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

(Communicated at the meeting of October 29, 1932.)

II. *Systems with a binary and with a unary invariant liquid.*

We now take an osmotic system

$$L\,(z)\,|\,inv.\,L'\,(W+X) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

in which the invariant liquid consists of the substances X and W only; it is represented in the partially drawn XYW-diagram (fig. 1) by a point i of side WX.

In this special system two paths of the bundle of this point i are known already at the beginning without any further experimental investigations. If namely we take the system

$$L\,(beg.\ Water)\,|\,inv.\,L'\,(W+X) \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

in which at the beginning of the osmosis the variable liquid L consists of pure water, this system will contain the substances X and W only; consequently the variable liquid will during the osmosis proceed along the straight line Wi, so that Wi is one of the paths of the bundle.

If we take the osmotic system

$$L\,(beg.\ u)\,|\,inv.\,L'\,(W+X) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

then it is clear that the variable liquid will now travel along the straight line ui so that ui and consequently Xi also, is one of the paths of this bundle.

From this follows, what can also be deduced in another way [1]), that side WiX must be one of the two axes of the bundle; the other axis has been represented by line ki, which we can imagine lengthened with a part ik' below side WX. As we have already stated in the preceding communication it depends upon the nature and the composition of the invariant liquid and upon the nature of the membrane, which of these two axes will be the principal and which the secondary axis; they determine the direction of the axis ki and the station of the two diffusing final mixtures d_1 and d_2 as well.

In connection with the osmotic systems, that will be discussed later on

[1]) F. A. H. SCHREINEMAKERS. These Proceedings **34**, 823 (1931).

and which, just as in the preceding communication will contain the substances.

$$X = Na\,Cl \qquad Y = Na_2\,CO_3 \qquad \text{and} \qquad W = \text{water}$$

we take *ki* as principal and *WiX* as secondary axis; all paths (except the straight-lined *Wi* and *Xi*) must, therefore, touch line *ki* in point *i*.

The experimental determinations show besides that point d_1 is situated on the undrawn prolongation *ik'* of the principal axis, and point d_2 on the undrawn prolongation of side *XW*, consequently on the left side of point *W*; so the two points d_1 and d_2 are situated outside the triangle *XYW*. If we compare fig. 1 of this communication with fig. 1 of the preceding

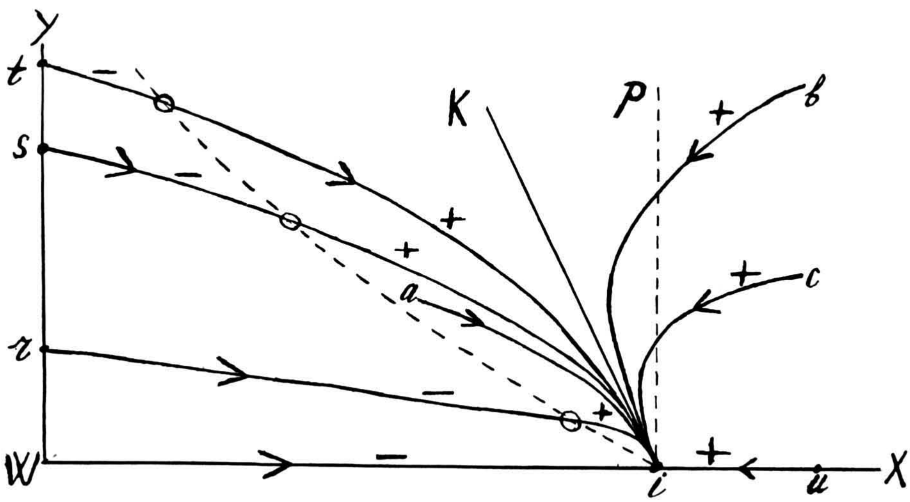

Fig. 1.

one, we see that in both figures the situation of the points d_1 and d_2 with respect to point *i* corresponds.

From the position of point d_1 it follows that the variable liquids of all paths (except *Wi* and *Xi*) will take in this mixture d_1 towards the end of the osmosis; consequently the quantity of the variable liquid of all these paths will increase towards the end of the osmosis.

From the position of point d_2 it follows that the variable liquid of path *Wi* will give off this mixture towards the end of the osmosis and that the variable liquid of path *ui* will take in this mixture.

In the preceding communication we have seen that a zero-curve runs through point *i*; here this is the case also. From the position of the points d_1 and d_2 it follows that this curve (at least in the vicinity of point *i*) will be situated within the angle *Wik*; in fig. 1 we imagine this curve drawn through the points indicated by the sign o; so, just as in the preceding communication this sign indicates again also the zeropoints of the osmosis-paths, namely the point of the path where the quantity of the variable liquid does not change.

It now appears from the experimental determinations that this zero-curve ends in a point of side WY and is situated completely within the angle Wik.

Now we are able to divide the paths into three groups, namely

1. paths in which the quantity of the variable liquid increases continuously (e.g. the paths *bi, ci* and *ui*).

2. path Wi in which the quantity of the variable liquid decreases continuously.

3. paths in which the quantity of the variable liquid first decreases and afterwards increases until the end of the osmosis (e.g. paths *ri, si* and *ti*).

Consequently there are no paths in this bundle in which the quantity of the variable liquid first increases and decreases afterwards until the end of the osmosis (in the bundle of fig. 1 of communication I such paths are indeed met with, e.g. path *ri*).

We now take the osmotic system

$$L\,(z)\,|\,inv.\ L'\,(i) \qquad M = pig's\ bladder \quad . \quad . \quad . \quad . \quad . \quad (4)$$

in which a membrane of pig's bladder; the invariant liquid has the composition

$$9.325\,\%\ Na\,Cl + 90.675\,\%\ Water$$

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

At the beginning of the osmosis we took for the variable liquid $L(z)$ the liquids which have been represented in fig. 1 by the points W, r, a, s, t, b, c and u; the compositions of these liquids are found in table 1.

TABLE I.

Liq.	% Na Cl	% $Na_2\,CO_3$	% Water	Path	Table
W	0	0	100	*Wi*	2
r	0	2.018	97.982	*ri*	3
a	5.078	1.999	92.923	*ai*	4
s	0	3.056	96.944	*si*	5
t	0	4.063	95.937	*ti*	6
b	14.213	5.035	80.752	*bi*	7
c	14.111	1.998	83.891	*ci*	8
u	14.129	0	85.871	*ui*	9

The data for these eight parts [1]) are found in the tables 2—9, which

[1]) The data for the paths *ai, bi* and *ci*, which have been determined in collaboration with H. H. SCHREINEMACHERS are also to be found in a slightly different way in the dissertation of L. J. VAN DER WOLK (Leiden, 1932); the five other paths were not determined until much later.

have been arranged in the same way as in the preceding communication.

If we draw these paths, we obtain a diagram like the schematical fig. 1 ; all paths namely (except *Wi* and *ui*) touch a line *ki*, which consequently forms the principal axis of this bundle.

The direction of this axis also depends upon the nature of the membrane, which, however, is slowly changing during the osmosis. The experimental determination of many bundles has taught us, however, that this change generally has such a small influence, that practically all the paths of a bundle have the same tangent in *i* notwithstanding.

In the system under discussion, however, this is different. In footnote (2) namely we have already pointed out that first the paths *ai*, *bi* and *ci* were determined ; the five other paths were not determined until later and besides an other bladder was used, because the first had become unserviceable.

Now, as was indeed to be expected, it appears from an accurate drawing of the paths, that the paths *ai*, *bi* and *ci* have a slightly different tangent in point *i* than the paths *ri*, *si* and *ti*. This difference, however, is so small that we may practically unite all paths into one and the same bundle.

From the last column of the tables 2—9 it appears that the quantity of the variable liquid

of path *Wi* decreases during the entire osmosis (sign — in fig. 1) ;

of the paths *bi*, *ci* and *ui* it increases during the entire osmosis (sign + in fig. 1) ;

and of the paths *ri*, *si* and *ti* it first decreases and afterwards increases until the end of the osmosis (signs — O + in fig. 1).

If, with the aid of the tables we draw the approximate position of the zero-points, we see that it approximates a straight line.

TABLE II. Path *Wi*.

N⁰.	t in hours	Composition of the variable liq.		Diffused to the variable liq.		$\triangle m$
		$\%$ X	$\%$ W	gr. X	gr. W	
1	0	0	100			
2	10	0.899	99.101	+ 2.551	— 7.903	— 5.352
3	29	2.676	97.324	+ 4.279	— 12.587	— 8.308
4	51	4.576	95.424	+ 3.913	— 11.674	— 7.761
5	72	5.999	94.001	+ 2.615	— 7.915	— 5.300
6	106	7.641	92.359	+ 2.736	— 8.349	— 5.613
7	166	8.881	91.119	+ 1.912	— 5.579	— 3.667

TABLE III. Path *r i*.

N⁰.	t in hours	Composition of the variable liq.			Diffused to the variable liq.			△ m
		% X	% Y	% W	gr. X	gr. Y	gr. W	
1	0	0	2.018	97.982				
2	11	1.248	1.889	96.863	+ 3.818	− 0.436	− 5.568	− 2.186
3	17	1.968	1.806	96.226	+ 1.898	− 0.242	− 2.701	− 1.045
4	27	3.182	1.673	95.145	+ 2.876	− 0.347	− 4.042	− 1.513
5	43	4.810	1.463	93.727	+ 3.222	− 0.445	− 4.239	− 1.462
6	63	6.488	1.204	92.308	+ 2.804	− 0.452	− 3.196	− 0.844
7	88	7.180	1.074	91.746	+ 2.271	− 0.430	− 1.959	− 0.118
8	135	8.084	0.848	91.068	+ 2.810	− 0.673	− 1.218	+ 0.919
9	231	8.844	0.528	90.628	+ 2.240	− 0.851	+ 0.848	+ 2.237
10	351	9.152	0.273	90.575	+ 0.884	− 0.538	+ 2.127	+ 2.473

TABLE IV. Path *a i*.

N⁰.	t in hours	Composition of the variable liq.			Diffused to the variable liq.			△ m
		% X	% Y	% W	gr. X	gr. Y	gr. W	
1	0	5.078	1.999	92.923				
2	17	6.115	1.745	92.140	+ 4.129	− 0.964	− 1.762	+ 1.403
3	38½	7.136	1.450	91.414	+ 3.755	− 1.010	− 0.569	+ 2.176
4	64½	7.967	1.151	90.882	+ 2.813	− 0.923	+ 0.351	+ 2.241
5	95	8.606	0.820	90.574	+ 2.015	− 0.874	+ 2.040	+ 3.181
6	129	8.994	0.527	90.479	+ 1.117	− 0.653	+ 2.145	+ 2.609
7	177½	9.212	0.232	90.556	+ 0.594	− 0.518	+ 2.184	+ 2.260

If we draw the starting-point *a* of path *ai* (table 4) then we see that this point is situated a little to the right side of the zero-curve (fig. 1) it appears indeed from table 4 that this path has no zero-point; if, however we had taken this starting-point to the left of the zero-curve (as the points *r*, *s* and *t*), we should indeed have found a zero-point.

TABLE V. Path *si*.

N⁰.	*t* in hours	Composition of the variable liq.			Diffused to the variable liq.			$\triangle m$
		% X	% Y	% W	gr. X	gr. Y	gr. W	
1	0	0	3.056	96.944				
2	14	1.014	2.898	96.088	+ 3.348	− 0.536	− 3.242	− 0.430
3	32	2.270	2.688	95.042	+ 3.761	− 0.641	− 3.448	− 0.328
4	52	3.537	2.463	94.000	+ 3.577	− 0.638	− 3.102	− 0.163
5	76	4.829	2.205	92.966	+ 3.454	− 0.682	− 2.540	+ 0.232
6	112	6.297	1.849	91.854	+ 3 642	− 0.845	− 1.631	+ 1.166
7	163	7.683	1.398	90.919	+ 3.356	− 0.986	+ 0.380	+ 2.750
8	252	8.735	0.834	90.431	+ 2.635	− 1.161	+ 3.065	+ 4.539
9	323	9.057	0.525	90.418	+ 0.923	− 0.587	+ 2.914	+ 3.250
10	419	9.223	0.270	90 507	+ 0.532	− 0.450	+ 2.454	+ 2.536

TABLE VI. Path *ti*.

N⁰.	*t* in hours	Composition of the variable liq.			Diffused to the variable liq.			$\triangle m$
		% X	% Y	% W	gr. X	gr. Y	gr. W	
1	0	0	4 063	95.937				
2	13	0.979	3.883	95.138	+ 3.128	− 0.592	− 2.931	− 0.395
3	30	2.250	3.623	94.127	+ 3.728	− 0.752	− 2.729	+ 0.247
4	48	3.505	3.366	93.129	+ 3.395	− 0.665	− 1.982	+ 0.748
5	76	5.066	2.909	92.025	+ 4.006	− 1.088	− 1.008	+ 1.910
6	119	6.724	2.339	90.937	+ 4.242	− 1.271	+ 1.056	+ 4 027
7	169	7.788	1.799	90.413	+ 2.794	− 1.134	+ 3.294	+ 4.954
8	252	8.644	1.109	90.247	+ 2.313	− 1.298	+ 6.009	+ 7.024
9	352	9.028	0.598	90.374	+ 1.085	− 0.921	+ 3.968	+ 4.132
10	492	9.213	0.217	90.570	+ 0.660	− 0.616	+ 3.837	+ 3.881

TABLE VII. Path *bi*.

N⁰.	*t* in hours	Composition of the variable liq.			Diffused to the variable liq.			△ *m*
		% *X*	% *Y*	% *W*	gr. *X*	gr. *Y*	gr. *W*	
1	0	14.213	5.035	80.752				
2	14	12.844	4.529	82.627	— 3.856	— 1.460	+ 20.601	+ 15.285
3	31	11.658	4.009	84.333	— 3.325	— 1.606	+ 18.650	+ 13.719
4	52	10.678	3.442	85.880	— 2.483	— 1.811	+ 17.909	+ 13.615
5	86	9.756	2.707	87.537	— 2.300	— 2.554	+ 19.063	+ 14.209
6	135	9.223	1.900	88.877	— 1.070	— 2.979	+ 15.318	+ 11.269
7	203	9.074	1.127	89.799	+ 0.431	— 2.806	+ 13.336	+ 10.961
8	274	9.146	0.573	90.281	+ 0.537	— 1.899	+ 4.513	+ 3.151
9	359	9.257	0.248	90.495	+ 0.381	— 0.993	+ 1.096	+ 0.484

TABLE VIII. Path *ci*.

N⁰.	*t* in hours	Composition of the variable liq.			Diffused to the variable liq.			△ *m*
		% *X*	% *Y*	% *W*	gr. *X*	gr. *Y*	gr. *W*	
1	0	14.111	1.998	83.891				
2	16	12.836	1.786	85.378	— 4.160	— 0.722	+ 13.432	+ 8.550
3	39	11.499	1.509	86.992	— 4.166	— 0.943	+ 14.230	+ 9.121
4	63	10.611	1.262	88.127	— 2.570	— 0.826	+ 9.919	+ 6.523
5	98½	9.823	0.932	89.245	— 1.984	— 1.054	+ 10.066	+ 7.028
6	144½	9.392	0.590	90.018	— 0.753	— 1.003	+ 7.659	+ 5.903
7	183½	9.299	0.359	90.342	— 0.014	— 0.577	+ 3.036	+ 2.445
8	274	9.301	0.084	90.615	+ 0.315	— 0.535	+ 3.577	+ 3.357

We now shall first consider the change of the X-amount of the variable liquid.

The paths *bi* and *ci* intersect the vertical axis *ip* and will after this intersection consequently have a point somewhere in which the tangent is vertical. From this it follows: the X-amount of the variable liquid of these paths, which at the beginning of the osmosis is greater than that of the invariant liquid i, becomes equal to it at a certain moment of the osmosis, afterwards this X-amount will decrease still further, reaches a minimum and increases afterwards again to that of liquid i (comp. column 3 of the tables 7 and 8). It is hardly possible to determine this increase experimentally in case of path ci, the minimum of which is situated close to point i.

From the tables 7 and 9 and the X-amount of liquid i it appears that the substance X diffuses successively according to the symbols:

$$\underset{\rightarrow}{>} \qquad \underset{\rightarrow *}{<} \qquad \underset{\leftarrow}{<}$$

so during a certain time there is a negative X-osmosis. It appears besides that the direction of diffusion turns round towards the end of the osmosis.

TABLE IX. Path ui.

N⁰.	t in hours	Composition of the variable liq.		Diffused to the variable liq.		Δm
		$^0/_0\ X$	$^0/_0\ W$	gr. X	gr. W	
1	0	14.129	85.871			
2	18	13.266	86.734	− 2.238	+ 5.903	+ 3.665
3	46	12.092	87.908	− 3.095	+ 7.785	+ 4.690
4	88	10.898	89.102	− 3.239	+ 7.718	+ 4.479
5	161	9.891	90.109	− 2.907	+ 5.198	+ 2.291
6	205	9.658	90.342	− 0.679	+ 1.059	+ 0.380

We see that this phenomenon viz. the occurrence of a minimum X-amount is connected with the position of the axis ki within angle piW. If this axis had been situated within angle piX, then these paths bi and ci would have had no minimum; the paths ri, ai si and ti on the other hand would have shown a maximum.

In order to consider the change of the W-amount of the variable liquid we imagine a line iq in fig. 1, so that $\angle Wiq = 45^\circ$; the points of this line represent liquids with the same W-amount as liquid i. As $\angle Wik = \pm 67^\circ$, this line iq, which has not been drawn, is situated within $\angle Wik$.

Path ti intersects this line iq and, therefore, after this intersection will have a point in which the tangent is parallel to iq. From this follows: the W-amount of the variable liquid, which at the beginning of the osmosis is greater than that of the invariant liquid i, becomes equal to it at a certain moment of the osmosis; afterwards this W-amount will decrease still further, reaches a minimum and afterwards increases again to that of liquid *i*. From column 5 of table 6 it appears that the minimum is situated in the vicinity of determination N⁰. 8.

From columns 5 and 8 of this table and from the *W*-amount of liquid *i* it also appears that the water diffuses successively according to the symbols:

$$\underset{\rightarrow}{\geq} \qquad \underset{\leftarrow}{\geq}{}^{*} \qquad \underset{\leftarrow}{\leq}$$

from this it appears that during a part of the osmosis the water diffuses negatively and that at a certain moment the direction of the *W*-diffusion turns round.

Of course all this obtains also for the paths *si, ai* and *ri* (tables 5, 4 and 3); from table 3 it appears, however, that this minimum of path *ri* is situated so close to point *i*, that it was not determined experimentally.

Now we take instead of (4) the system

$$L\,(z)\,|\,inv.\,L'\,(i_1) \qquad M = pig's\ bladder \quad . \ . \ . \ . \quad (5)$$

in which the invariant liquid i_1 has the composition

$$5.641\,^0/_0\ Na_2\,CO_3 + 94.359\,^0/_0\ Water$$

So this liquid is no longer represented now by a point of side, *WX*, but by a point i_1 on side *WY* of fig. 1, which has not been drawn.

We are able to deduce that side Wi_1Y now must be one of the axes of the bundle. It appeared from the experimental determination of four paths that they all touch side *WY* in point i_1 so that this side is the principal axis of the bundle.

In the osmotic system

$$L\,(z)\,|\,inv.\,(Water) \qquad M = pig's\ bladder \quad . \ . \ . \ . \quad (6)$$

the invariant liquid consists of pure water; consequently it is represented by point *W* (fig. 1). We are able to deduce that the sides *WX* and *WY* now must be the axes of the bundle. From the experimental determination of three paths it appeared that they all touch side *WY* in point *W*, so that *WY* is the principal axis and *WX* the secondary axis of this bundle.

For a closer consideration of these paths of systems (5) and (6), which have also been determined in collaboration with H. H. SCHREINEMACHERS we refer to the dissertation mentioned in note 2.

By the support of the "Bataafsch Genootschap der Proefondervindelijke Wijsbegeerte te Rotterdam" we were enabled to examine the paths *Wi, ri, si, ti* and *ui* (tables 2, 3, 5, 6 and 9) for which we express our thanks to this "Genootschap".

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