

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

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Ternary systems with vapour-phases.

We now consider an osmotic system:

$$G \mid G_1 \dots \dots \dots (1)$$

in which a vapour occurs on both sides of the membrane. We represent the composition of the vapour G by:

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

and that of the vapour G_1 by:

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

If we assume that the membrane allows the substance W only to pass through, then we find that system (1) is in osmotic equilibrium, when:

$$\zeta - x \frac{\partial \zeta}{\partial x} - y \frac{\partial \zeta}{\partial y} = \zeta_1 - x_1 \frac{\partial \zeta_1}{\partial x_1} - y_1 \frac{\partial \zeta_1}{\partial y_1} \dots \dots (2)$$

As we find, therefore, for the osmotic equilibrium of two vapours the same equations as for the osmotic equilibrium of two liquids, we can say, therefore, that the *O.W.A.* of a vapour is defined by:

$$\varphi = \zeta - x \frac{\partial \zeta}{\partial x} - y \frac{\partial \zeta}{\partial y} \dots \dots (3)$$

and consequently we can apply to those osmotic vapour-systems the same considerations as formerly to the osmotic liquid-systems.

Let us take f.i. fig. 1 Comm. II and let us assume that at given temperature and pressure all binary and ternary mixtures are gaseous, then the curves ad , eh etc. can represent isotonic vapour-curves. All vapours of curve ad then are mutually isotonic, also those of eh etc.; of course vapours of different curves are not mutually isotonic, as the *O.W.A.* of the vapours of an isotonic curve is larger, the more this curve is situated farther from the point W .

Previously (Communication II) we have deduced that the isotonic liquid curves are in the vicinity of point w (fig. 1. II) straight lines which cut equal parts of the sides WX and WY ; on greater distance of point W , however, they are curved, as is drawn in the figure. If we assume, however, as we shall do always in the following, that the vapours follow the law of BOYLE GAY-LUSSAC, then the isotonic vapour-curves

are not only straight lines in the vicinity of the point W , but everywhere. For a vapour, which follows the law of BOYLE GAY-LUSSAC, we have viz.

$$\zeta = x C_x + y C_y + (1-x-y) C_w + \left. \begin{array}{l} \\ + RT [x \log x + y \log y + (1-x-y) \log (1-x-y)] \end{array} \right\} \quad (4)$$

Hence follows for the osmotic equilibrium (1):

$$\varphi = C_w + RT \log (1-x-y) \quad \varphi_1 = C_w + RT \log (1-x_1-y_1) \quad (4^a)$$

consequently:

$$x + y = x_1 + y_1 \quad (5)$$

If we give a definite composition to the vapour G_1 then it appears from (5) that the vapour G is represented by the points of a straight line, which goes through the point which represents the point G_1 . The isotonic vapour-curves, therefore, are straight lines, parallel to the side XY .

As $1-x-y$ is the concentration of the water in the vapour G and $1-x_1-y_1$ that in the vapour G_1 , it follows, therefore:

the vapours G and G_1 have the same *O.W.A.* if the concentration of the water and, therefore, also the partial vapour-pressure of the water is equal in both vapours.

It now is evident that properties and phenomena, which we have previously deduced, with assumption that the isotonic liquid-curves are curved, are no more valid now. Previously we have seen a.o. that the *O.W.A.* of the liquid t (fig. 1. II) does not increase immediately with addition of the substance Y ; its *O.W.A.* viz, firstly becomes smaller, till it becomes a minimum in g and only at further addition of Y the *O.W.A.* increases. Of course a similar phenomenon cannot occur with vapours.

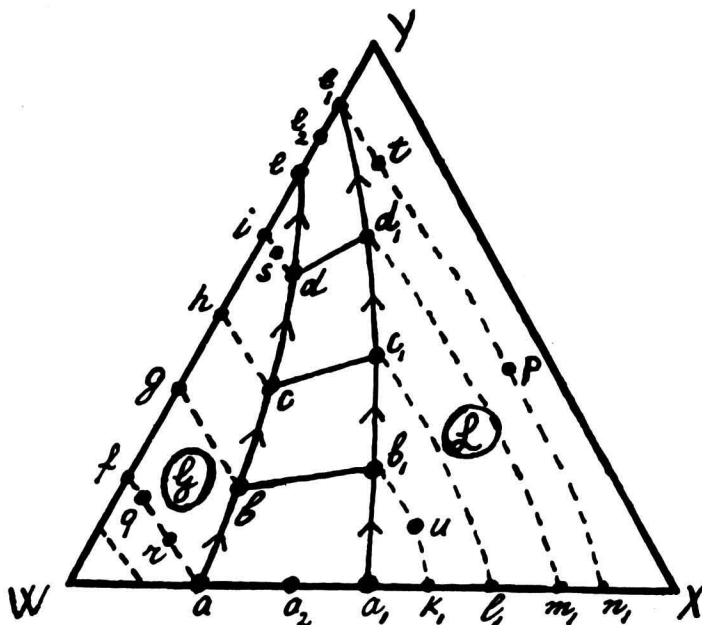
Now we shall assume that with a given temperature and pressure a part of the mixtures is liquid and another part gaseous, so that also may occur equilibria: $G + L$ viz. vapour + liquid. Of the many cases which can occur with this ¹⁾ we shall discuss only some.

If we assume that at the given T and P the substance W is gaseous, but the substances X and Y are liquid, then we may get a diagram as fig. 1, in which Wae represents the vapour-region and $a_1 e_1 YX$ the liquid-region; the first one is indicated by an encircled G , the latter one by an encircled L . Consequently at the given T and P all mixtures of the region Wae are gaseous and those of the region $a_1 e_1 YX$ are liquid. With every vapour of curve $a_1 e_1$ a definite liquid of curve $a_1 e_1$ can be in equilibrium, f.i. vapour a with the liquid a_1 ; vapour b with

¹⁾ For considerations more in detail on ternary systems, in which vapour occurs, compare; F. A. H. SCHREINEMAKERS. Zeitschrift f. Phys. Chem. 36 257, 413, 710 (1901); 37 129 (1901); 38 227 (1901); 43 671 (1903) Archives Néerlandaises. These Proceedings. Equilibria in ternary systems. Comm. I—XVIII (1912—1915).

the liquid b_1 ; etc.; some of the vapours and liquids which are in equilibrium with one another are united with one another in the figure by straight lines (conjugation-lines: vapour-liquid).

The field $a a_1 e_1 e$ situated between the curves $a e$ and $a_1 e_1$ is a heterogeneous field; each point of this field represents viz. a complex of a vapour of curve $a e$ and a liquid of curve $a_1 e_1$; f.i. a point of the line $b b_1$ represents an equilibrium $G_b + L_{b_1}$; a point of the line $c c_1$ an equilibrium $G_c + L_{c_1}$; etc.



The two binary conjugation-lines $a a_1$ and $e e_1$ of course go through the point W ; referring to the position of the ternary conjugation lines we may distinguish two cases, viz.:

- a) one (or some) of the conjugation-lines goes through the point W .
- b) none of the conjugation-lines goes through the point W .

In fig. 1 the latter case is drawn; with this we have assumed that all conjugation-lines intersect the side WY in points between W and Y . In connection with this assumption we may say, as in the previous communications, that we move away from the point W along the curves $a e$ and $a_1 e_1$ if we proceed along these curves in the direction of the arrows viz. from a towards e and from a_1 towards e_1 .

We now take an equilibrium :

$$G + L \dots \dots \dots (6)$$

of which G and L are represented, therefore, in fig. 1 by two conjugated points, the one of which is situated on curve $a e$ and the other on curve $a_1 e_1$. As G and L are in equilibrium with one another, they are isotonic with respect to all components and, therefore, also with respect to the

diffusing component *W*. Consequently the vapour *a* has the same *O.W.A.* as the liquid *a*₁; the vapour *b* the same as the liquid *b*₁; etc. Consequently we have a.o. the following osmotic equilibria:

$$G_a \mid L_{a_1} \quad G_b \mid L_{b_1} \quad G_c \mid L_{c_1} \dots \dots \dots (7)$$

in which, however, we can also omit the membrane.

In the previous communication we have deduced:

the *O.W.A.* of a stable system becomes smaller at taking in of water and greater at losing of water.

If we apply this rule to the equilibria (6) above-mentioned then we find:

the *O.W.A.* of the vapours of curve *a e* and that of the liquids of curve *a₁e₁* increases in the direction of the arrows, viz. from *a* towards *e* and from *a₁* towards *e₁*.

In the osmotic system:

$$G_b + L_{b_1} \overset{\mid}{\underset{\mid}{\rightleftarrows}} G_c + L_{c_1} \dots \dots \dots (8)$$

the system at the right of the membrane has, therefore, a greater *O.W.A.* than the left system; consequently the water will diffuse in the direction of the arrow, viz. from left to right.

The curves dotted in fig. 1 represent isotonic curves; if we limit ourselves to stable states then we find in the vapour-region *W a e* only isotonic vapour-curves and in the liquid-region *a₁ X Y e₁* only isotonic liquid-curves. In the heterogeneous region *a a₁ e₁ e* all isotonic curves are metastable. The isotonic curves situated in the vapour-region are straight lines parallel to the side *XY*; the isotonic curves of the liquid-region are more or less curved.

Isotonic curves with a smaller *O.W.A.* than that of the vapour *a* are situated within the triangle *W a f*; the isotonic curve with the same *O.W.A.* as that of the vapour *a* consists of curve *a f* and the isolated point *a₁*. Consequently we can have the osmotic equilibrium:

$$G(a f) \mid L_{a_1} \dots \dots \dots (9)$$

in which *G(a f)* represents an arbitrary vapour of the curve *a f*. Consequently we may have a.o. the following osmotic equilibria:

$$G_f \mid G_a ; G_q \mid G_r ; G_q \mid L_{a_1} ; G_f \mid L_{a_1} \dots \dots (10)$$

In the last of those systems a binary vapour, consisting of *W + Y*, is in osmotic equilibrium with a binary liquid consisting of *W + X*.

The isotonic curve with a same *O.W.A.* as the vapour *b* consists of two branches viz. of the vapour-branch *g b* and the liquid-branch *b₁ k₁*, which are united with one another by the conjugation-line *b b₁*. Consequently all vapours of branch *g b* have the same *O.W.A.*, also all

in which G'_q is represented by the point of intersection of Wq and hc and L'_p by the point of intersection of Wp and $c_1 l_1$.

If the equilibrium is formed on the isotonic curve im_1 , then (11) passes into the osmotic equilibrium:

$$G_d + L_{d_1} \mid L'_p \dots \dots \dots (14)$$

in which L'_p is represented by the point of intersection of Wp and $d_1 m_1$.

In the osmotic system:

$$G_r \overset{\mid}{\rightarrow} L_p \dots \dots \dots (15)$$

as is apparent from the figure, the liquid has a greater *O.W.A.* than the vapour, so that water must diffuse in the direction of the arrow. If we assume that the line Wr intersects the conjugation-line bb_1 also, then (15) may pass into the osmotic equilibrium:

$$G_b + L_{b_1} \mid G_b + L_{b_1} \dots \dots \dots (16)$$

If the equilibrium is formed on curve $c_1 l_1$ then (15) passes into the osmotic equilibrium:

$$L'_r \mid L'_p \dots \dots \dots (17)$$

consequently into an equilibrium of two liquids which are represented by the points of intersection of the lines Wr and Wp with curve $c_1 l_1$. Therefore, the vapour G_r of system (15) is totally condensed with loss of water.

In the osmotic system:

$$G_r \overset{\mid}{\rightarrow} L_t \dots \dots \dots (18)$$

as is apparent from the figure, the liquid has a greater *O.W.A.* than the vapour, so that the water diffuses in the direction of the arrow. If we choose the ratio of the quantities of both phases in such a way that the equilibrium is formed on the isotonic curve hl_1 , then (18) passes into the osmotic equilibrium:

$$L'_r \mid G'_t \dots \dots \dots (19)$$

in which L'_r is represented by the point of intersection of Wr and $c_1 l_1$ and G'_t by the point of intersection of Wt and hc . The result of the diffusion is, therefore, that in (18) the vapour (at the left side of the membrane) passes into a liquid and that the liquid (at the right side of the membrane) passes into a vapour.

We now take an osmotic system of two vapours f.i.

$$G_r \overset{\mid}{\rightarrow} G_s \dots \dots \dots (20)$$

in which, as is apparent from the figure, the vapour s has a greater

O.W.A. than the vapour r . If the equilibrium is formed on the isotonic curve gk_1 then (20) passes into the osmotic equilibrium:

$$G_b + L_{b_1} \mid G'_s \dots \dots \dots (21)$$

in which G'_s is represented by the point of intersection of Ws and gb . The vapour G_r of system (20) is partly condensed, therefore, with loss of water.

The vapour G_r of system (20) can also condense totally; this is the case f.i. if we choose the ratio's of the quantities of the phases in (20) in such a way that the equilibrium is formed on the isotonic curve hl_1 . Then system (20) passes into the osmotic equilibrium:

$$L'_r \mid G'_s \dots \dots \dots (22)$$

in which L'_r is represented by the point of intersection of Wr and $c_1 l_1$ and G'_s by the point of intersection of Ws and hc . The vapour G_r of system (20) is totally converted into liquid, therefore.

At last we still consider an osmotic system of two liquids, f.i.:

$$L_u \overset{\mid}{\rightarrow} L_t \dots \dots \dots (23)$$

in which, as appears from the figure, the water must diffuse from left to right. If we choose the ratio of the quantities of both phases in such a way that the equilibrium is formed on the isotonic curve hl_1 , then (23) is converted into the osmotic system:

$$L'_u \mid G'_t \dots \dots \dots (24)$$

in which L'_u is represented by the point of intersection of Wu and $c_1 l_1$ and G'_t by the point of intersection of Wt and hc . Consequently the liquid at the right side of the membrane in (23) is totally passed into vapour with taking up water.

In fig. 1 we have assumed that at the given T and P the vapour-region is represented by Wae and the liquid-region by $a_1 e_1 YX$. We now shall suppose, however, the reverse, viz. that Wae represents a liquid-region and $a_1 e_1 YX$ a vapour-region; we have to interchange, therefore, in fig. 1 the encircled letters L and G ; also we have to imagine the curves $b_1 k_1$, $c_1 l_1$, etc. to be replaced by straight lines, parallel to the side XY .

The previous considerations remain all valid now, but of course we have to interchange everywhere vapour and liquid and in the osmotic systems and equilibria (9)–(24) we have to replace the G by L and reversally. If we take f.i. the osmotic system (20) then this now becomes an osmotic system of two liquids viz.:

$$L_r \overset{\mid}{\rightarrow} L_s \dots \dots \dots (25)$$

which, if the equilibrium is formed on the isotonic curve $h l_1$, passes into the osmotic equilibrium

$$G'_r \mid L'_s \quad (26)$$

instead of into (22).

One of the liquids of system (25) viz. L_r now passes with loss of water into the unsaturated vapour G'_r , which is represented in the figure by the point of intersection of $W r$ and $c_1 l_1$.

The ternary conjugation-lines are drawn in fig. 1 all in such a way that none of them passes through the point W ; if we assume, however, that one of those conjugation-lines f.i. the line $c c_1$ goes through the point W , then, if we proceed along the curves $a e$ and $a_1 e_1$, the *O.W.A.* in c and c_1 is maximum or minimum. We can deduce this in the same way as in communication XIV the corresponding property for the contact of an isotonic curve with the binodal-curve. In previous communications on vapour-tensions in ternary systems¹⁾ we find many diagrams in which conjugation-lines: vapour-liquid go through the point W .

As in fig. 1 stable states only are indicated, we find the isotonic vapour-curves only in the region $W a e$ and the isotonic liquid-curves only in the region $a_1 e_1 Y X$. The first is divided by curve $a f$, the second by $e_1 n_1$ into two parts, which behave themselves differently with respect to osmotic equilibria. A vapour of part $W a f$ viz. can be isotonic only with vapours, and a liquid of part $e_1 n_1 X Y$ only with liquids; however, a vapour of part $a f e$ can be isotonic as well with vapours as with liquids; the same is valid for a liquid of part $a_1 e_1 n_1$.

Otherwise it is, however, if we consider metastable states also; then the vapour-region does not terminate in curve $a e$ and the liquid-region not in curve $a_1 e_1$; it depends on the T and P for which the figure is valid, how far both are prolonged. If we choose, as we shall assume further, the T and P in such a way that the components and all their mixtures may be as well liquid as gaseous, then each of both the regions covers the total triangle. Within the region $a e e_1 a_1$ then is situated a curve $a_2 e_2$ of which only the terminating-points a_2 and e_2 are drawn; its interpretation appears from the following. If we leave out of consideration the heterogeneous region $a e e_1 a_1$, then all vapours of the region $W a_2 e_2$ and all liquids of the region $a_2 e_2 Y X$ are stable and consequently all liquids of $W a_2 e_2$ and all vapours of $a_2 e_2 Y X$ are metastable. If we take into consideration, however, also the heterogeneous region, then the vapours of $a e e_2 a_2$ and the liquids of $a_1 e_1 e_2 a_2$ are metastable with respect to the equilibria $L + G$.

Of the many cases, which may occur, if we consider metastable phases

¹⁾ l. c.

also, we shall discuss a few only. We represent the composition of a vapour G by:

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

and that of a liquid L by:

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

The thermodynamical potential ζ of the vapour is then defined by (4); in order to represent the thermodynamical potential ζ_1 of the liquid we have to add to (4) still a term which we shall write in the form $RT\mu_1$; further of course we have to replace in (4) x and y by x_1 and y_1 . If the vapour is stable with respect to a liquid of the same composition, then is $\zeta < \zeta_1$ and μ_1 is positive, therefore; in the opposite case μ_1 is negative. We now find for the vapour G :

$$\varphi = C_w + RT \log (1 - x - y) \dots \dots \dots (27)$$

and for the liquid L :

$$\varphi_1 = C_w + RT \log (1 - x_1 - y_1) + RTm \dots \dots \dots (28)$$

in which:

$$m = \mu_1 - x_1 \frac{\partial \mu_1}{\partial x_1} - y_1 \frac{\partial \mu_1}{\partial y_1} \dots \dots \dots (29)$$

We now take a vapour G_0 of the composition $x_0 y_0$ and we consider the osmotic systems:

$$G_0 \mid G \dots (30^a) \quad G_0 \mid L \dots \dots \dots (30^b)$$

For (30^a) follows from (27) the equation:

$$x_0 + y_0 = x + y \dots \dots \dots (31)$$

for (30^b) we find with the aid of (27) and (28):

$$1 - x_0 - y_0 = (1 - x_1 - y_1) e^m \dots \dots \dots (32)$$

As we can always satisfy (31) also always an osmotic equilibrium (30^a) exists, therefore; that is to say: always a series of vapours exists (totally or partly metastable) which are isotonic with G_0 .

However, as we shall see further, it is not always possible to satisfy (32) [viz. by values of x_1 and y_1 which represent points within the triangle]. If we represent the second part of (32) by K then K is a function of x_1 and y_1 which has the value e^{μ_1} in the point W ($x_1 = 0$ and $y_1 = 0$). If we give to x_1 and y_1 such values that the liquid moves away from point W along a straight line going through W , then, as we shall show further, the value of K decreases from e^{μ_1} to zero. (In accordance with fig. 1 we leave here out of consideration dimixtion into 2 of 3 liquids).

We now take the osmotic system (30^b) and we assume, in accordance with fig. 1, that T and P have been chosen in such a way that the watervapour is stable and, therefore, the liquid water is metastable. In point W , therefore, μ_1 is positive and consequently $K = e^{\mu_1} > 1$. As the

first part of (32) is smaller than 1 and as K decreases, when the liquid moves away from W along a line going through point W , consequently on each straight line going through point W is situated a liquid L , which is isotonic with the vapour G_0 . Consequently we find:

if at given T and P water-vapour is the stable state of the water, then with every vapour G_0 a series of vapours and a series of liquids can be isotonic.

We now imagine in fig. 1 vapour- and liquid-region to be interchanged then the water is in liquid-state more stable than in vapour-state. In point W , therefore, μ_1 is negative and consequently $K = e^{\mu_1} < 1$. It now depends on the values of x_0 and y_0 which of the two cases

$$1 - x_0 - y_0 < e^{\mu_1} \qquad 1 - x_0 - y_0 > e^{\mu_1}$$

will occur. In the first case we can satisfy again (32), in the second case, however, not. Hence follows:

if at given T and P the water in stable state occurs as liquid, then with every vapour G_0 a series of vapours can be in equilibrium; however, it depends on the composition of the vapour G_0 whether there is a series of liquids, isotonic with this vapour, or not.

If the liquid L of the osmotic system (30^b) consists of water only, then (32) passes into:

$$1 - x_0 - y_0 = e^{\mu_1} \dots \dots \dots (33)$$

If the liquid water is stable, then is $\mu_1 < 0$ therefore $e^{\mu_1} < 1$; if, however, the liquid water is metastable then is $\mu_1 > 0$ and consequently $e^{\mu_1} > 1$. In the first case, therefore, we can satisfy (33) by positive values of x_0 and y_0 , in the second case we cannot do so. Hence follows:

if water is stable in liquid state, then a series of vapours exists, which have the same *O.W.A.* as this liquid water. (Those vapours, however, are all metastable).

If the vapour G_0 in (30^b) consists of water-vapour only, then (32) passes into:

$$1 = (1 - x_1 - y_1) e^m \dots \dots \dots (34)$$

in which the second part has the value $K = e^{\mu_1}$ for $x_1 = 0$ and $y_1 = 0$. In a similar way as above, it now appears:

if water-vapour is the stable state of the water, then a series of liquids exists, which have the same *O.W.A.* as this water-vapour. (Those liquids, however, are all metastable).

The property, used above, on the change of K viz. the second part of (32) can be deduced on the following way. It follows viz. from the value of K :

$$dK = - \left[1 + (1 - x_1 - y_1) \left(x \frac{\partial^2 \mu}{\partial x^2} + y \frac{\partial^2 \mu}{\partial x \partial y} \right)_1 \right] e^m dx - \left[1 + (1 - x_1 - y_1) \left(x \frac{\partial^2 \mu}{\partial x \partial y} + y \frac{\partial^2 \mu}{\partial y^2} \right)_1 \right] e^m dy \quad (35)$$

If we deduce from ζ_1 the values of $r_1 s_1$ and t_1 then it appears that we may write also for (35):

$$RT \cdot dK = -(1-x_1-y_1) [(rx + sy)_1 dx_1 + (sx + ty)_1 dy_1] e^m . \quad (36)$$

If we choose dx_1 and dy_1 in such a way that the liquid moves away from W along a line going through point W then is:

$$dx_1 : x_1 = dy_1 : y_1 = d\lambda$$

in which $d\lambda$ is positive; (36) now passes into:

$$RT \cdot dK = -(1 - x_1 - y_1) (rx^2 + 2sxy + ty^2)_1 e^m \cdot d\lambda.$$

If we exclude dimixtion into two or more liquids, then follows that dK is negative, from which follows the above-mentioned property.

We may easily deduce the results obtained in this and previous communications and many other also with the aid of the ζ -surface of the vapours and liquids.

(To be continued).