Chemistry. — *Influence of the nature of the membrane and the temperature on the osmotic system of water and oxalic acid.* By F. A. H. SCHREINEMAKERS, Miss J. C. LANZING and C. L. DE VRIES.

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§ 1. *Introduction.*

1. In the osmotic iso-p-complex

$$inv.\ L\ (water)\ |\ L'\ (beg.\ q)\ (X+W) \quad . \quad . \quad . \quad . \quad . \quad (1)$$

viz. an osmotic complex in which the two liquids have the same pressure p, there is an invariant liquid consisting of pure water found on the left side of the membrane, which is permeable for all substances. On the right side is a variable liquid L' which at the beginning of the osmosis has the composition q; this liquid is saturated with solid X or with a hydrate $X.nH_2O$ which we shall indicate by the letter q; this solid substance, however, is not present in (1). If we leave this complex alone, liquid L' will change its composition and at the end of the osmosis also consist of water only.

As during the entire osmosis no X is present on the left side of the membrane, X will diffuse $\leftarrow$, viz. congruently and positively during the entire osmosis.

Water being present on both sides of the membrane during the entire osmosis, it can during the whole process diffuse $\rightarrow$, viz. congruently and positively, or $\leftarrow 0^*$, viz. incongruently and negatively, or first in the one and afterwards in the other direction.

The moment the direction of the W-diffusion changes, the variable liquid L' is in its W-stopping point; for this liquid then does not take in water, neither does it give off water; its W-amount, however, does change at this moment, as this liquid L' gives off X to liquid L.

2. In the osmotic iso-p-complex

$$L\ (beg.\ water)\ |\ inv.\ L'\ (q)\ (X+W) \quad . \quad . \quad . \quad . \quad . \quad (2)$$

the left side liquid is variable and at the beginning of the osmosis it consists of pure water; the right side liquid is invariant and consists of the solution q discussed above; during the osmosis we can easily keep it invariant by adding solid X or $X.nH_2O$. If we leave this complex alone, liquid L will now change its composition and at the end of the osmosis get the composition q of the invariant liquid.

Of course, the substance X must diffuse $\leftarrow$ at the beginning of the osmosis and this may continue during the entire osmosis; as soon as liquid *L* has got a certain *X*-amount, however, it is also possible that the direction of the *X*-diffusion changes; at the moment of this change of direction the variable liquid *L* is in its *X*-stopping-point.

As during the entire osmosis there is water on both sides of the membrane, the same rules as sub 1. obtain for the possible directions of the *W*-diffusion. We have to bear in mind here, however, that $X \rightarrow 0^*$ and $W \leftarrow 0^*$ are not possible at the same time, viz. that they cannot both pass through the membrane incongruently and negatively.

3. We are now able to divide the binary systems into different groups or types according to the directions in which *X* and *W* move in the complexes (1) and (2) during the osmosis; all the systems investigated until now in the Leiden Laboratory belong to one of the types we have called I, IIa, II*b*, and IIc. In each of these types the substance *X* diffuses ← during the entire osmosis; as has been indicated in table I, they may be distinguished however by the direction of the *W*-diffusion.

In the first column of this table we find the type to which the system belongs; in columns 2 and 3 the arrows indicate the directions in which during the osmosis the water diffuses in the osmotic complexes (1) and (2) respectively.

TABLE I.

Direction of the *W*-diffusion.

Type	inv. *L* (*W*) | *L'* (beg. *q*)	*L* (beg. *W*) | inv. *L'* (*q*)
I	→	→
IIa	← 0 *	← 0 *
IIb	← 0 *	← 0 * →
IIc	→ ← 0 *	→

When there is one arrow only, the water diffuses in the direction indicated during the entire osmosis; when there are two arrows the water diffuses first in the direction of the first arrow and afterwards in the direction of the second, then the variable liquid has a *W*-stopping-point [1]) as in complex (2) of type II*b* and in complex (1) of type IIc.

It is clear now that it does not only depend upon the nature of the membrane *M* but also upon the temperature *T* to which type a given system belongs. In the system oxalic acid + water the osmosis proceeds according

[1]) For a survey of the systems belonging to types I, II*b* and IIc and the influence of the membrane cf. F. A. H. SCHREINEMAKERS, Rec. Trav. Chim. Pays Bas **51**, 218 (1932); Miss J. C. LANZING, Dissertation Leiden, 1933.

to type I when M = cellophan and T = c. 20°, according to type IIa when M = pig's bladder and T = 0°, and according to type IIb when M = pig's bladder and T = c. 20°.

§ 2. *The osmotic system Oxalic acid + water;*
M = cellophan, T = c. 20°.

1. In the osmotic complex

$$inv.\ L\,(W)\,|\,L'\,(beg.\ q = 8.686\ \%\ Ox.\ acid) \quad . \quad . \quad . \quad . \quad (3)$$

in which M = cellophan and T = c. 20°, the variable liquid L' contains 8.686 % of Oxalic acid at the beginning of the osmosis, so that it is about saturated with the hydrate $H_2C_2O_4 . 2H_2O$.

It now appeared from the determination [2]) that the amount of Oxalic acid of this variable liquid decreased continuously during the osmosis and had after 274 hours dropped already to 0.093 %. It appeared besides that during the entire osmosis the Oxalic acid had diffused ← and the water →, consequently according to the D.T.

$$\leftarrow Ox.\ acid \rightarrow Water \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

in which both substances pass through the membrane congruently.

2. In the osmotic complex

$$L\,(beg.\ water)\,|\,inv.\ L'\,(q)\,(Ox.\ acid + W) + Ox.\ ac.\ 2\,H_2O \quad . \quad (5)$$

the hydrate Ox. acid $2H_2O$ is also present on the right side of the membrane, so that liquid L' is saturated with this hydrate.

It now appeared [3]) that the amount of Ox. acid of the variable liquid L, consisting of pure water at the beginning of the osmosis, increased continuously and had already risen to 8.308 % after 470 hours. It appeared besides that during the entire osmosis the Oxalic acid and the water diffused in the same direction as sub 1.

3. As in both complexes the water diffuses → during the entire osmosis, this system consequently belongs to type I.

§ 3. *The osmotic system Oxalic acid + water;*
M = pig's bladder, T = 0°.

1. In the osmotic complex

$$inv.\ L\,(W)\,|\,L'\,(beg.\ q = 3.476\ \%\ Ox.\ acid) \quad . \quad . \quad . \quad . \quad (6)$$

in which M = pig's bladder and T = 0°, at the beginning of the osmosis the variable liquid L' contains 3.476 % of Ox. acid, so that it is about saturated with the hydrate Ox. acid. $2H_2O$.

The data for this osmosis are found in table II; in the first column we find the number of the successive determinations, in column 2 the time,

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viz. the number of hours passed after the beginning of the osmosis; owing to accidental circumstances, however, this time should be considered as an approximination only. In columns 3 and 4 we find the number of grams of Ox. acid and of water respectively, which have diffused between 2 successive determinations; the arrows indicate the direction in which these substances have passed through the membrane; in column 5 we find the composition of the variable liquid L'.

TABLE II. $T = 0°$.

No.	t in hours	Diffused		% Ox. ac. of the var. liq. L'
		gm. Ox. ac.	gm. Water	
		←	← 0 *	
1	0			3.476
2	18	0.381	1.667	3.389
3	55	1.798	7.235	2.957
4	100	1.887	8.663	2.476
5	150	0.181	1.041	2.429
6	213	0.982	5.227	2.160
7	306	2.526	14.846	1.403
8	399	1.492	10 660	0.903
9	492	0.848	7.556	0.588
10	609	0.644	5.938	0.322
11	870	0.613	3.117	0.035

It appears from this table that the amount of Ox. acid of this variable liquid decreased continuously during the osmosis and had dropped to 0.035 % after 870 hours. Further it appears that during the entire osmosis the Ox. acid had diffused ←, viz. congruently and positively, and the water also ← 0*, but consequently incongruently and negatively; the water namely passes from the solution towards the pure water. So in this complex the osmosis proceeds according to the mixed D.T.

$$\leftarrow \textit{Ox. acid} \quad \leftarrow 0 * \textit{Water} \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

From this table can among other things also be deduced that after 870 hours 11.356 gms of Ox. acid and 65.954 gms of water had diffused towards the left.

2. In the osmotic complex

$$L\,(beg.\ water)\,|\,inv.\ L'\,(q)\,(Ox.\ ac. + W) + Ox.\ ac.\ 2\,H_2O\ .\quad .\quad (8)$$

the amount of Oxalic acid in the variable liquid L, consisting of pure water at the beginning of the osmosis, increased continuously and had already risen to 3.362 % after 951 hours.

The data for this osmosis are found in table III, which is arranged in the same way as table II; the composition of the variable liquid L, however, is here indicated in column 3.

It appears from the direction of the arrows that during the entire osmosis both substances diffuse in the same direction as was the case in complex (6), viz. according to the D.T. (7). From this table may be deduced as well that after 951 hours 10.197 gms of Ox. acid and 12.567 gms of water had diffused towards the left.

3. As during the entire osmosis the water diffuses $\leftarrow 0^*$ in both complexes, this system consequently belongs to type II*a*.

§ 4. *The osmotic system Oxalic acid + water; M = pig's bladder, T = c. 20°.*

1. In the osmotic complex

$$inv. L(W) \mid L' (beg.\ q = 8.077\ \%\ \text{of}\ Ox.\ ac.) \quad . \quad . \quad . \quad . \qquad (9)$$

in which, as in the complex of § 3, M = pig's bladder but now T = c. 20°, the variable liquid L' contained 8.077 % of Ox. acid at the beginning of the osmosis.

TABLE III. $T = 0°$.

No.	t in hours	% Ox. ac. of the var. liq. L	Diffused	
			gm. Ox. ac.	gm. Water
			$\leftarrow$	$\leftarrow 0^*$
1	0	0		
2	26	0.437	1.455	2.466
3	48	0.759	1.028	1.616
4	89.5	1.247	1.535	2.146
5	137.5	1 648	1.252	1.663
6	203	2.030	1.156	1.084
7	253	2.328	0.875	0.808
8	319	2.640	0.895	0.784
9	408	2.930	0.823	0.651
10	502	3.101	0.482	0.535
11	619	3.217	0.324	0.535
12	781	3.309	0.240	0.092
13	951	3.362	0.132	0.187

It appeared from the determinations [4]) that the amount of Ox. acid in the variable liquid L' had after 190 hours already dropped to 0.024 % and that the osmosis took place according to the D.T.

$$\leftarrow Ox.\,acid \qquad \leftarrow 0 * \,Water \;.\;.\;.\;.\;.\;. \quad (10)$$

So during the entire osmosis the Oxalic acid passes through the membrane congruently and positively, the water, however, incongruently and negatively.

2. The variable liquid L of the osmotic complex

$$L\,(be_J.\ Water)\,|\,inv.\ L'\,(q)\,(Ox.\ ac. + W) + Ox.\ ac.\ 2\,H_2O \;. \quad (11)$$

consisting of pure water at the beginning of the osmosis, contained 8.342 % of Ox. acid after 637 hours; it appeared besides [5]) that the osmosis had taken place during the first 57 hours according to the D.T.

$$\leftarrow Ox.\,ac. \qquad \leftarrow 0 * \,Water \;.\;.\;.\;.\;.\;. \quad (12)$$

and afterwards according to the D.T.

$$\leftarrow Ox.\,ac. \qquad \rightarrow Water \;.\;.\;.\;.\;.\;.\;. \quad (13)$$

So the variable liquid L of complex (11) has a W-stopping-point at a certain moment of the osmosis and then contains c. 5 % of Ox. acid.

3. As in complex (9) during the entire osmosis the water passes through the membrane $\leftarrow 0^*$ and in complex (11) first $\leftarrow 0^*$ and afterwards $\rightarrow$, this system must belong to type II*b*.

§ 5. *Some considerations.*

It appears from the above that the nature of the membrane can influence the type to which an osmotic system belongs. A system of water + Oxalic acid and $T =$ c. 20°, namely, belongs to type I with $M =$ cellophan (§ 2) and to type II*b* with $M =$ pig's bladder (§ 4).

The same thing is shown also by the osmotic systems water + succinic acid [6]) and water + tartaric acid [7]), for the first belongs to type I with $M =$ cellophan or parchment and the second with $M =$ cellophan; however, with $M =$ pig's bladder both belong to type II*c*.

The nature of the membrane, however, can also influence the process of an osmosis without necessarily changing the type of the system. This appears e.g. from the system water + tartaric acid, which belongs to

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[5]) Miss J. C. LANZING l.c.

[6]) Miss J. C. LANZING l.c.

[7]) J. P. WERRE, Dissertation, Leiden. F. A. H. SCHREINEMAKERS and J. P. WERRE: These Proceedings **35**, 42, 162 and 477 (1932).

type IIc with $M =$ pig's bladder, as has already been said above; consequently in the osmotic complex

$$inv.\ L\,(W)\,|\,L'\,(beg.\ q)\,(W + tart.\ ac.) \quad . \quad . \quad . \quad . \quad . \quad (14)$$

the water will during the osmosis diffuse first $\rightarrow$ and afterwards $\leftarrow 0^*$, so that the variable liquid L' has a W-stopping-point.

The amount of tartaric acid of the liquid with the W-stopping-point depends, however, upon the nature of the bladder used; three determinations gave for it c. 21, 17 and 14 %. With a membrane consisting of a layer of cellophan and a layer of pig's bladder [8]) and on turning the first layer towards the var. liq. L', this W-stopping-point was situated lower, viz. at c. 10 % of tartaric acid.

2. It appears from § 3 and § 4 that the osmotic system of water + Oxalic acid with $M =$ pig's bladder has a different type at 0° and 20°; at 20° this system, namely, belongs to type II*b*, so that in the osmotic complex

$$L\,(beg.\ W)\,|\,inv.\ L'\,(q)\,(W + Ox.\ ac.) \quad . \quad . \quad . \quad . \quad . \quad (15)$$

the water diffuses at first $\leftarrow 0^*$ and later on $\rightarrow$; the variable liquid L, namely, has a W-stopping-point at c. 5 % of Ox. ac. (4). At 0°, however, this system belongs to type IIa, so that in complex (15) the water diffuses $\leftarrow 0^*$ during the entire osmosis.

The W-stopping-point occurring at 20° has consequently disappeared at 0°.

Perhaps this would make us think that a fundamental difference exists between the process of the osmosis at 20° and that at 0°. However, this is not the case, for we have to bear in mind here that several factors play a part, viz. the influence of the temperature upon:

a. the composition of the saturated solution $L'(q)$;

b. the amount of Oxalic acid of the W-stopping-point of the variable liquid L.

c. the nature of the membrane.

As liquid $L'(q)$ contains c. 8.7 % of Oxalic acid at 20°, the variable liquid L will consequently at 20° have all concentrations from 0 % to 8.7 % of Oxalic acid.

The W-stopping-point of this liquid L being situated at c. 5 %, it follows for the W-movement

$$\text{from } 0\,\% \text{ to } 5\,\% \text{ of } \textit{Oxalic acid} \leftarrow 0 * W. \quad . \quad . \quad . \quad (16)$$

$$\text{from } 5\,\% \text{ to } 8.7\,\% \text{ of } \textit{Oxalic acid} \rightarrow W \quad . \quad . \quad . \quad . \quad (17)$$

As, however, liquid $L'(q)$ at 0° contains only c. 3,5 % of Oxalic acid, the variable liquid now passes through all concentrations from 0 % to 3,5 % of Oxalic acid. Since the factors *b* and *c* have no influence on the

8) F. A. H. SCHREINEMAKERS and H. A. SCHREINEMACHERS: These Proceedings **36**, 634 (1933).

amount of Ox. ac. of the *W*-stopping-point, it will be clear that this has disappeared at 0°, so that the water will only diffuse according to (16), viz. ← 0*.

The same rule obtains also when the factors mentioned sub *b* and *c* are active, provided the amount of Oxalic acid of the *W*-stopping-point does not drop below 3,5 %.

Of course, this *W*-stopping-point would exist at 0°, but only in metastable state; we might find it, if it would be possible to substitute for the inv. liquid $L'(q)$ of complex (15) an invariant supersaturated solution with a sufficiently high amount of Oxalic acid. One of us will refer to this later on.

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Botany. — *The Chemical Nature of Some Growth Hormones as determined by the Diffusion Method.* By A. N. J. HEYN. (Communicated by Prof. G. VAN ITERSON JR.)

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KÖGL, HAAGEN SMIT and ERXLEBEN about a year ago described a growth hormone of the same activity as auxin, which was present in urine and was also produced by certain fungi and which proved to be identical with β-indolyl acetic acid ("hetero-auxin").

Many different chemical substances have been found in the last year which are also active in influencing cell elongation (KÖGL and KOSTERMANS, 1935; THIMANN, 1935; HAAGEN SMIT and WENT, 1935).

An investigation, on the other hand, of the chemical nature of the different growth substances, which may be obtained from different plants and different parts of the plant, has not yet been undertaken (with the exception of the hormone of the coleoptile tip of Avena and the hormone produced by some fungi).

The results of such investigations are now given for the hormone of root tips and the hormone of the regenerated tip of the Avena coleoptile, which data appeared to be of particular interest.

Method.

It was impossible to obtain large quantities of the hormone to be investigated and in the case of the hormone of the regenerated tip even very small quantities only were obtained. The only way of identification,