Chemistry. — *Osmotic systems with water, NaCl and Na_2CO_3 in which one invariant liquid.* I. By F. A. H. SCHREINEMAKERS and L. J. VAN DER WOLK.

(Communicated at the meeting of September 24, 1932).

I. *Systems with a ternary invariant liquid.*

In the ternary osmotic system :

$$L(z) \mid inv.\ L'(X+Y+W) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

is a membrane permeable for the three substances X, Y and W(water). On the right side of this membrane is an invariant liquid L', containing the three substances X, Y and W; we imagine this liquid represented in fig. 1 by point i; the angle-points and sides of this XYW-diagram have not been drawn in this figure. On the left side of the membrane is a variable liquid $L(z)$, also containing the substances X, Y and W or in which at the beginning of the osmosis one or two of these substances may also be missing.

If we leave this system alone, the variable liquid $L(z)$ will change its composition and will during the osmosis consequently travel along a path in the XYW-diagram. As we have assumed that the membrane is permeable for all substances, the variable liquid will towards the end of the osmosis get the same composition as the invariant one [1]; so the path of the variable liquid will end in point i (fig. 1).

As at the beginning of the osmosis we may give an infinite number of varying compositions to the variable liquid $L(z)$ (e.g.: f, u, p, q, etc. fig. 1), an infinite number of paths may meet in point i; together they form the bundle of point i. We now may deduce [2]:

all paths meeting in an invariant point i have only two tangents in this point, which we may call the axes of this bundle;

an infinite number of paths touches one of these axes (the principal axis); the other axis (the secondary axis) is touched only by two paths and in special cases by one only;

the position of these axes is defined by the nature and the composition of the invariant liquid i and by the nature of the membrane.

If in fig. 1 we imagine the principal axis represented by kik' and the secondary axis by hih', then all paths will touch the axis kik' in i; only the paths fi and $f'i$ touch the axis hih' in i.

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[1]) We assume namely that in the system $X+Y+W$ no dimixture into two liquids can occur.

[2]) F. A. H. SCHREINEMAKERS, These Proceedings **34**, 341, 524 and 823 (1931).

During the osmosis the variable liquid will not only change its composition, but also its quantity ; in connection with experimental investigations, to be discussed further on, we shall also consider this change in quantity.

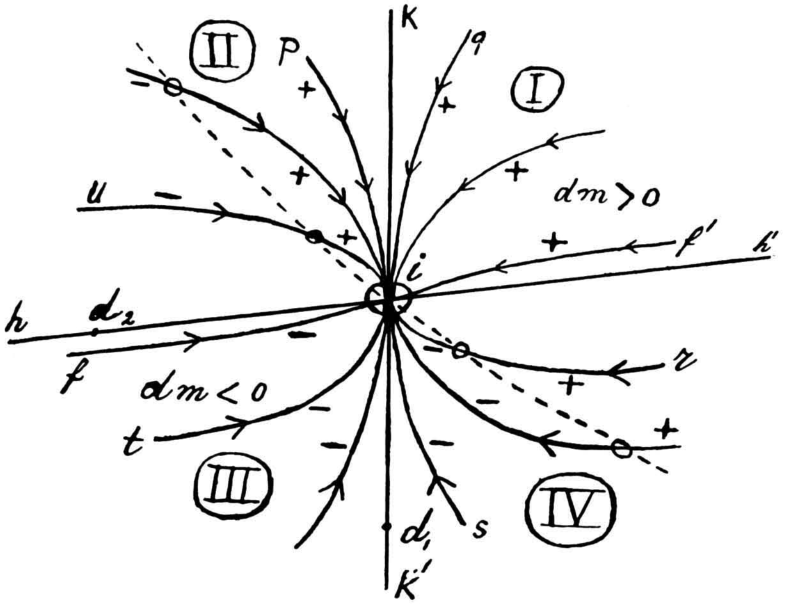

Fig. 1

At some moment of the osmosis we imagine the variable liquid of system (1) represented by a point z of one of the paths of fig. 1 ; the mixture diffusing at this moment is then represented by a point d of the tangent, which in this point z may be drawn to the path of the variable liquid.

If we take point z in one of the paths, touching the principal axis kik', then this tangent will coincide with the principal axis towards the end of the osmosis, namely when point z has arrived in the immediate vicinity of point i. So the mixture diffusing at this moment, and which we shall call the diffusing final-mixture, will be represented by a point of the principal axis ; we are able to deduce that all paths, touching the principal axis, must have the same diffusing final mixture. In accordance with experimental determinations to be discussed later on in an osmotic system containing the substances NaCl, Na_2CO_3 and water, this mixture has been represented in fig. 1 by a point d_1 on the part ik' of the principal axis.

We now shall first consider the paths touching part ik of the principal axis in i (e.g. path $u\ i$ or pi or qi). It follows from the position of point d_1 that a liquid, travelling along one of these paths, must take in this mixture d_1 towards the end of the osmosis ; consequently the quantity of the variable liquid increases towards the end of the osmosis. This has been indicated in fig. 1 by the sign +, put with these paths.

As according to our deduction this increase of quantity is only valid, however, when the variable liquid has arrived in the vicinity of point *i*; it is of course possible that this quantity will decrease at some distance from point *i*. Further on we shall see that this happens indeed, so that we can distinguish two cases, viz.:

a. the quantity of the variable liquid increases during the entire osmosis (e.g. in paths *pi* and *qi* with which only the sign + has been placed).

b. during the osmosis the quantity of the variable liquid first decreases, next remains constant for a moment and then increases until the end of the osmosis (e.g. along path *ui* with which we find the signs — and +; the sign o indicates the liquid, the quantity of which does not change; we shall call this point the "zeropoint" of this path).

We now take the paths touching part *ik'* of the principal axis in point *i* (e.g. the paths *ri*, *si* and *ti*). It now follows from the position of point d_1 that a liquid travelling along one of these paths will give off this mixture d_1 towards the end of the osmosis; consequently the quantity of the variable liquid decreases towards the end of the osmosis. This has been indicated in the figure by placing the sign — with these paths.

Now it is clear that also here we may distinguish two cases, namely

c. the quantity of the variable liquid decreases during the entire osmosis (e.g. in the paths *si* and *ti*, with which only the sign — has been placed).

d. during the osmosis the quantity of the variable liquid first increases, next remains constant for a moment and then decreases until the end of the osmosis (e.g. along path *ri* with the signs +, o and —).

We now imagine the variable liquid *z* of system (1) represented by a point *z* of path *fi* or *f'i*, touching the secondary axis *hih'*. In a similar way as indicated above we now find that the diffusing final mixture must be situated somewhere on this secondary axis *hih'*. In accordance with the experimental determinations to be discussed later on (and the position of the zero-points in the paths touching the principal axis) this mixture has been represented in fig. 1 by a point d_2 on part *ih* of the secondary axis. From this it follows that the quantity of the variable liquid of path *fi* will decrease towards the end of the osmosis and the quantity of the variable liquid of path *f'i* will increase towards the end of the osmosis.

If we summarise the above considerations on the change in quantity of the variable liquid, it appears that in fig. 1 we may distinguish four groups of paths, namely

1. paths, along which the quantity of the variable liquid increases continuously (e.g. the paths *pi* and *qi*).

2. paths, along which the quantity of the variable liquid decreases continuously (e.g. the paths *si* and *ti*).

3. paths, along which during the osmosis the quantity of the variable liquid first increases and afterwards decreases (e.g. path *ri*).
4. paths, along which during the osmosis the quantity of the variable liquid first decreases and afterwards increases (e.g. path *ui*).

In order to illustrate the above, we represent the composition of the variable liquid $L(z)$ of the osmotic system :

$$L\,(z) \mid inv.\, L'\,(X+Y+W) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

by

$$x\, gr\, X + y\, gr\, Y + (1-x-y)\, gr\, W \quad . \quad . \quad . \quad . \quad . \quad (3)$$

We now assume that in this system

$$(\alpha \,.\, dt)\, gr.\, X + (\beta \,.\, dt)\, gr.\, Y + (\gamma \,.\, dt)\, gr.\, W \quad . \quad . \quad . \quad . \quad (4)$$

flow through the membrane between the moments t and $t+dt$. We take α positive when the substance X diffuses towards the left and is consequently taken in by the variable liquid ; if, however, the substance X diffuses towards the right and is consequently given off by the variable liquid, α will be negative. The same obtains for β and γ with respect to the directions in which Y and W diffuse.

If we represent the quantity of the variable liquid at the moment t by m and at the moment $t+dt$ by $m+dm$, we have, therefore :

$$dm = (\alpha + \beta + \gamma)\, dt \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

The quantity of the variable liquid will increase, therefore, between the moments t and $t+dt$ when $\alpha+\beta+\gamma>0$, decrease when $\alpha+\beta+\gamma<0$ and remain constant when $\alpha+\beta+\gamma=0$.

The quantity of X, running through the membrane in system (2) between the moments t and $t+dt$, depends upon the composition of the variable liquid, on the composition of the invariant liquid and on the nature of the membrane. So we may put :

$$\alpha = \varphi\,(x\, y) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

which function also contains the composition of the invariant liquid and the magnitudes, determining the nature of the membrane. For the diffusing quantities Y and W obtains also :

$$\beta = f\,(x\, y) \quad \text{and} \quad \gamma = F\,(x\, y) \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

for which functions the same obtains as for (6). Instead of (5) we may write, therefore :

$$dm = [\varphi\,(x\, y) + f\,(x\, y) + F\,(x\, y)]\, dt \quad . \quad . \quad . \quad . \quad . \quad (8)$$

From this it appears that the quantity of a variable liquid will not change during a moment dt, when its composition (xy) satisfies:

$$\varphi(x\,y) + f(x\,y) + F(x\,y) = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

From this it follows that in fig. 1 there is an infinite number of variable liquids, the quantity of which does not change at a certain moment of the osmosis; or in other words: there must be an infinite number of zero-points in fig. 1. All these zero-points are situated on a curve, determined by (9); we shall call this curve the "zero-curve".

We imagine this zero-curve drawn in fig. 1 through the points, indicated by the sign o (the zeropoints of the paths). It is clear that this curve must also run through point i; if namely we imagine the variable liquid in point i, then, as both liquids will have the same composition at that time, the osmosis has ended and the quantity of the variable liquid consequently will remain constant (in this special case not only $\alpha + \beta + \gamma = 0$, but also at the same time $\alpha = 0$, $\beta = 0$ and $\gamma = 0$).

The shape of the zerocurve, as we have seen above, is determined by (9); as each of the three functions of (9) besides contains the magnitudes determining the nature of the membrane, this curve may have different shapes.

Above namely we have tacitly assumed that every path intersecting this curve, has only one single point of intersection with this curve. We may also suppose, however, that there are paths, intersected by this curve in two points; this will surely be the case e.g. when the zerocurve is a closed curve. Then we have paths with two zeropoints, so that during the osmosis the quantity of the variable liquid of such a path does not change for a moment in two points. If e.g. we imagine still another zeropoint in path ui (fig. 1), then during the osmosis the quantity of the variable liquid will first increase, afterwards it will decrease for some time and at last it will increase again until the end of the osmosis.

It also appears from the preceding considerations that between the position of the two diffusing final mixtures d_1 and d_2 and the direction of the zerocurve in point i there will exist some relation. We may deduce namely:

the points d_1 and d_2 are situated on the same side of the tangent that can be drawn to the zerocurve in point i.

From this it follows that the zerocurve (at least in the vicinity of point i) must be situated in fig. 1 within the angles hik and $h'ik'$; as we shall see later on, our experimental investigations agree with this.

We now shall discuss some of the paths, which have been experimentally determined in an osmotic system with the substances

$$X = NaCl \qquad Y = Na_2CO_3 \qquad \text{and } W = water.$$

From the determinations of these paths etc. it appears that the bundle of the system

$$L\,(z)\,|\,inv.\,L'\,(W + NaCl + Na_2CO_3)$$

can be represented schematically by fig. 1, in which we imagine the X-axis ($NaCl$-axis) horizontal and the Y-axis (Na_2CO_3-axis) vertical. The principal axis kik' and the paths fi and $f'i$, touching the secondary axis hih', divide fig. 1 into four fields, which have been indicated by the encircled ciphers I, II, III and IV; in order to simplify the subsequent discussion we shall call them the fields I, II etc.

First we take the osmotic system

$$L\,(z)\,|\,inv.\,L'\,(i) \quad M = pig's\ bladder\ \alpha \quad . \quad . \quad . \quad . \quad (10)$$

in which a membrane of pig's bladder, which we shall call α and an invariant liquid $L'(i)$ with the composition:

$$11.72\ \%\ NaCl + 6.72\ \%\ Na_2CO_3 + 81.56\ \%\ H_2O$$

which we imagine represented in fig. 1 by point i.

For the variable liquid $L(z)$ we took the liquids a, b, c and d, which at the beginning of the osmosis had the compositions indicated in table 1.

TABLE I.

	% $NaCl$	% Na_2CO_3	% H_2O
L (*beg a*)	6.053	3.474	90.473
L (*beg b*)	5.496	6.686	87.818
L (*beg c*)	18.150	3.502	78.348
L (*beg d*)	18.014	6.863	75.123

So we determined the paths of the systems:

$$L\,(beg\ a)\,|\,inv\ L'\,(i) \qquad L\,(beg\ b)\,|\,inv\ L'\,(i)$$
$$L\,(beg\ c)\,|\,inv\ L'\,(i) \qquad L\,(beg\ d)\,|\,inv\ L'\,(i)$$

The data for these systems are found in the tables 2—5. In the first column we find the numbers of the successive determinations, in the second column the time, viz. the number of hours passed after the beginning of the osmosis. In the third, fourth and fifth columns we find the composition of the variable liquid in procents of weight ($X = NaCl$, $Y = Na_2CO_3$); in the three following columns we find sub X, Y and W the number of grams of $NaCl$, Na_2CO_3 and Water, which have passed through the membrane between two successive determinations; the sign + indicates that this quantity has been taken in by the variable liquid; the sign — indicates that this quantity has been given off by the variable liquid.

TABLE 2. L (*beg. a*) | *inv.* L' (i)

N⁰.	t in hours	Comp. of the variable liquid			Diffused to the variable liquid			$\triangle m$
		$^0/_0$ X	$^0/_0$ Y	$^0/_0$ W	gr X	gr Y	gr W	
1	0	6.053	3.474	90.473				
2	16.5	7.069	3.625	89.206	+ 3.088	+ 0.127	— 16.146	— 12.931
3	39.5	8.391	3.846	87.763	+ 3.502	+ 0.197	— 19.623	— 15.924
4	64.3	9.555	4.090	86.355	+ 2.622	+ 0.257	— 16.713	— 13.834
5	110.	11.002	4.505	84.493	+ 2.510	+ 0.473	— 21.426	— 18.443
6	157.6	11.777	4.874	83.349	+ 0.755	+ 0.448	— 13.445	— 12.242
7	252.3	12.183	5.483	82.334	— 0.727	+ 0.776	— 14.646	— 14.597
8	419.3	11.992	6.153	81.855	— 1.772	+ 0.899	— 10.159	— 11.032
9	634.3	11.820	6.512	81.668	— 1.051	+ 0.400	— 5.097	— 5.748

From these three columns follows at once what has been indicated in the last column, namely the total quantity ($\triangle m$) taken in (sign +) by the variable liquid between two successive determinations or given off (sign —).

If we now draw the osmosis-paths with the aid of these tables we see that they have the same tangent in their final point i; this tangent, therefore, is the principal axis kik' of the bundle.

We now see that path ai is situated in field III. The W-amount of the variable liquid decreases during the entire osmosis, as is apparent from table 2 (column 3—5), whereas the Y-amount increases; the X-amount, however, first increases (nos 1—7) and afterwards decreases.

So the X-amount of the variable liquid passes through a maximum, consequently the path must have a vertical tangent somewhere.

From table 2 (column 6—8) it appears besides that during the entire osmosis water is given off by the variable liquid, whereas the substance Y is taken in; the substance X, however, is first taken in (nos 2—6) and afterwards given off.

From the last column it appears that during the entire osmosis the variable liquid gives off the diffusing mixture, so that the quantity of the variable liquid decreases continuously; this is in accordance with the position of this path ai in field III.

Path bi is situated in field II. It appears from table 3, that this path has a maximum Y-amount; that during the entire osmosis the variable liquid takes in the substance X, gives off the substance Y, but first gives off water and afterwards takes water in again. It appears from the last column that the quantity of the variable liquid first decreases and increases again towards the end of the osmosis; consequently the path has a zeropoint in the vicinity of point i, like e.g. path ui of fig. 1.

TABLE 3. L (*beg b*) | *inv* $L('i)$.

N⁰.	t in hours	Composition of the variable liq. $^0/_0 X$	$^0/_0 Y$	$^0/_0 W$	Diffused to the varable liq. gr. X	gr. Y	gr. W	$\triangle m$
1	0	5.496	6.686	87.818				
2	22.7	6.769	6.796	86.435	+ 4.324	— 0.228	— 13.799	— 9.703
3	45.7	7.827	6.856	85.317	+ 3.345	— 0.310	— 10.826	— 7.791
4	81.5	9.088	6.928	83.984	+ 3.768	— 0.322	— 11.801	— 8.355
5	127.7	10.163	6.961	82.876	+ 2.993	— 0.326	— 8.962	— 6.295
6	211.5	11.130	6.984	81.886	+ 2.628	— 0.215	— 6.551	— 4.138
7	287	11.446	6.939	81.615	+ 0.910	— 0.164	— 1.179	— 0.433
8	497.3	11.656	6.823	81.521	+ 0.810	— 0.221	+ 1.120	+ 1.709

The paths ci and di are both situated in field IV. It appears from table 5 that path di has a minimum Y-amount. It appears from the tables 4 and 5 that during the entire osmosis the variable liquids of the two paths give off the substance X, take in the substance Y, but first take in the water and afterwards give it off. It appears from the last column that during the osmosis the quantity of the variable liquid of both paths first increases and

TABLE 4. L (*beg. c*) | *inv.* $L'(i)$.

N⁰.	t in hours	Composition of the variable liq. $^0/_0 X$	$^0/_0 Y$	$^0/_0 W$	Diffused to the variable liq. gr. X	gr. Y	gr. W	$\triangle m$
1	0	18.150	3.502	78.348				
2	22.2	17.039	3.637	79.324	— 4.230	+ 0.630	+ 5.649	+ 2.049
3	46.7	16.052	3.779	80.169	— 3.794	+ 0.592	+ 3.957	+ 0.755
4	86.5	14.883	4.044	81.073	— 4.647	+ 0.946	+ 2.236	— 1.465
5	153	13.650	4.473	81.877	— 5.421	+ 1.255	— 2.643	— 6.809
6	246.5	12.772	5.039	82.189	— 4.469	+ 1.358	— 8.353	— 11.464
7	415.7	12.154	5.841	82.005	— 3.696	+ 1.717	— 12.261	— 14.240
8	558	11.906	6.260	81.834	— 1.659	+ 0.729	— 6.959	— 7.889
9	743	11.809	6.510	81.681	— 0.855	+ 0.354	— 4.489	— 4.990

afterwards decreases. Consequently both paths have a zeropoint as e.g. path *ri* of fig. 1.

From this we see that the variable liquids of the paths *ci* and *di* behave in all respects differently (viz. reversely) from the one of path *bi*.

TABLE 5. *L (beg. d) | inv. L'(i)*.

N^0.	t in hours	Composition of the variable liq. $^0/_0\,X$	$^0/_0\,Y$	$^0/_0\,W$	Diffused to the variable liq. gr. X	gr. Y	gr. W	$\triangle\, m$
1	0	18.014	6.863	75.123				
2	16	17.268	6.773	75.959	— 1.938	+ 0.074	+ 8.436	+ 6.572
3	39.5	16.222	6.698	77.080	— 2.878	+ 0.277	+ 11.390	+ 8.789
4	66.5	15.195	6.612	78.193	— 3.025	+ 0.177	+ 10.881	+ 8.033
5	109.6	14.061	6.510	79.429	— 3.315	+ 0.165	+ 12.023	+ 8.873
6	168.5	13.114	6.483	80.403	— 2.936	+ 0.330	+ 9.371	+ 6.765
7	277	12.256	6.450	81.294	— 2 941	+ 0.140	+ 7.047	+ 4.246
8	346.7	12.068	6.491	81.441	— 0.701	+ 0.189	+ 0.930	+ 0.418
9	658.2	11.808	6.609	81.583	— 1.300	+ 0.300	— 1.424	— 2.424

If we substitute the pig's bladder α, used in system (10) by an other pig's bladder β or by parchment or cellophane, we get the three systems

$$L\,(z)\,|\,inv.\,L'\,(i) \quad M = pig's\ bladder\ \beta \, . \quad . \quad . \quad . \quad . \qquad (11)$$

$$L\,(z)\,|\,inv.\,L'\,(i) \quad M = parchment \quad . \quad . \quad . \quad . \quad . \quad . \qquad (12)$$

$$L\,(z)\,|\,inv.\,L'\,(i) \quad M = cellophane \quad . \quad . \quad . \quad . \quad . \quad . \qquad (13)$$

in which the invariant liquid has the same composition as in system (10). It appears from the experimental[1]) determinations that the bundle of each of these systems can be represented again schematically by fig. 1; the principal axis *kik'* (and the secondary axis *hih'*), however, has in each of these systems a slightly different direction, as was to be expected.

A system

$$L\,(z)\,|\,inv\,L'\,(i) \qquad M = pig's\ bladder\ \gamma \quad . \quad . \quad . \quad . \qquad (14)$$

was also examined, in which the invariant liquid had a composition differing entirely from that in the preceding systems; it contained namely

$$4.68\,^0/_0\,NaCl + 10.10\,^0/_0\,Na_2CO_3 + 85.22\,^0/_0\,H_2O.$$

It appeared from the experimental determinations that the bundle of

1) Comp. L. J. v. D. WOLK, Diss. Leiden 1932. The bundles of this system and of the system (10) already discussed above are found in the figs. 8, 9, 10 and 12.

this system [1]), in which only paths were determined, situated in the fields III and IV, can also be represented schematically by fig. 1.

We shall not discuss these systems here, but only summarise some results ; see table 6. In the first column we find the number, by which these systems have been indicated in this communication ; in the last column we find the number of the figures in the dissertation (l.c.).

TABLE 6

Syst.	*Sign of dm*				Diss. l. c.
	+	— 0 +	—	+ 0 —	
10	*n*	1	1	2	fig. 9
11	1	2	2	1	fig. 8
12	*n*	1	1	*n*	fig. 10
13	*n*	*n*	1	1	fig. 12
14	*n*	*n*	5	2	fig. 7

Above we have seen that, according to the change (dm) in the quantity of the variable liquid during the osmosis, we can divide the paths into four groups ; we find these groups indicated in the columns 2—5 by the sign of dm and also the number of the paths determined in every group ; n means that no path of this group has been determined.

Among other things it now appears from this table 6 that in system (11) six paths have been determined ; along one of these paths the quantity of the variable liquid increases during the entire osmosis ($dm = +$) ; along two of these paths the quantity of the variable liquid first decreases and afterwards increases till the end of the osmosis ($dm = -0+$) ; along two paths the quantity of the variable liquid decreases ($dm = -$) during the entire osmosis and along one of these paths the quantity of the variable liquid first increases and afterwards decreases till the end of the osmosis ($dm = +0-$).

For normal and anormal changes in concentration, positive and negative osmosis and other phenomena, which may occur in these systems during the osmosis, we refer to the dissertation (l.c.).

(To be continued).

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[1]) L. J. v. d. Wolk l. c. fig. 7.