OSMOSIS OF LIQUIDS.

General Considerations.

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The present paper is a continuation of the series entitled "Equilibria in systems, in which the phases are separated by a semipermeable membrane," which have appeared in the proceedings of the Koninklijke Akademie van Wetenschappen (Amsterdam, Holland). In this paper I shall discuss in a simple form some of these results, *viz.* the osmosis of ternary liquids. The reader can find the thermodynamic deductions in the original communication.[1]

I.

Graphical Representation.

We shall begin by discussing briefly in what way ternary liquids are represented. We take a liquid, consisting of the substances X, Y, and W, for example, of sugar, urea, and water, or of salt, soda, and water, etc. If 1 gm. of this liquid contains x gm. of the substance X and y gm. of the substance Y, then it will consequently contain $1 - x - y$ gm. of the substance W, and we represent its composition by

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

Instead of 1 gm. of this liquid we may also take a quantity consisting of 1 gm. mol in all; if in it x gm. mol X and y gm. mol Y are present and consequently $1 - x - y$ gm. mol W, then we represent it by

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

[1] Schreinemakers, F. A. H., *Proc. K. Akad. Wetensch. Amsterdam*, Part 27, 701, and the 22 following communications.

In general, therefore, we may represent the composition of a liquid by x quantities of $X + y$ quantities of $Y + (1 - x - y)$ quantities of W in which "quantities" may denote gm. as well as gm. mol.

We represent the composition of this liquid by a point of a rectangular triangle $W\,X\,Y$ (Fig. 1); we take $W\,X = W\,Y = 1$.

As the liquid contains x quantities of X and y quantities of Y, we take $W\,b = x$ and $W\,a = y$; then point q represents the X and Y quantities of the liquid, we now have $qa = x$ and $qb = y$. From the figure follows $qb = Wa$ and $qa + qc = ac = aY$; as $Wa + ay = 1$, we find:

$$qa + qb + qc = 1$$

or

$$x + y + qc = 1$$

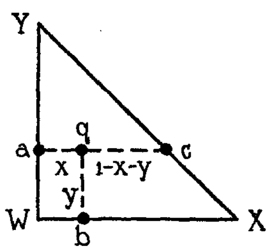

FIG. 1.

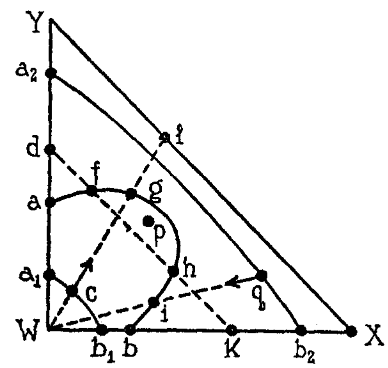

FIG. 2.

Consequently $qc = 1 - x - y$. The line qc represents, therefore, the W amount of the liquid. Consequently the point q represents a liquid which contains $qa = x$ quantities of X, $qb = y$ quantities of Y, and $qc = (1 - x - y)$ quantities of W; therefore it not only indicates the X and Y quantities but also the W quantity of the liquid. If point q is situated on side $W\,X$ then $y = 0$; the liquid then contains only W and X. If point q is situated on side $W\,Y$ then $x = 0$; the liquid then contains only W and Y. If q is situated on side XY then $(1 - x - y) = 0$; the liquid then contains only X and Y.

If q coincides with the angular point W, then $x = 0$ and $y = 0$

and $(1 - x - y) = 1$; the liquid then consists of W (water) only. In a corresponding way we see that point X represents the pure substance X and point Y the pure substance Y.

Consequently we find the angular points of the triangle represent the three pure substances, W, X, and Y: the sides represent binary liquids, *viz.* liquids which contain either $W + X$ only or $W + Y$ only or $X + Y$ only; the points within the triangle represent the ternary liquids which contain $X + Y + W$.

In Fig. 1 we draw an imaginary line through point q, parallel to XY; then in all points of this line $1 - x - y$ has the same value; this means that all liquids of this line have the same W amount. This W amount grows larger the nearer this line runs to point W.

If in Fig. 2 we imagine, for example, dK parallel to XY then the liquids d, f, h, and K must have the same W amount; this will be larger than that of the liquids g, p, q, etc., which are situated on one side of this line, but smaller than that of the liquids a, b, c, i, etc., which are situated on the other side.

We take two liquids, L_1 and L_1', with the respective compositions:

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

If we mix n_1 quantities of L_1 with n_1' quantities of L_1' we get $n_1 + n_1'$ quantities of a new liquid L, the composition of which we represent by

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

As those $n_1 + n_1'$ quantities of L contain in all $n_1 x_1 + n_1' x_1'$ quantities of X and $n_1 y_1 + n_1' y_1'$ quantities of Y, it follows that:

$$x = \frac{n_1 x_1 + n_1' x_1'}{n_1 + n_1'} \qquad y = \frac{n_1 y_1 + n_1' y_1'}{n_1 + n_1'} \tag{1}$$

so that the composition of the new liquid L is known. We represent those liquids L_1 and L_1' in Fig. 3 in which the sides $W X$ and $W Y$ have only been drawn partially by the points 1 and 1′, and liquid L by point e. With the aid of (1) we now can show: point e is situated on line 1-1′ and divides it into the parts 1-e and 1′-e; for the length of those parts is valid:

$$1\text{-}e : 1'\text{-}e = n_1' : n_1 \tag{2}$$

Of the many things which may be deduced from this we shall only discuss those which will serve our purpose later on; among other things we find: If we continuously add to a certain quantity of liquid L_1' liquid L_1, then L_1' proceeds along the line 1-1′ starting from point 1′ towards point 1. If to liquid q of Fig. 2 water is added, it will, therefore, proceed along line qW in the direction of the arrow; consequently it is continually coming nearer to point W. If we withdraw water from a liquid, then this will move in the opposite direction; if, for example, we withdraw water from liquid c (Fig. 2) then this will proceed along the line $c\,l$ in the direction indicated by the arrow.

We shall now call $n_1 \times L_1 + n_1' \times L_1'$ a complex of n_1 quantities of L_1 and n_1' quantities of L_1'. This is represented in Fig. 3 by point e. It is of no account here whether the liquids of this complex mix with one another totally or partially or not at all or whatever might result from them. If, for example, n_2 quantities of L_2 and n_2' quantities of L_2' (in Fig. 3, represented by the points 2 and 2′) should be formed, then line 2-2′ must, therefore, also go through point e and we have:

$$2\text{-}e : 2'\text{-}e = n_2' : n_2 \tag{3}$$

The same is valid when from this complex the liquids 3 and 3′ or 4 and 4′ or others are formed.

II.

Osmosis of One Substance.

Positive and Negative, Normal and Anomalous Osmosis.

We imagine the liquids L and L_g separated from one another by a membrane; we represent this by:

$$L \mid L_g \tag{4}$$

We call this an "osmotic system" and we shall say that the liquids are in "osmotic contact." We now assume that temperature and pressure are equal on both sides of the membrane and that this is permeable only for W (water) and consequently not for X and Y.

We now can distinguish two cases, *viz.* either W diffuses in the one or the other direction through the membrane or nothing happens. In the latter case the system is in "osmotic equilibrium;" then we may say also that the liquids are "isotonic" or that they have the same O.W.A. (osmotic water attraction).

If we imagine L_g to be represented in Fig. 2 by point g then we may put the question: what liquids have the same O.W.A. as liquid g? We may deduce an infinite number of liquids satisfying this condition; they are all situated on a curve, going through point g, and indicated in Fig. 2 by $a\ b$. All liquids of this curve, therefore, have the same O.W.A. and are consequently isotonic; for this reason we call this curve an "isotonic curve." If we take the liquids f and g, for example, we consequently have the system:

$$L_f \mid L_g \tag{5}$$

in which no water diffuses through the membrane and which, therefore, is in osmotic equilibrium.

If we take, for example, the osmotic system

$$L_a \mid L_b \tag{6}$$

we have on the left side a liquid consisting of $W + Y$ only and on the right side a liquid consisting only of $W + X$; both, however, have the same O.W.A. and are, therefore, isotonic. Each of these liquids a and b is also isotonic with all other liquids of curve $a\ b$, consequently with liquids containing the three substances X, Y, and W.

It is evident now that in Fig. 2 an infinite number of isotonic curves may be drawn; we find in this figure the curves $a_1\ b_1$, $a\ b$, and $a_2\ b_2$. All liquids of $a_1\ b_1$ have, therefore, the same O.W.A., also all liquids of $a\ b$ and also those of $a_2\ b_2$. The O.W.A. of the liquids of curve $a_1\ b_1$ is smaller, however, than that of curve $a\ b$ and their O.W.A. is smaller again than that of the liquids of curve $a_2\ b_2$. We now can show that the O.W.A. of the liquids of an isotonic curve grows, the farther this curve is away from point W.

We may among others deduce the following properties of those curves.

1. Two isotonic curves never can intersect or touch one another.

2. Every straight line going through point W intersects a curve in one point only.

3. The O.W.A. of the liquids of an isotonic curve is greater, the farther this curve lies from point W.

4. The isotonic curves are straight lines in the vicinity of point W; at a greater distance they are curved and may take various shapes. We shall refer to this later on.

Now we may put the question: What will happen if we bring two liquids in osmotic contact with one another?

We can show now that: if both liquids have the same O.W.A. nothing happens; if both liquids have a different O.W.A. water diffuses from the liquid with the smaller O.W.A. towards that with the larger. This osmosis continues till both liquids get the same O.W.A.

An isotonic curve, for example $a\ b$, divides the triangle into two parts; from the above mentioned property, (3) follows: all liquids of field $W\ a\ b$ have a smaller, and all liquids of field $a\ b\ X\ Y$ have a larger O.W.A. than those of curve $a\ b$.

If, therefore, we take the osmotic system:

$$L_c \mid L_q \rightarrow \tag{7}$$

(Fig. 2) then the right side liquid has a larger O.W.A. than the left side liquid; consequently the water diffuses through the membrane towards the right, as has been represented in (7) by an arrow.

As liquid q absorbs water, it, therefore, proceeds along line $q\ W$ in the direction of the arrow in Fig. 2; as liquid c loses water, it proceeds along line $c\ l$ in the direction of the arrow in point c. Consequently the O.W.A. of liquid q decreases continuously (*viz.* it comes continuously on isotonic curves, which are situated closer to point W); the O.W.A. of liquid c, however, increases continuously; the diffusion of the water will continue till both liquids get the same O.W.A.; this is the case when they come on the same isotonic curve. If we assume that $a\ b$ is this curve, then at the end of the osmosis liquid c must come in g and liquid q in i. Consequently system (7) passes into the osmotic equilibrium:

$$L_g \mid L_i \tag{8}$$

(Fig. 2) in which no water diffuses any more through the membrane. Consequently during the osmosis liquid c has proceeded along the straight line $c\ g$ and liquid q along the line $q\ i$; we call those lines the "osmosis path" of the liquids or of the system. Later on we shall see that those paths are not straight lines, but curves, when more than one substance diffuses through the membrane.

From our considerations it follows that liquids with a similar W amount need not yet be isotonic. This is clear; as we can show that the O.W.A. also depends on the nature of the other substances, present in the liquid.

Let us take Fig. 2, for example, in which line $d\ K$ is parallel to side $X\ Y$, so that all liquids of this line have the same W amount. On this line we take a liquid, h. Of all other liquids of this line $d\ K$ there is, therefore, only one, *viz.* f, which has the same O.W.A. as liquid h. All liquids which are situated between f and h have a smaller O.W.A. than liquid h and all which are situated either between d and f or between K and h have a larger O.W.A. than liquid h.

Consequently if we take a liquid u between f and h we have a system:

$$L_u \mid L_h \rightarrow \tag{9}$$

in which the water diffuses towards the right; if we take u between d and f or between K and h, we have a system:

$$L_u \mid L_h \leftarrow \tag{10}$$

in which the water goes through the membrane towards the left. In both systems (9) and (10) the liquids on the left and the right side of the membrane have the same W amount; yet in (9) water diffuses towards the right and in (10) towards the left. Consequently it is apparent from this that if two liquids with a similar W amount are in osmotic contact with one another, in most cases diffusion of water will occur after all.

It is also possible that the water diffuses from a liquid with smaller W amount towards a liquid with larger W amount. Let us, for example, take the system:

$$L_p \mid L_h \rightarrow * \tag{11}$$

(Fig. 2) in which the left side liquid p has a smaller W amount than the right side liquid h. If, however, we imagine an isotonic curve through p, then we see that this is situated closer to point W than curve a b on which point h is found. Consequently liquid h has a larger O.W.A. than liquid p; therefore, in (11) the water diffuses towards the right, that is to say from the liquid with the smaller to the liquid with the larger W amount.

In order to distinguish easily the many cases which may occur with the osmosis of one, but especially of more substances, we shall use some signs. We shall indicate by the sign $<$ that the left side liquid has a smaller amount of W than the right side liquid; consequently the sign $>$ indicates that the left side liquid has a larger amount of W. We now distinguish four cases. The first two we represent by

$$(a) \qquad \xleftarrow{<} \qquad \xrightarrow{<}* \qquad (12)$$

In both cases the liquid on the left side of the membrane has, therefore, a smaller W amount than the liquid on the right side; the arrows indicate the direction, in which the water diffuses.

In the first case, therefore, the water diffuses from a liquid with larger to a liquid with smaller W amount; we call this a "positive" osmosis.

In the second case the water diffuses in the opposite direction, *viz.* from the liquid with smaller to that with larger W amount; we call this a "negative" osmosis. In order to make this strike the eye at once, we shall henceforth put an asterisk with arrows, which indicates a negative osmosis.

The two other cases are:

$$(b) \qquad \xleftarrow{>}* \qquad \xrightarrow{>} \qquad (13)$$

Intrinsically they absolutely resemble the first two; the only difference being that now the left side liquid has a greater W amount than the right side liquid. Indeed, in the first of these cases the osmosis is negative, in the second positive. In (11) we have already discussed an example of negative osmosis; this is indicated by the sign * with the arrow.

As, during the osmosis, the liquids are changing their concentrations all the time, we shall also represent those changes by schemes. Later on, especially when more substances diffuse, we shall see that this will give us a clear survey. We assume that the liquid on the left side of the membrane has a smaller W amount than the liquid on the right side. We now distinguish four cases:

1. During the osmosis the amount of W increases on the left side of the membrane and decreases on the right side. We represent this by

$$\uparrow < \downarrow \tag{14}$$

The left side arrow which is pointed upward indicates that the amount of W of the left side liquid increases; the right side arrow which is pointed downward indicates that the amount of W of the right side liquid decreases.

2. The W amount of both liquids increases; we represent it by

$$\uparrow < \uparrow * \tag{15}$$

To the meaning of the sign * we shall refer later on.

3. The W amount of both liquids decreases,

$$* \downarrow < \downarrow \tag{16}$$

4. The W amount of the left side liquid decreases and that of the right side liquid increases

$$* \downarrow < \uparrow * \tag{17}$$

In subsequent communications we shall discuss experimental examples of such cases.

Now we shall say:

A. The W amount of a liquid changes "normally" (1) if it increases when the liquid on the other side of the membrane has a larger amount of W; (2) if it decreases when the liquid on the other side of the membrane has a smaller amount of W.

B. The W amount of a liquid changes "anomalously" (1) if it increases although the liquid on the other side of the membrane has a smaller amount of W; (2) if it decreases, although the liquid on the other side of the membrane has a larger amount of W.

All we have discussed above as regards the W amount of a liquid, is valid also for its X and Y amount. We see that in scheme (14) both liquids change normally; now we shall say that the system changes normally-normally.

In scheme (15) the left side liquid changes normally, the right side liquid, however, changes anomalously. In order to make this clear at once, we put an asterisk near the arrow, which indicates an anomalous change of a concentration. We say that this system changes normally-anomalously.

In scheme (16) we shall say that the system changes anomalously-normally.

In scheme (17) it changes anomalously-anomalously.

Of course, the words normal and anomalous should not lead us to look upon the one phenomenon as more normal than the other.

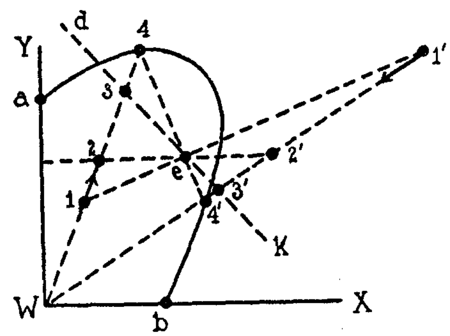

FIG. 3.

We imagine the liquids L_1 and L_1' of the osmotic system

$$L_1 \mid L_1' \tag{18}$$

(Fig. 3) to be represented by the points 1 and 1'. If curve *a* 4-4' *b* is an isotonic curve, then it follows that the right side liquid L_1' will have a larger O.W.A. than the left side liquid L_1, consequently the water diffuses toward the right. The left side liquid loses water; consequently starting from point 1 it goes in the direction of the arrow; the right side liquid, which absorbs water, must go in the direction of the arrow starting from point 1'. When both liquids on curve *a b* get the same O.W.A. then the left side liquid L_1 will proceed along the line 1-4 and the right side liquid along the line 1'-4'.

If the left side liquid is at a certain moment somewhere in a point *u* of the line 1-4, then the right side liquid is somewhere in a point *u'* of the line 1'-4'. Those points *u* and *u'* are not situated arbitrarily, however, for if we have n_1 quantities of L_1 and n_1' quantities of L_1', then, as we have seen before, the complex $n_1 \times L_1 + n_1' \times L_1'$ is represented by a definite point e of the line 1-1′; as the liquids u and u' arise from this complex, the line u u' must always go through point e. If liquid u is found in 2, then u' must be in point 2′; when liquid u is found in 3, then u' must be in point 3′, etc.

During this osmosis the X, Y, and W amounts of the liquid change; we shall begin by considering the X amount.

From Fig. 3 it appears that the X amount of the left side liquid increases from point 1 until 4; the X amount of the right side liquid decreases from point 1′ until 4′. We also see that the X amount of the left side liquid during all the osmosis is smaller than that of the right side liquid. Consequently we can represent this by

$$\uparrow < \downarrow \tag{19}$$

We can say, therefore, that the X amount of the liquids changes normally-normally.

From Fig. 3 it appears also that the Y amount of the left side liquid increases from point 1 until point 4 and that the Y amount of the right side liquid decreases from point 1′ until 4′. We now imagine the line 2-2′ to be horizontal; we may now distinguish two cases.

If the left side liquid is found on part 1-2 and the right side liquid, therefore, on 1′-2′ then the left side liquid must have a smaller Y amount than the right side liquid; consequently we get the scheme:

$$\text{1-2} \quad \uparrow < \downarrow \tag{20}$$

in which is indicated also that this is valid for part 1-2 of the path.

If, however, the left side liquid is on the part 2-4 and hence the right side liquid on 2′-4′ then the left side liquid has a greater Y amount than the right side liquid, we then have the scheme:

$$\text{2-4} \quad *\uparrow > \downarrow* \tag{21}$$

Although the Y amount on the left side of the membrane is larger than on the right side, yet it increases on the left side and it decreases on the right side; hence the Y amount changes on part 2-4 anomalously-anomalously.

It appears from Fig. 3 that the W amount of the left side liquid decreases from point 1 until point 4; the W amount of the right side liquid increases from point $1'$ until point $4'$. We now imagine the line $d\ K$ to be parallel to the side $X\ Y$, which has not been drawn; we can distinguish two cases.

If the left side liquid is on part 1-3 and the right side liquid, therefore, on $1'$-$3'$ then the left side liquid must have a larger W amount than the right side liquid, so that we have the scheme:

$$1\text{-}3 \quad \underrightarrow{\downarrow > \uparrow} \tag{22}$$

in which is indicated also the direction in which the water diffuses through the membrane.

If, however, the left side liquid is on part 3-4 then it has a smaller W amount than the right side liquid, which is then on part $3'$-$4'$; we then get the scheme:

$$3\text{-}4 \quad \underset{\longrightarrow *}{{*}\downarrow < \uparrow{*}} \tag{23}$$

Although the W amount is smaller on the left side of the membrane than on the right side, the water diffuses toward the right, notwithstanding; consequently we have a negative W osmosis; also both liquids change their W amount anomalously; consequently we might say that the system changes its W amount anomalously-anomalously-negatively.

It is not necessary to use the horizontal arrows in the schemes (22) and (23), for it follows already from the vertical ones that the W amount decreases on the left side and increases on the right side, so that we may conclude that the water diffuses toward the right. If, however, more than one substance passes through the membrane, then, as we shall see later on, we are not allowed to draw a conclusion from the vertical arrows as to the direction in which the substance passes through the membrane; this conclusion might be totally mistaken and make it absolutely necessary to indicate this direction by a horizontal arrow.

We may summarize what has been deduced above in a single scheme (24)

Fig. 3	X	Y	W	
1-2	$\uparrow < \downarrow$	$\uparrow < \downarrow$	$\underrightarrow{\downarrow > \uparrow}$	
2-3	"	${*}\uparrow > \downarrow{*}$	"	(24)
3-4	"	"	$\underset{\longrightarrow *}{{*}\downarrow < \uparrow{*}}$	

In this scheme we find the three parts into which we must divide the line 1-4; under each of the substances X, Y, and W has been indicated what we have deduced above with regard to these substances; in it, therefore, we find everything that may be deduced from Fig. 3.

We see, for example, that on part 1-2 all concentrations change normally; on part 2-3 and 3-4, however, the Y amount and on part 3-4 the W amount change anomalously. On the parts 1-2 and 2-3 we have a positive osmosis, on part 3-4, however, a negative osmosis. In systems, in which more substances diffuse through the membrane, we have already found experimentally several examples of anomalous change of concentration and of negative osmosis.