic  $W$ -curves are situated the nearer to the point  $W$ , the greater  $\zeta_{(W)}$  is. When  $\zeta_{(W)}$  becomes  $=\zeta_W$  (viz. the thermodynamical potential of the liquid  $W$ ) then this curve shrinks to the point  $W$  itself.

5 The diffusion-pressure of the substance  $W$  is equal in all liquids of an isotonic  $W$ -curve; however, it is greater, the nearer this curve is situated to the point  $W$ .

It is only too clear that all this is also true for the substances  $X$  and  $Y$ .

In order to find the form of the curves in the vicinity of the point  $W$ , we put:

$$\zeta = \varphi + RT(x \log x + y \log y).$$

(14) then passes into:

$$\varphi - x \frac{\partial \varphi}{\partial x} - y \frac{\partial \varphi}{\partial y} - RT(x + y) = \zeta_{(W)} \quad . \quad . \quad (15)$$

when we represent the value of  $\varphi$  for  $x=0$  and  $y=0$  by  $\varphi_0$ , then (15) passes into:

$$RT(x + y) = \varphi_0 - \zeta_{(W)} \quad . \quad . \quad . \quad . \quad (16)$$

in which data of second and higher order are neglected and the second part has a small positive value. The isotonic  $W$ -curve is, therefore, in the vicinity of the point  $W$  a small straight line, which intercepts equal parts from the two axes. On further distance of the point  $W$  those curves are curled generally. In the vicinity of the point  $W$  the liquids, in which the diffusion-pressure of the substance  $W$  is the same, have also the same concentration of this substance  $W$ ; at a greater distance this is no more the case.

We now take two liquids  $b$  and  $k$  (fig. 1) which are situated on a straight line, going through point  $W$  and we separate those liquids by a semi-permeable membrane, which allows to pass the substance  $W$  only. As the diffusion-pressure of the substance  $W$  is larger in the liquid  $b$  than in  $k$ , consequently  $W$  shall diffuse from  $b$  to  $k$ ;



the two liquids move, therefore, towards one another in the direction of the little arrows. The diffusion-pressure of the substance  $W$  decreases, therefore, continually in the moving liquid  $b$ , in  $k$ , however, it increases. Consequently the diffusion will continue till both liquids reach the same isotonic  $W$ -curve; therefore, till they get the same composition. When  $u$  is the complex of the two liquids  $b$  and  $k$  then the result of the membrane-diffusion is, therefore, that both the liquids get the composition  $u$ . Of course the same is true also for binary liquids  $WX$  and  $WY$ .

Quite another case it is, however, when both the liquids are not situated on a straight line, going through  $W$ ; let us take f.i. the liquids  $c$  and  $l$ , the complex of which we shall represent by point  $s$ . At the membrane-diffusion of  $W$  therefore  $c$  shifts in the direction of the little arrow away from point  $W$  and  $l$  shifts in the direction of the little arrow towards point  $W$ ; of course the complex remains represented by point  $s$ . This membrane diffusion will continue till the one liquid is arrived in  $f$  and the other one in  $g$ ; the points  $f$ ,  $s$  and  $g$  are situated on a straight line and  $f$  and  $g$  on the same isotonic  $W$ -curve; the diffusion-pressure is then equal in both liquids. Consequently the result of the membrane diffusion is the birth of the liquids  $f$  and  $g$ .

The line  $fsg$  is drawn in fig. 1 approximately parallel to the line  $XY$ ; the liquids  $f$  and  $g$  have, therefore, approximately the same concentration of the substance  $W$ ; however, this line can be situated also in such a way that the concentration of  $W$  in the liquid  $f$  is larger than in  $g$  and reversally.

Now we will say of two substances the one of which has a larger concentration of the substance  $W$  than the other one, that the one is  $W$ -concentrated and the other one  $W$ -poor. We may say now:

at membrane-diffusion of the substance  $W$  between two liquids the  $W$ -concentrated may rest in this state, but it may become also  $W$ -poor.

Let us take in fig. 1 the liquids  $K$  and  $n$ , of which  $K$  is the  $W$ -concentrated and  $n$  the  $W$ -poor liquid. Imagining the isotonic  $W$ -curve drawn through  $n$ , then it appears that the diffusion-pressure of the substance  $W$  is larger in liquid  $n$  than in  $K$ ; consequently the substance  $W$  shall diffuse from  $n$  to  $K$ . We find, therefore:

at membrane-diffusion a substance  $W$  can go from a  $W$ -poor liquid to a  $W$ -concentrated liquid.

It follows from those considerations that the diffusion-pressure of a substance  $W$  in a liquid is not only dependent on the concentration of this substance  $W$ , but also on other substances, which are present in this liquid.

Let us take now the binary liquid  $d$  and let us add to this the new substance  $Y$ . Going from point  $d$  towards  $Y$  we now intersect isotonic  $W$  curves of steadily diminishing diffusion-pressure; consequently addition of  $Y$  causes decrease of the diffusion-pressure of the substance  $W$ .

However, when we add the new substance  $Y$  to the liquid  $t$ , then the phenomena become different; we assume viz. that the line  $tY$  touches the curve  $eh$  in  $g$ . We imagine in fig. 1 to be drawn through point  $t$  the isotonic  $W$ -curve, which intersects the line  $tY$  in  $v$ . Consequently the diffusion-pressure increases starting from  $t$ , reaches a maximum in  $g$  and decreases at further addition of  $Y$ ; then in  $v$  the diffusion-pressure is again the same as in  $t$ ; in  $q$  it is lower.

We find, therefore:

the diffusion-pressure of a substance in a binary mixture can as well decrease as increase by addition of a new substance; in the latter case this pressure goes through a maximum, so that at last it decreases again.

We take the liquids  $L_1$  and  $L_2$  with the composition:

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

and

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

and we keep the pressure  $P$  constant. When the pure liquid  $W$  under a pressure  $P_1$  is in osmotic equilibrium with the liquid  $L_1$  then is the osmotic pressure  $\pi_1 = P - P_1$  of  $L_1$  defined by:

$$\left( \zeta_1 - x_1 \frac{\partial \zeta_1}{\partial x_1} - y_1 \frac{\partial \zeta_1}{\partial y_1} \dots \right)_P = (\zeta_0)_{P_1} \dots \dots (17)$$

in which the second part represents the  $\zeta$  of the pure liquid  $W$  under the pressure  $P_1$ . The osmotic pressure  $\pi_2 = P - P_2$  of the liquid  $L_2$  with respect to the pure liquid  $W$  under a pressure  $P_2$  is defined by:

$$\left( \zeta_2 - x_2 \frac{\partial \zeta_2}{\partial x_2} - y_2 \frac{\partial \zeta_2}{\partial y_2} \dots \right)_P = (\zeta_0)_{P_2} \dots \dots (18)$$

when we represent the first part of (17) by  $\zeta_{(W_1)}$  and that of (18) by  $\zeta_{(W_2)}$  then follows:

$$\zeta_{(W_1)} - \zeta_{(W_2)} = (\zeta_0)_{P_1} - (\zeta_0)_{P_2} = \int_{P-P_2}^{P-P_1} v_0 dP \dots \dots (19)$$

in which  $v_0$  is the volume of the pure liquid. When this volume changes only little with the pressure, then with approximation (19) passes into:

$$\zeta_{(W_1)} - \zeta_{(W_2)} = (\pi_2 - \pi_1) v_0 \dots \dots \dots (20)$$

According to the sign of the first part of (19) or (20) being positive or negative, the membrane-diffusion-pressure of the substance  $W$  in the liquid  $L_1$  is larger or smaller than in  $L_2$ .

Consequently we may say:

the membrane-diffusion-pressure of a substance  $W$  in a liquid  $L$  under a pressure  $P$  is the larger (smaller), the smaller (larger), the osmotic pressure of this liquid  $L$  with respect to the pure liquid  $W$  is.

When the substance  $W$  diffuses by a membrane from the liquid  $L_1$  to  $L_2$ , we have said that the diffusion-pressure of the substance  $W$  in liquid  $L_1$  is larger than in  $L_2$ . However, we might say also that the "osmotic  $W$ -attraction" of liquid  $L_1$  is smaller than that of  $L_2$ . Then in the previous deductions we have to substitute everywhere larger (smaller) diffusion-pressure by smaller (larger) "osmotic attraction". Therefore the property mentioned sub 5 f.i. will become:

the osmotic  $W$ -attraction is the same for all liquids of an isotonic  $W$ -curve; however, the nearer this curve approaches point  $W$  the smaller the osmotic  $W$ -attraction is.

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*(To be continued).*