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THE PHENOMENON OF OSMOSIS IN PERMEABLE MEMBRANES

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SUMMARY

Two effects give rise to osmosis in a permeable membrane: the coupling effect between the ion streams and water, demonstrated by binary isotonic osmosis, and the osmotic difference between the outside solutions. But, in contrast to a semipermeable membrane, it is not the difference in the outside concentrations but the difference in the Donnan ions inside the membrane that produces the flux of water.

OSMOTIC PRESSURE

If a semipermeable membrane separates a solution from the pure solvent in an osmotic cell, a flux of water runs from the solvent into the solution. This flux is caused by the lower vapour pressure of the solution. On the other hand, the flux entering a closed osmotic cell gives rise to a hydrostatic pressure, which causes an increase in the vapour pressure of the solution and diminishes the decrease that arises from the solute. A state of equilibrium is reached if the vapour pressure has the same value on both sides of the membrane. This fact can be expressed by the equation

$$\mu_L^0 = \mu_L^{0'} + V_L P \quad (1)$$

which states that the chemical potential, μ_L^0 , of the pure solvent on one side of the membrane must be equal to the chemical potential, $\mu_L^{0'} + V_L P$, on the other side. Therefore, $\mu_L^{0'}$ represents the chemical potential of the water in a solution in the absence of a pressure (superscript zero) and $V_L P$ is an additional potential originating from the (hydrostatic) pressure P ($V_L =$ molar volume).

Until equilibrium is reached, $\mu_L^0 > \mu_L^{0'} + V_L P$ and a flux of water from the higher to the lower potential is the result. Restricting the situation to a "strip dx ", i.e., a section of a membrane, Fick's first law can be written as

$$j_L/q = -D_H \text{grad} (\mu_L^0 + V_L P) \quad (2)$$

where D_H is the hydrodynamic permeability and q the cross-section of the membrane. Setting $j_L = 0$, we obtain

$$d\mu_L^0 = V_L dP \quad (3)$$

where

$$d\mu_L^0 = \mu_L^0 - \mu_L^{0'}$$

The hydrostatic difference dP (in the strip dx) which corresponds to the osmotic difference $d\mu_L^0$ between the pure solvent and the solution is called the osmotic pressure difference, dP_{os} .

OSMOSIS

In addition to semipermeable membranes, there are permeable membranes which are permeable for the solute also. In contrast to the semipermeable membranes, where the flux of solvent always runs in the direction of the osmotic gradient, we frequently observe in the case of permeable membranes a flux of water opposed to this gradient. Employing a pig's bladder to separate a concentrated solution of salicylic acid from pure water, both the salicylic acid and the water pass through the membrane in the same direction from the solution into the pure solvent. Surprisingly, the flux of water is 10,000 times greater than the flux of salicylic acid.

Effects in which water fluxes are opposed to the osmotic gradient are termed anomalous negative osmosis. In order to explain this behaviour, Graham¹ suggested that these effects originate from electric potentials.

ELIMINATION OF THE OSMOTIC PRESSURE: ISOTONIC OSMOSIS

In order to separate the flux of water originating in the osmotic difference from the flux, presumably caused by an electric potential, we used isotonic solutions, *i.e.*, solutions of different composition but equal activity of water. Our experiments were performed with membranes of condensed phenolsulphonic acid and binary isotonic mixtures of HCl with different alkalimetalchlorides². Although there was no osmotic difference, $d\mu_L$, between the solutions bordering the boundaries of the membrane, strong fluxes of water, j_L , were observed. Using small concentrations, the flux of water increases proportionally to the ion fluxes and the ratio j_L/j_i is given in Table I. However, on increasing the total concentration, c , the flux of water reaches a maximum and changes sign at $c > 4n$ (ref. 3) (see Fig. 1). In these experiments, pure solutions of HCl were used on one side of the membrane and mixtures of HCl and LiCl on the other side. By changing the $H^+ : Li^+$ ratio, a more or less steep gradient, $\Delta c_H/\Delta x$, which is the parameter of the family of curves in Fig. 1, was produced in the membrane. A surprising result was the independence of the inversion point on $\Delta c_H/\Delta x$ and on stirring of the solutions (plotted curve). This behaviour is explained in a further section on isotonic osmosis below.

APPLICABILITY OF THEORIES

While there is no lack of theories of osmosis, we have found no theory that is in accordance with our experiments. A large number of theories are based on an arrangement of the thermodynamics of irreversible processes (T.I.P.)⁴:

$$j_i = \sum^k L_{ik} X_k \quad (i = 1, 2, \dots, N) \quad (4)$$

where the unknown streams j_i are linear functions of arbitrary forces represented by X_k and L_{ik} are coefficients obeying the Onsager reciprocal relationship $L_{ik} = L_{ki}$.

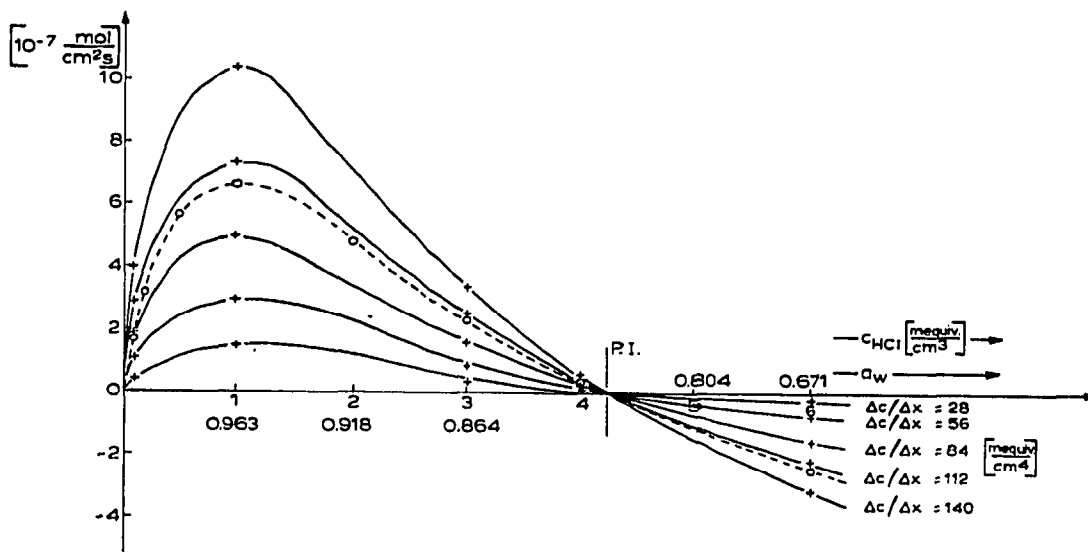


Fig. 1. Isotonic osmosis at higher concentrations. Water flux as a function of the concentration gradient. System: LiCl + HCl-HCl. Parameter: concentration gradient.

Unrestricted confidence in the reciprocal relations can give rise to a failure of such theories. As stated by Gyarmati⁵, the Onsager relations do not need to be valid in the case of constraints. An example of a constraint is the condition

$$\sum z_i^\pm F j_i = I \quad (5)$$

which states that the electric current, I , is given by the number of elementary charges, $z_i^\pm F$ (F = Faraday constant), carried away with the ion fluxes. When $I = 0$, eqn. 5 is called the condition of electroneutrality, which gives rise to an electric field (Nernst's diffusion potential). As this field is not an independent and arbitrary force, it cannot be used on the right-hand side of eqn. 4.

The consequence of the above is that eqn. 4 and the Onsager equation can no longer be used and another principle must be sought. As all transport processes obey a variational principle (Fermat's principle of least time is the classical example) we have used this method to obtain correct equations of transport.

BRAUN-LE CHATELIER PRINCIPLE

The complete deduction of all transport equations requires an exhaustive knowledge of the calculus of variations. As such a procedure exceeds the scope of this paper, we give a short explanation of two equations which we have deduced elsewhere⁶.

If in a solution two fluxes j_1 and j_2 flow in opposite directions through a membrane, an interaction with the solvent (water) takes place. The water evades the constraint originating from the frictional interaction and moves so as to reduce the force

exerted on it to a minimum. In this case, the flux of water is given by the equation

$$j_L = \frac{c_L}{2} \frac{\sum R_i j_i}{\sum R_i c_i} \quad (6)$$

if R_i is the frictional coefficient of the ion i .

Imagining that the particles are electrically neutral and $R_1 > R_2$, the force K_1 necessary to transport particle 1 through the membrane must be greater than the force K_2 exerted on particle 2. In this case, a difference $dK = K_1 - K_2$ is the result. But in the case of ions, an electric field

$$c_F F \text{ grad } \varphi = - \frac{1}{2q} \sum R_i j_i \quad (7)$$

takes place and the result is that the difference dK disappears. This unexpected result is a consequence of the Braun–Le Chatelier principle of least constraint.

Comparing eqns. 6 and 7, the electric field as well as the flux of water can be expressed by the term $\sum R_i j_i$, which results in a formal connection between the osmosis and the electric field (eqn. 7). However, we cannot conclude from this fact that the osmosis arises from an electric field.

FURTHER CONSIDERATION OF ISOTONIC OSMOSIS

Eqn. 6 was used to evaluate the results of our experiments, presented in Table I. The frictional coefficients recorded in Table I were determined with the aid of reverse osmosis² by pressing the pure solvent through the membrane charged with ions 1 and 2. In addition to the ratio $(R_1 - R_2)/(R_1 + R_2)$, Table I gives the corresponding ratios of the ion mobilities, l_1 and l_2 , in solutions which do not differ essentially from the ratio found in the membrane. The last column gives the ratio f of the experimentally determined fluxes of water and the values calculated from eqn. 6. It is not clear whether there is a systematic error or an actual deviation from theory.

In order to understand the inversion of the water flux, it can be noted that eqns. 6 and 7 are valid for an arbitrary number of particles, N . In the case of the isotonic osmosis presented in Fig. 1, there are three particles, H^+ , Li^+ and Cl^- ,

TABLE I
ISOTONIC OSMOSIS AT LOW CONCENTRATIONS
Comparison of experimental and theoretical j_L/j_i values.

System	j_L/j_i (<i>exptl.</i>)	$\frac{R_1 - R_2}{R_1 + R_2}$	$\frac{l_2 - l_1}{l_2 + l_1}$	c_L/c_F	j_L/j_i (<i>theor.</i>)	f
Li-H	6.70	0.76	0.81	18.6	3.5	0.52
Na-H	4.80	0.57	0.76	16.3	2.3	0.48
K-H	3.60	0.47	0.67	16.0	1.9	0.52
Li-K	2.10	0.45	0.32	(13.0)	1.5	0.71
Na-K	1.40	0.14	0.19	(11.5)	0.4	0.20
NH ₄ -K	0.02	—	0.00	—	—	—

from which result the fluxes j_{H^+} and j_{Li^+} of the counter ions and j_{HCl} and j_{LiCl} of the Donnan ions. Eqn. 6 must be written in this case as

$$j_L \sum^N R_i c_i = \frac{c_L}{2} (R_H^+ j_{H^+} + R_{HCl} j_{HCl} + R_{Li^+}^+ j_{Li^+} + R_{LiCl} j_{LiCl}) \quad (8)$$

Using low outside concentrations, the Donnan fluxes can be ignored and osmosis flows in the direction of the Li^+ flux, as $R_{Li^+} > R_{H^+}$. Increasing the outside concentrations, a flux of Donnan ions takes place. As the experiments have shown³, a strong flux of HCl arises, whereas the flux of LiCl can be ignored. This behaviour results from the well known fact that the mobility of H^+ is more than ten times greater than the mobility of Li^+ . To this flux, the second term on the right-hand side of eqn. 8 is coordinated and as the flux j_{Cl^-} together with flux j_{H^+} is opposed to the flux j_{Li^+} , inversion of the osmosis takes place with an increasing concentration of Donnan ions. The independence of the inversion point on the parameter dc/dx follows from the fact that at this point the electric potential disappears and all fluxes j_i are dependent on dc/dx only. Having $j_L = 0$, we can divide both sides by dc/dx and obtain an equation that is independent of dc/dx at the inversion point. The osmotic inversion demonstrates that the electric field coordinated to the osmosis flux (see eqns. 6 and 7) is not Nernst's diffusion potential as assumed by Schlögl⁷. This is a consequence of the fact that $\text{grad } \varphi$ changes sign without the frictional coefficients or the gradients of chemical potentials changing sign, as would be necessary in the case of a diffusion potential.

ELECTROKINETIC RELATIONSHIPS

While on the one hand there is no agreement between our own results and those of prior concepts involving osmosis, on the other hand the investigations of Schmid⁸ on electrokinetic effects completely support our results.

Taking into consideration the definition

$$D_H = -c_L / \sum R_i c_i \quad (9)$$

and restricting eqns. 6 and 7 to a single ion $i = 1$, we obtain

$$\frac{j_L}{q} = -D_H c_F F \text{ grad } \varphi \quad (10)$$

where D_H represents the hydrodynamic permeation, which is inversely proportional to the frictional coefficient. This equation, involving the correct coefficient $c_F F$, was first found by Schmid⁸.

A result of our theory is the following simple electrokinetic relationship. If any solution passes a sintered glass under the influence of a hydrostatic pressure, the velocities v_i and v_L of the solute i and solvent L fulfil the obvious relationship

$$v_L / v_i = 1 \quad (11)$$

If the sintered glass is replaced by a cation-exchange membrane and the pressure gradient by an electric field, it follows from the theory in the case of a single electrolyte^{2,6} that

$$v_L/v_i = 0.5 \quad (12)$$

The evaluation of earlier measurements⁹ yields a value of 0.54 (instead of 0.5), while more recent measurements¹⁰ give a value of 0.49.

PROBLEMS OF SUPERPOSITION OF FLUXES

Comparing eqns. 6 and 7, we can express the isotonic osmosis by an electric field. Proceeding to the non-isotonic osmosis, it seems obvious that the following equation results:

$$j_L/q = -D_{11} \text{grad} (\mu_L^0 + V_L P) - \frac{c_L}{\sum R_i c_i} c_F F \text{grad} \varphi \quad (13)$$

which gives a superposition of the water flux arising from the osmotic difference $d(\mu_L^0 + V_L P)$ (see eqn. 2) and the electric field (eqns. 6 and 7). This equation cannot be correct, however, as the first term on the right-hand side is related to a reversible process concerning a semipermeable membrane and the second term is related to an irreversible process concerning a permeable membrane. The correct equation results from the variational principles. In this paper, we will try to obtain the correct equation by means of phenomenological considerations.

CONSTRAINT RESULTING FROM THE MATRIX

It is the usual method in the theory of osmotic pressure to replace the osmotic difference, $d\mu_L^0$, by the concentration difference of the solute with the aid of the Gibbs-Duhem equation. Using this method for a permeable membrane, we obtain, in the case of a single counter ion 1, the equation

$$c_L \frac{d\bar{\mu}_L^0}{dc_L} \text{grad} c_L = -c_{1F} \frac{d\mu_{1F}}{dc_{1F}} \text{grad} c_{1F} - c_{1D} \frac{d\mu_{1D}}{dc_{1D}} \text{grad} c_{1D} \quad (14)$$

In the following discussion, $\bar{\mu}_L^0$ represents the chemical potential of the solvent inside any membrane. The first term on the right-hand side includes the gradient of the counter ions, which must be zero in a membrane. In order to understand this very important fact, we must take into consideration that the concentration of the fixed ions in a membrane is constant, as is the concentration of the counter ions. Bearing in mind that the gradient implies differentiation and as the differentiation of a constant always results in zero, the term involving the fixed ions and the counter ions must also become zero in eqn. 14.

AN OSMOTIC PARADOX

At both boundaries of the membrane, the condition $\bar{\mu}_L^0 = \mu_L^0$ must be satisfied. From this it follows that $d\bar{\mu}_L^0 = d\mu_L^0$. But if the outside difference $d\mu_L^0$ is high and

as a result of a low concentration of the Donnan ions the difference $d\bar{\mu}_L^0$ is small, the latter condition cannot be satisfied and we have $d\bar{\mu}_L^0 < d\mu_L^0$. This paradox is an apparent one, as we have not paid attention to an essential condition which can be explained as follows. In contact with pure water, a membrane adsorbs water until the chemical potential of the water inside the membrane is equal to the chemical potential of the pure water. Taking the membrane for a simple polyelectrolyte, this state would first be attained at infinite dilution. Indeed, the non-cross-linked polystyrenesulphonic acid exhibits this behaviour. When divinylbenzene is added to the latter, a cross-linked gel is formed. The matrix of the membrane resulting from this reaction opposes a constraint P_c against the infiltrating water. The reaction against this stress is the swelling pressure P_s , which acts on the water according to the equation

$$P_s = -P_c \quad (15)$$

and increases the chemical potential of the latter according to eqn. 1. Hence the paradox mentioned above is resolved, as the phase equilibrium between both boundaries of the strip dx and the solutions must be written as

$$d\mu_L^0 = d(\bar{\mu}_L^0 + V_L P_s) \quad (16)$$

If there is an outside (hydrostatic) pressure gradient $\text{grad } P$, the expression $V_L dP$ must be added to both sides of eqn. 16. In contrast to an outside pressure gradient, a gradient of the swelling pressure does not perform any work, as P_c and P_s are constraining forces. It follows from these considerations that eqn. 13 is valid if we replace μ_L^0 by $\bar{\mu}_L^0$. The latter value results from the concentration gradient of the Donnan ions according to eqn. 14.

ILLUSTRATION OF A PERMEABLE MEMBRANE

In Fig. 2, curve A demonstrates the distribution of the concentration in an inactive membrane if the latter separates solutions of an electrolyte with different concentrations. This "normal" distribution breaks down if the membrane becomes "active" and adsorbs the bulk of ions (in exchange for other ions that diffuse away), as represented by curve C.

The remaining Donnan ions form a normal distribution (curve D). Curves B and E represent the osmotic gradients coordinated to curve A and D. The counter ions show a constant distribution of the concentration and do not give rise to any gradient.

OSMOTIC LAWS CONCERNING SEMIPERMEABLE AND PERMEABLE MEMBRANES

In order to emphasize the difference between a semipermeable and a permeable membrane, we can state that if a membrane separates two solutions showing an osmotic difference $d\mu_L^0$, the following effects take place in a closed osmotic cell:

(1) If the membrane is semipermeable, a hydrostatic pressure difference dP , given by eqn. 3 and called the osmotic pressure takes place in the equilibrium state.

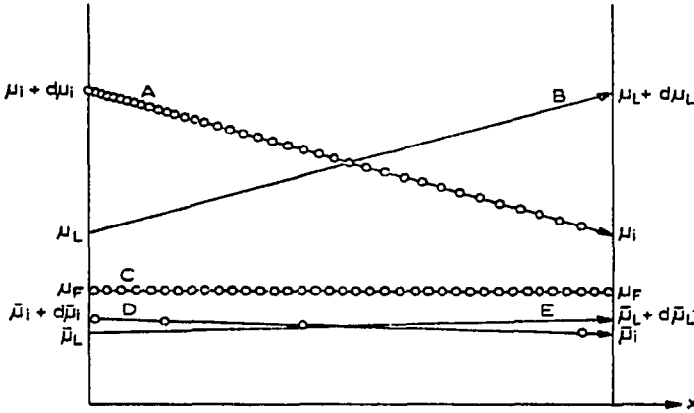


Fig. 2. Osmotic behaviour of semipermeable and permeable membranes. A, normal gradient $d\mu_i/dx$ of the ions; B, osmotic gradient $d\mu_L/dx$ in a semipermeable membrane; C, gradient of the fixed ions $d\mu_F/dx$ in a permeable membrane; D, gradient $d\bar{\mu}_i/dx$ of Donnan ions in a permeable membrane; E, intrinsic osmotic gradient $d\bar{\mu}_L/dx$ in a permeable membrane.

(2) Replacing the semipermeable membrane by a permeable membrane, a hydrostatic pressure difference dP is present in the stationary state. This pressure represents the apparent osmotic pressure and is given by the equation

$$\text{grad } P_a = -c_L \text{ grad } \bar{\mu}_L^0 - c_F F \text{ grad } \varphi \quad (17)$$

which follows from eqn. 13 if we write $\bar{\mu}_L^0$ instead of μ_L^0 , equate j_L to zero and take into consideration eqn. 9. The first term on the right-hand side of eqn. 17 represents the intrinsic osmotic difference which results from the gradient of the Donnan ions according to eqn. 14. From this arises the intrinsic osmotic pressure

$$\text{grad } P_i = -c_L \text{ grad } \bar{\mu}_L^0 = c_{iD} \text{ grad } \mu_{iD} \quad (18)$$

The second term in eqn. 17 represents the electroosmotic potential, which gives rise to the electroosmotic pressure difference

$$\text{grad } P_{el} = \frac{1}{2q} \sum R_i j_i \quad (19)$$

The right-hand side follows from eqns. 7.

(3) In all instances, the chemical potential of the water passes the boundaries of the membrane as stated by the condition

$$d(\mu_L^0 + V_L P) = d(\bar{\mu}_L^0 + V_L P_s + V_L P) \quad (20)$$

(4) In the case of a semipermeable membrane, dP_s vanishes and the intrinsic osmotic difference $d\bar{\mu}_L^0$ is equal to the outside osmotic difference.

(5) In the case of a permeable membrane, the outside osmotic difference performs a jump, which is given by the equation

$$d\mu_L^0 - d\bar{\mu}_L^0 = V_L dP_s \quad (21)$$

We call this effect the osmotic jump. It results from the fact that the constraining force dP_s represents a reaction against the outside osmotic difference $d\mu_L^0$, which reduces the latter to the inside osmotic difference, $d\mu_L^0$.

CONCLUSION

In this paper we have considered a particular aspect in the field of osmosis, in as much as we have restricted ourselves to a "strip dx " of a membrane. The extension to a membrane of finite thickness is a further problem of the calculus of variations. The solution which we have found represents a function of the concentration on the boundaries of the membrane and not a function of the gradients, as is the case in the strip dx .

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