

Chemistry. — “Equilibria in systems, in which phases, separated by a semi-permeable membrane.” IV. By F. A. H. SCHREINEMAKERS.

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Ternary equilibria with solid phases.

In the previous communication we have discussed the *O.W.A.* (osmotic water-attraction) etc. of liquids in ternary systems, when one of the components occurs as solid phase. Now we shall assume that a binary compound viz. a hydrate component *Y* occurs.

The saturation-curve of this hydrate is represented for a definite *T* and *P* by curve *w d v*; point *H* represents the hydrate; every straight line starting from point *H* is allowed to intersect this curve in one point only. We shall call *w* the terminating-point of the curve rich in water and *v* the terminating-point poor in water. Just as in the previous communication we shall say also here that point *a* is situated closer to *w* than *b*, etc. It is not allowed, however, to prove from this (compare the previous communication) that a liquid of this curve contains the more (less) water, the closer (further) it is situated to (from) the point *w*. The dotted curves *w m*, etc. are the isotonic *W*-curves.

In a similar way as in the previous communication we may deduce:

1^o. An isotonic curve and the saturation-curve of the hydrate can intersect one another in one point only, they never can touch one another.

2^o. The *O.W.A.* of a liquid of a saturation-curve of a hydrate is greater (smaller) the more this liquid is situated further from (closer to) the terminating-point rich in water of this curve.

The *O.W.A.* increases, therefore, along curve *w v* in the direction of the arrows.

3^o. An isotonic curve and the saturation-curve of a hydrate are situated in the vicinity of their point of intersection either both within the conjugation-angle or both within the supplement-angle. When the one curve touches one side of that angle, than the other curve touches the other side.

In point *c* (fig. 1) the conjugation-angle is *W c H*; as the saturation-curve touches *WC* in *c*, the isotonic curve *n n'* must touch *cH* in *c*.

We are able to deduce the property mentioned sub. 2^o a.o. also in the following way. When we represent the composition of *H* by: $\beta \text{ Mol } Y + (1 - \beta) \text{ Mol } W$, then the saturation-curve *w v* is defined by:

$$\zeta - x \frac{\delta \zeta}{\delta x} + (\beta - y) \frac{\delta \zeta}{\delta y} = \zeta_H \dots \dots \dots (1)$$

in which ζ_H is the ζ of the substance H . The *O.W.A.* of a liquid is defined by:

$$\varphi = \zeta - x \frac{\delta \zeta}{\delta x} - y \frac{\delta \zeta}{\delta y} \dots \dots \dots (2)$$

From (1) follows:

$$[-x r + (\beta - y) s] dx + [-x s + (\beta - y) t] dy = 0 \dots \dots (3)$$

From (2) follows in connection with (3)

$$\frac{1}{\beta} d\varphi = -s dx - t dy \dots \dots \dots (4)$$

We now take a system of coordinates with the point H as pole and the line HW as axis; we represent the radius vector by ρ and the angle by μ ; consequently in w is $\mu = 0$, in v is $\mu = 180^\circ$. In order to simplify the calculation we imagine angle $WXY = 90^\circ$, which has not any influence on the result. We now have:

$$\begin{aligned} \rho \sin \mu &= x & \rho \cos \mu \cdot d\mu + \sin \mu \cdot \delta \rho &= dx \\ \rho \cos \mu &= \beta - y & -\rho \sin \mu \cdot d\mu + \cos \mu \cdot \delta \rho &= -\delta y. \end{aligned}$$

When we substitute those values in (3) and (4) then follows:

$$\begin{aligned} \rho [(t - r) \sin \mu \cdot \cos \mu + s (\cos^2 \mu - \sin^2 \mu)] d\mu &= \{ \dots \dots \dots (5) \\ &= [r \sin^2 \mu - 2s \sin \mu \cos \mu + t \cos^2 \mu] d\mu \} \end{aligned}$$

$$\frac{1}{\beta} \cdot \delta \varphi = -\rho (s \cos \mu + t \sin \mu) d\mu - (s \sin \mu - t \cos \mu) \delta \rho \dots (6)$$

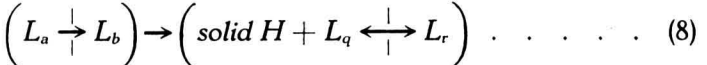
Outside a region of dimixtion $rt - s^2$ and consequently also the coefficient of $\delta \rho$ in (5) is always positive and never zero; therefore $\delta \mu$ can not become zero. A radius vector going through point H , therefore never can touch the saturation-curve wv , only in one point it may intersect this curve.

By elimination of $\delta \rho$ it follows from (5) and (6):

$$\frac{d\varphi}{d\mu} = -\frac{\beta \rho (rt - s^2) \sin \mu}{r \sin^2 \mu - 2s \sin \mu \cos \mu + \cos^2 \mu} \dots \dots \dots (7)$$

so that the second part of (7) is negative. Consequently φ decreases along curve wv starting from w towards v , so that *O.W.A.* increases starting from w towards v .

Point c , viz. the point of contact of the tangent to curve wv drawn from point W , divides wv into two parts. We now bring into osmotic contact two liquids L_a and L_b of part wc ; as L_b has a greater *O.W.A.* than L_a , water is diffusing from L_a towards L_b . Consequently the inversion is:



In this L_q represents a saturated solution between a and b and L_r an unsaturated solution; of course L_q and L_r are situated on the same osmotic curve.

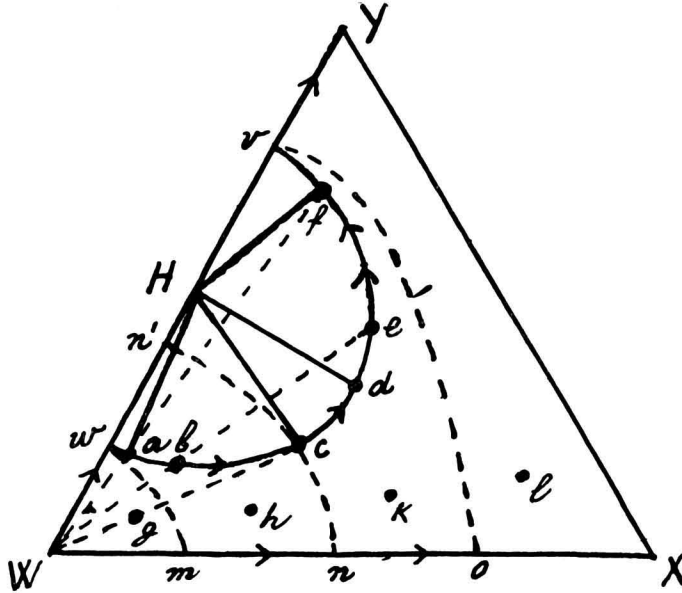


Fig. 1.

When we bring into osmotic contact L_e and L_f of part cv , then the inversion is:

$$\left(L_e \begin{array}{c} \rightarrow \\ | \\ \rightarrow \end{array} L_f \right) \rightarrow \left(L_s \begin{array}{c} \leftarrow \\ | \\ \rightarrow \end{array} L_t + \text{solid } H \right) (9)$$

in which L_t represents a liquid between e and f and L_s an unsaturated liquid.

When we take two liquids, the one of which is situated on part wc and the other on part cv , f.i. L_b and L_f , then the inversion is:

$$\left(L_b \begin{array}{c} \rightarrow \\ | \\ \rightarrow \end{array} L_f \right) \rightarrow \left(\text{solid } H + L_u \begin{array}{c} \leftarrow \\ | \\ \rightarrow \end{array} L_u + \text{solid } H \right) . . . (10)$$

The position of L_u depends on the situation of the complex of L_b and L_f ; when f.i. this complex is situated on the line Hd , then is $L_u = L_d$.

With inversion (8) the solid substance arises on that side of the membrane on which water is removed from; in (9) on that side to which water is diffusing; in (10) the solid substance arises on both sides of the membrane.

We bring the two binary liquids L_w and L_v into osmotic contact. As L_v has a greater *O.W.A.* than L_w the inversion is:

$$\left(L_w \begin{array}{c} \downarrow \\ \uparrow \\ \downarrow \end{array} L_v \right) \rightarrow \left(\text{solid } H + L_w \begin{array}{c} \downarrow \\ \uparrow \\ \downarrow \end{array} \text{solid } H \right) (11)$$

or :

$$\left(L_w \begin{array}{c} \downarrow \\ \uparrow \\ \downarrow \end{array} L_v \right) \rightarrow \left(\text{solid } H \begin{array}{c} \downarrow \\ \uparrow \\ \downarrow \end{array} L_v + \text{solid } H \right) (12)$$

In both cases viz. water is diffusing from L_w towards L_v and L_w passes with loss of water, L_v with increase of water into solid H . This diffusion continues till all the liquid either on the one or on the other side of the membrane, has disappeared. When we bring L_w and L_v in definite ratio into osmotic contact, then the inversion may become also :

$$\left(L_w \begin{array}{c} \downarrow \\ \uparrow \\ \downarrow \end{array} L_v \right) \rightarrow \left(\text{solid } H \begin{array}{c} \downarrow \\ \uparrow \\ \downarrow \end{array} \text{solid } H \right) (13)$$

The liquids then disappear on both sides of the membrane with separation of solid H .

We now bring into osmotic contact L_w with a liquid L_q ; consequently we have a system $\left(L_w \begin{array}{c} \downarrow \\ \uparrow \\ \downarrow \end{array} L_q \right)$. In the same way as in the previous communication it now appears :

1^o. when L_q is situated within the region Wwm , then water is diffusing from L_q to L_w ; then L_w passes into an unsaturated liquid between w and W .

2^o. when L_q is situated on the isotonic curve wm , then L_q and L_w are in osmotic equilibrium and nothing happens.

3^o. when L_q is situated within the region $wmXYvdw$, then water is diffusing from L_w to L_q ; then L_w shall separate the substance H and shall dry up totally or partially.

When we bring L_v into osmotic contact with a liquid L_q , then we have to bear in mind that, as appears also from fig. 1, L_v separates the solid hydrate H with increase of water, and that L_v passes into an unsaturated solution losing water.

We now find :

1^o. when L_q is situated within the region $WovdwW$, then water is diffusing from L_q to L_v ; then L_v separates solid H and dries up totally or partially.

2^o. when L_q is situated on the isotonic curve vo then nothing happens.

3^o. when L_q is situated within the region $voXY$ then water is diffusing from L_v to L_q ; then L_v becomes an unsaturated solution between v and Y .

Different results may be deduced from those considerations. A.o. this: all liquids within the region $wmovidw$ make as well L_w as L_v to dry up totally or partially into the solid substance H .

In accordance with our definition of the osmotic water-attraction of solid substances (see the previous communication) we have to mean by the *O.W.A.* of the hydrate *H* the *O.W.A.* of the liquid which arises when a very small quantity of water is added to the substance *H*; consequently here this is the liquid L_w . Therefore curve wm is the curve ($O.W.A. = H$).

Just as in the previous communication we now find:

1°. the hydrate *H*, in osmotic contact with a liquid within the region Wwm , shall remove water from this liquid.

2°. the hydrate *H*, in osmotic contact with a liquid outside the region Wwm , can not remove water from this liquid.

Consequently when we bring solid *H* in osmotic contact with liquid L_g (fig. 1) then water diffuses to the solid substance and is formed either: solid $H + L_w$ or an unsaturated liquid between w and W .

When we bring solid *H* in osmotic contact with one of the liquids h, k, l, n or o (fig. 1) then nothing happens. When, however, we bring in osmotic contact one of those liquids with L_w , then L_w is drying up totally or partially with separation of solid *H*.

In fig. 2 point *D* represents a ternary compound, f.i. a hydrous double-salt. The saturation-curve of *D* is represented by the closed curve $wbvfw$. In accordance with a well-known property all lines starting from point *D* intersect this curve in one point only. As w and v represent the solutions of *D* in pure water, we may call w the point of solubility of substance *D* rich in water and v the point poor in water

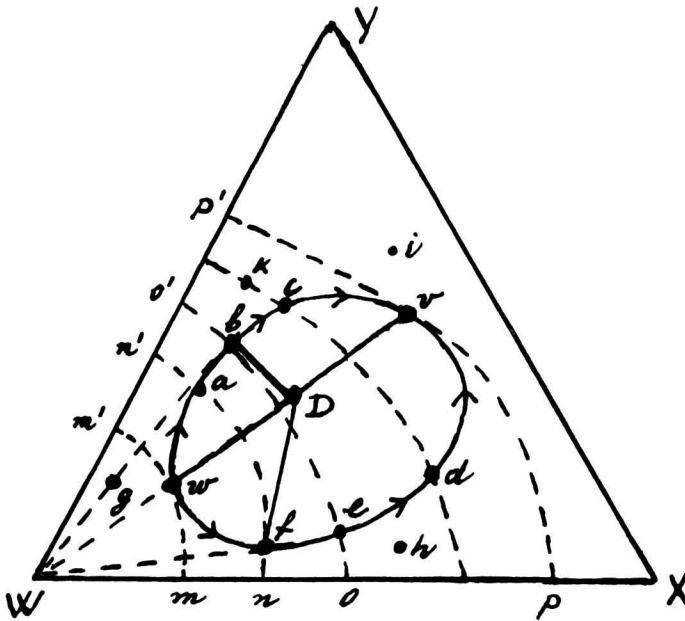


Fig. 2.

Further we shall call wbv the branch of the saturation-curve rich in Y and wfv the branch rich in X . The dotted curves mm' , nn' , etc. are isotonic curves.

We now easily may deduce:

1^o. An isotonic curve intersects the saturation-curve of a ternary compound in two points; the one point of intersection is situated on the branch rich in X , the other on the branch rich in Y . The isotonic curves going through w and v touch the saturation-curve in w and v .

Consequently with each solution of the branch rich in X , a definite solution of the branch rich in Y may be in osmotic equilibrium; f. i. L_a with L_f , L_b with L_e , L_c with L_d etc.

2^o. The *O.W.A.* of a liquid of the saturation-curve is greater (smaller) the more it is situated further from (closer to) the point w .

Consequently the *O.W.A.* increases on both branches of the curve in the direction of the arrows.

3^o. For an isotonic curve and the saturation-curve of a ternary substance in the vicinity of their point of intersection the same is true as for an isotonic curve and the saturation-curve of a component or of a hydrate.

Consequently the curves nn' and oo' must touch the lines fD and bD in f and b .

We also may deduce the property, mentioned sub 2^o, a. o. in the following way. We represent the composition of D by: a Mol $X + \beta$ Mol $Y + (1-a-\beta)$ Mol W . Then the saturation-curve wv is defined by:

$$\zeta + (a-x) \frac{\delta\zeta}{\delta x} + (\beta-y) \frac{\delta\zeta}{\delta y} = \zeta_D \quad (14)$$

in which ζ_D is the ζ of the solid substance D . The *O.W.A.* of a liquid is defined by:

$$\varphi = \zeta - x \frac{\delta\zeta}{\delta x} - y \frac{\delta\zeta}{\delta y} \quad (15)$$

It follows from (14):

$$[(a-x)r + (\beta-y)s] dx + [(a-x)s + (\beta-y)t] dy = 0. \quad . (16)$$

From (15) follows, in connection with (16):

$$d\varphi = -(ar + \beta s) dx - (as + \beta t) dy \quad (17)$$

We now take a system of coordinates, the pole of which is represented by point D , the axis by the line DW . We let the radius vector to turn at increasing value of μ in the direction of the hands of a clock, consequently starting from w , along a, b, c towards v and backwards along d towards w . When we put angle $DWX = \vartheta$ and when we take for the sake of simplicity angle $XWY = 90^\circ$, then we have:

$$\begin{aligned} a-x &= \varrho \cos(\mu - \vartheta) & \beta-y &= -\varrho \sin(\mu - \vartheta) \\ dx &= \varrho \sin(\mu - \vartheta) \cdot d\mu - \cos(\mu - \vartheta) \delta\varrho \\ dy &= \varrho \cos(\mu - \vartheta) \cdot d\mu + \sin(\mu - \vartheta) \cdot \delta\varrho \end{aligned}$$

Substituting those values in (16) and (17) and putting $\mu - \vartheta = \mu'$, then we find;

$$\left. \begin{aligned} \varrho [(r - t) \sin \mu' \cos \mu' + s (\cos^2 \mu' - \sin^2 \mu')] d\mu &= \} \\ &= [r \cos^2 \mu' - 2s \sin \mu' \cos \mu' + t \sin^2 \mu'] \delta \varrho \} \end{aligned} \right. \quad \dots \quad (18)$$

$$d\varphi = -\varrho [R \sin \mu' + S \cos \mu'] d\mu + [R \cos \mu' - S \sin \mu'] d\varrho \quad \dots \quad (19)$$

in which:

$$R = ar + \beta s \quad \text{and} \quad S = as + \beta t$$

From (18) again follows the same as is deduced from (5). When we eliminate $d\varrho$ from (18) and (19) and when we substitute again μ' by $\mu - \vartheta$, then follows:

$$\frac{d\varphi}{d\mu} = -\frac{\varrho (rt - s^2) [a \sin (\mu - \vartheta) + \beta \cos (\mu - \vartheta)]}{A} \quad \dots \quad (20)$$

in which A represents the coefficient of $d\varrho$ from (18). As further:

$$\frac{\beta}{a} = \text{tg } \vartheta. \quad \dots \quad (21)$$

(20) passes into:

$$\frac{d\varphi}{d\mu} = -\frac{\varrho (rt - s^2) a \sin \mu}{A} \quad \dots \quad (22)$$

Consequently φ is maximum or minimum for $\sin \mu = 0$, therefore when $\mu = 0^\circ$ and $\mu = 180^\circ$, consequently in w and v . For points on branch $w b v$ $\sin \mu$ is positive and therefore φ decreases starting from w towards v ; for points on branch $v e w$ $\sin \mu$ is negative and consequently φ increases from v towards w or reversally it decreases from w towards v . As the *O.W.A.* of a liquid increases with decreasing values of φ , the property mentioned sub 2^o follows from this.

With the aid of fig. 2 the reader now may deduce several properties; briefly we shall discuss a single one.

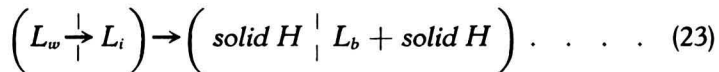
We bring into osmotic contact L_w with a liquid L_q .

1^o. when L_q is situated within the region $W m w m'$, then water diffuses from L_q to L_w ; L_w passes into an unsaturated liquid between w and W .

2^o. when L_q is situated on the osmotic curve $m w m'$, then nothing happens.

3^o. when L_q is situated outside the region $W m w m'$, then water diffuses from L_w to L_q ; then L_w separates solid D and dries up totally or partially.

When a complex of L_w and L_i is represented f.i. by a point of bD , then we have the inversion:



Here we have to mean by the *O.W.A.* of the ternary compound the

O.W.A. of the liquid L_w . Consequently curve mwm' is the curve (O.W.A. = D). We now find:

1^o. a ternary compound D , in osmotic contact with a liquid within the region $Wmwm'$, removes water from this liquid, with formation of $L_w + D$ or an unsaturated solution between w and W .

2^o. a ternary compound D , in osmotic contact with a liquid out of the region $Wmwm'$, does not remove water from this liquid.

Consequently when we bring into osmotic contact solid D with a liquid L_q (fig. 2) then water diffuses to the solid substance. When we bring into osmotic contact solid D with one of the liquids b, v, d, h, k or i , then nothing happens. When, however, we bring into osmotic contact one of those liquids with L_w , then L_w is drying up totally or partially with separation of solid D .

Finally we still have to consider the occurrence of a binary compound between the components X and Y . As, however, the results are in accordance with the now mentioned, we shall not discuss this case.

We have assumed with our considerations that water may diffuse from a liquid through a membrane towards other liquids and solid substances. Till now, we have supposed, however, that water can not diffuse through the membrane from solid hydrous substances (f. i. from the hydrate H in fig. 1 or the hydrous compound D in fig. 2). In many cases this is surely possible; we shall refer to this later.

When we assume this now, then some deductions must be changed in connection with the O.W.A. of the hydrate H (and compound D).

Let us take the osmotic system



When a little water diffuses from H to L then H passes into L_v (fig. 1) with loss of water; on the left side of the membrane then arises $H + L_v$; consequently system (24) passes into:



Therefore, it now depends on the O.W.A. of L_v with respect to that of L , which shall happen. When L is situated in the region $v o X Y$ then L has a greater O.W.A. than L_v ; consequently water diffuses from L_v to L . As L_v should become unsaturated then, H is dissolving, so that the quantity of H decreases. When H has totally disappeared, before L has reached curve ov , then on the left side a liquid unsaturated and poor in water arises (viz. between v and Y).

We have deduced from fig. 1: a hydrate H in osmotic contact with a liquid L :

1^o. removes water and flows away, when L is situated within the region Wwm .

2^o. rests unchanged, when L is situated within the region $mXYvdw$.
 We now have to replace region $mXYvdw$ in 2^o. by the region $movidw$; in that case is also:

3^o. separates water and flows away when L is situated within the region $voXY$.

Therefore we can assume that the hydrate H has two different *O.W.A.*'s viz.

1^o. the *O.W.A.* of the solution L_w , saturated and rich in water, which arises when H takes water.

2^o. the *O.W.A.* of the solution L_v , saturated and poor in water, which arises when H loses water.

When it is necessary to distinguish the two *O.W.A.*, we shall call the second one the maximum or *M—O.W.A.*

We may also apply those considerations to a mixture of solid substances. In general we may say:

the *O.W.A.* of a solid substance or of a mixture of solid substances is that of the new system, which arises by taking water in;

the *M—O.W.A.* is that of the new system, which arises by losing water.

It is evident that only in that case there may be question of a *M—O.W.A.* when one or more of the solid substances contain water.

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(To be continued).