

THE KINETICS OF OSMOSIS.

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(Accepted for publication, April 27, 1927.)

The equilibrium conditions in osmotic pressure experiments have been thoroughly investigated both theoretically and experimentally. The kinetics of the process, however, has received little attention although the general theory is known. The process of osmosis is essentially one of diffusion of the solvent into the solution and so should follow in general the diffusion laws. In ordinary diffusion experiments, however, such as the solution of a solid or the diffusion of salt through a vessel of water, the solute is the component which moves while in osmosis it is the solvent. In the former case, since the number of solute molecules is ordinarily only a small fraction of the total number, the total number of molecules remains practically constant, while in osmosis, the total number of molecules in the solution changes during the experiment. It might be expected therefore that the equation for osmosis would differ slightly from that of diffusion of the solute since the terms containing the total number of molecules, *i.e.* the volume, which are constant in the ordinary diffusion formula are now variables. As will be seen this is the case experimentally.

The desired relation may be derived in a number of ways, but the following derivation, although not mathematically rigorous, appears to the writer to be the simplest.

Assume the solution separated from the solvent by a membrane permeable only for the solvent, as shown in Fig. 1. The mole fraction of the solute is assumed small and the solution is assumed to obey the laws of ideal solutions. Solvent will pass through the membrane from the pure solvent into the solution. The volume and hence the hydrostatic pressure on the solution will be increased and the process

will stop when the hydrostatic pressure equals the osmotic pressure. It is desired to know the quantity of solvent which passes through the membrane at any time.

According to the general law of diffusion (or flow) the rate of flow per unit area is proportional to the pressure gradient, or, in this case, to the pressure divided by the resistance; or

$$\frac{dv}{dt} \sim \frac{P}{R_1}$$

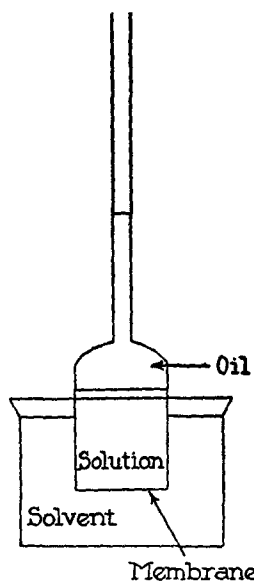


FIG. 1. Apparatus for the determination of the rate of osmosis.

in which v is the volume, t the time, P the pressure, and R the resistance offered to the flow.

In order to integrate this equation the variable terms must be expressed as functions of v or t . The pressure is evidently equal to the osmotic pressure, which tends to force the water in, less the hydrostatic pressure, which tends to force it out,

$$P = OP - HP.$$

The osmotic pressure is defined by the equation,¹

$$OP = \frac{RT}{V_m} (-\ln(I - x))$$

which for dilute solutions reduces to

$$OP = \frac{RTx}{V_m} \quad (1)$$

where R is the gas constant, T the absolute temperature, x the mole fraction of the solute, and V_m the molal volume of the solvent in the solution.² Assume there are g gm. of solute of molecular weight M dissolved in V cc. of water. The mole fraction of the solute, then, will be the moles of solute divided by the total moles, or

$$x = \frac{\frac{g}{M}}{\frac{V}{V_m} + \frac{g}{M}}$$

Since $\frac{g}{M}$ is assumed small in comparison to $\frac{V}{V_m}$, the equation may be written $x = \frac{gV_m}{MV}$. Substituting this value of x in (1),

$$OP = \frac{RT}{V_m} \cdot \frac{gV_m}{MV}$$

¹ Cf., for instance, Washburn, E. W., Physical chemistry, New York, 1st edition, 1915, 155.

² Since we are interested only in the *amount* of water that diffuses into the system, *i.e.*, the amount that passes through the plane at the outside surface of the membrane, it is not necessary to consider the pressure gradient within the solution. The pressure may therefore be assumed proportional to the average pressure, *i.e.*, to the pressure that would exist if the solution were homogeneous. That this is so may be seen from the fact that the pressure gradient would depend on the diffusion coefficient, which does not affect the form of the equation but only the value of the constant. Mathematical proof of this statement may be found in the fact that if the equation is solved according to the general form of Fourier's theorem, which takes into account the pressure gradient and gives the amount of water which passes through a plane at any distance y , from the surface of the membrane, and y is then made equal to zero, the equation reduces to the same form as the integral of (1). Cf. Mellor, J. W., Higher mathematics for students of chemistry and physics, New York, 4th edition, 1913, 488.

or, since in any one experiment R , T , M and also g are all constant and may be combined into one constant P_o ,

$$OP = \frac{P_o}{V}. \quad (2)$$

The hydrostatic pressure will be equal to the initial pressure, n' , plus the additional pressure caused by the rise of the solution in the capillary. If 1 cc. increase in volume causes the liquid to rise K' mm., and f is the relative specific gravity of the liquid compared to mercury, then the hydrostatic pressure at any time expressed in mm. of mercury will be equal to $fn' + fK'(v - v_o)$, or $HP = n + K(v - v_o)$, where v is the volume at any time and v_o is the initial volume; n is the initial pressure expressed as mm. mercury; and K is the increase in pressure per cc. increase in volume, expressed also as mm. mercury.

Evaluation of R_1 .— R_1 may be expressed in different ways depending on the mechanism assumed for the passage of water through the membrane. If the water is assumed to dissolve in the membrane and so pass by diffusion, R_1 is a function of the diffusion coefficient. If the water is assumed to flow through capillaries, then R_1 is a function of the size and number of the capillaries.

1. The Water Dissolves in the Membrane.

The thickness of the layer of solution for a cylindrical vessel with the membrane at one end will be $\frac{v}{\pi r^2}$, where r is the radius of the cylinder. If the thickness of the membrane is h then the total average distance the water has to diffuse will be $h + \frac{v}{2\pi r^2}$, and the total resistance offered to its flow per unit of area will be the distance times the specific resistance; or if R_m is the resistance offered by unit thickness of collodion and R_w the resistance offered by unit thickness of the solution, the total resistance $R_1 = hR_m + \frac{v}{2\pi r^2} R_w$. If the membrane is of such a nature therefore that the solvent can diffuse through it as rapidly or nearly so as through the solution, it is evident that the resistance offered by the membrane may be neglected, since the

distance passed through in the membrane is very small compared to the total distance, and $R = \frac{v}{2\pi r^2} R_w$. In the case of collodion membranes and most other artificial membranes the resistance offered by the membrane is enormously greater than that offered by the solution, so that the term representing the resistance of the solution may be neglected and $R = hR_m$. Since the diffusion coefficient is the reciprocal of the specific resistance, $R = \frac{h}{C}$ where C is the diffusion coefficient of the solvent in the membrane.

2. *The Water Flows through Capillaries in the Membrane.*

In the evaluation of the resistance given above the solvent was assumed to diffuse through the membrane in the same way as through the solution and the increase in resistance was ascribed to the difference in the rate of diffusion of the solvent molecules in the membrane and in the solution. There is some reason to believe, however, that collodion membranes at any rate may be considered as consisting of pores in a solid and that the water passes only through the pores. From this point of view the resistance offered by the membrane will be determined by Poiseuille's law.³ The resistance offered by the solution can again be neglected. If there are p pores of radius r_1 per unit of surface, and they are assumed to be the same length as the thickness of the membrane, the quantity of water that will pass under unit pressure according to Poiseuille's law will be proportional to $\frac{pr_1^4}{h\eta}$, η being the viscosity, and the resistance offered to the passage of the water will be the reciprocal of this or $\frac{h\eta}{pr_1^4}$. Since for any one solvent and membrane η , p and r_1 are constant the resistance will be $\frac{h}{C}$ as before.

In either case, then, the total amount of water passing through will be proportional to $\frac{SC}{h}$ where S is the total surface of the membrane.

³ Cf. Hitchcock, D. I., *J. Gen. Physiol.*, 1925-27, viii, 71.

Substituting these values of R and P , equation (1) becomes

$$\frac{dv}{dt} = \frac{CS}{h} \left[\frac{P_o}{v} - [n + K(v - v_o)] \right]. \quad (3)$$

C is the quantity of solvent that will pass through a unit area of membrane of unit thickness in unit time under unit pressure. Changes in the value of C are due then either to changes in the rate of diffusion in the membrane or to changes in the pore size or number, or the viscosity of the solvent, depending on which mechanism is assumed for the passage of the solvent through the membrane.

If there is no hydrostatic pressure on the solution at the beginning of the experiment the equation in this form predicts that the quantity of solvent passing through the membrane in the first few minutes will be proportional to the osmotic pressure of the solution. This relation has been shown to be true by a number of workers and has been used to measure the pressure in cases where the equilibrium value could not be obtained.⁴

At equilibrium no solvent passes through the membrane, *i.e.*

$\frac{dv}{dt} = 0$, so that

$$\frac{P_o}{v_o} = n + K(v_o - v_o), \quad (4)$$

or

$$Kv_o = n + Kv_o - \frac{P_o}{v_o},$$

where v_o is the volume of solution at equilibrium.

Equation (3) may be integrated in a number of forms depending on which constants are used. Mathematically the simplest expression is obtained in terms of P_o , v_o and K . In order to obtain the equation in these terms the value of Kv_o , from equation (4), is substituted in equation (3). Collecting terms and simplifying, the equation becomes $\frac{dv}{dt} = \frac{CSP_o(1+bv)(v_o-v)}{hv_o v}$, where $b = \frac{Kv_o}{P_o}$, which, on integration, gives

$$C = \frac{2.3 hv_o}{(1+bv_o)SP_o t} \left(v_o \log \frac{v_o - v}{v_o - v_o} - \frac{1}{b} \log \frac{1+bv}{1+bv_o} \right); \quad (5)$$

⁴ Cf. Findlay, A., Osmotic pressure, London and New York, 2nd edition, 1919.

or if $K = 0$, that is when the experiment is so arranged that the hydrostatic pressure is constant,

$$C = \frac{hv_e}{SP_e t} \left(v_o - v + 2.3 v_e \log \frac{v_e - v_o}{v_e - v} \right). \quad (6)$$

TABLE I.

Rate of Osmosis 30°C.

Experiment 1.

$v_o = 3.0$ $P_o = 52.5$ $K = 2.28$ $n = 1.1$ $v_e = 6.2$ $b = .27$
 $S = 10$ sq. cm.

T	v	$K_m \times 10^4$	$\frac{C}{h} \times 10^4$
<i>hrs.</i>	<i>cc.</i>		
0	3.0		
24	3.70	47.5	2.27
48	4.20	44.0	2.19
96	4.85	38.0	1.96
192	5.60	36.0	1.98

Experiment 2

3.2 cc. a "soluble" gelatin in thistle tube closed with collodion membrane.

$v_o = 3.2$ $P_o = 288$ $K = 0$ $n = 50$ $v_e = 5.85$ $S = 4.5$ sq. cm.

T	v	$K_m \times 10^4$	$\frac{C}{h} \times 10^4$
<i>hrs.</i>	<i>cc.</i>		
0	3.2		
24	3.75	42.5	1.53
48	4.15	40.0	1.53
96	4.72	38.7	1.62
192	5.22	32.0	1.51
300	5.85		

This condition would also be true if the solvent outside the membrane were replaced by a large volume of solution having a lower osmotic pressure than that of the solution inside. The osmotic pressure of the outside solution would enter into the equation in the same way as does the initial hydrostatic pressure, n , in equation (3).

A number of experiments were performed to test the accuracy of these equations, and they were found to hold within the experimental error.

Table I and Fig. 2 give the results of two such experiments. In the first experiment solutions of egg albumin in $m(\text{NH}_4)_2\text{SO}_4$ were placed in a rocking osmometer,⁵ with the same concentration of ammonium sulfate outside, and left until equilibrium was established.

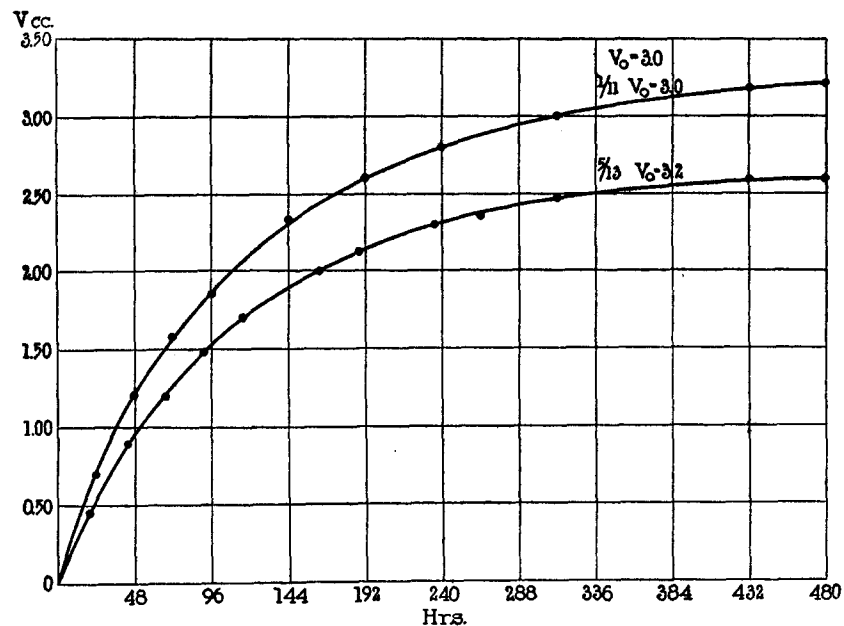


FIG. 2. The rate of osmosis of protein solutions in collodion membranes.

3 cc. of the solution was then placed in a tube closed with a membrane, the upper part of the tube filled with oil and the membrane immersed in the solution of ammonium sulfate with which the albumin solution had previously been in equilibrium. The pressure in the manometer was set at the equilibrium value and the system left for 2 days so that the permeability of the membrane might become constant. The manometer level was then lowered and the rise of the

⁵ Northrop, J. H., and Kunitz, M., *J. Gen. Physiol.*, 1925-26, ix, 351; also 1926-27, x, 161.

oil in the manometer noted. The experiment was carried on in a water bath at 30°C. In the presence of this concentration of ammonium sulfate the osmotic pressure of albumin is nearly proportional to its concentration, so that it may be assumed to obey the ideal solution law. The ammonium sulfate also prevents bacterial growth. The second experiment was done in the same way except that a solution of "soluble" gelatin⁵ was used. In this case the manometer tube was bent so as to be horizontal. There was therefore no change in pressure during the experiment and equation (6) should fit. The table shows in both cases that the monomolecular constant K_m given for comparison shows a regular decrease while the constants calculated by equations (5) and (6) do not vary outside of the experimental error. This was found to be the case in all of the experiments made. The monomolecular constant dropped slowly in every case.

In the first experiment the value of $\frac{C}{h}$ was found to be 2×10^{-4} .

If the derivation given is correct this should be the cc. of water that will flow through 1 sq. cm. of the membrane in 1 hour under 1 mm. mercury pressure. At the end of the experiment the membrane was washed, filled with water and the rate of flow of water through it determined under 10 cm. mercury pressure. A value for the rate of flow of 1.5×10^{-4} cc. per hour per mm. mercury pressure was obtained, which agrees as well as could be expected with the figure calculated from the osmotic pressure experiment.

In this experiment the surface of the membrane is constant. In experiments with cells such as those of McCutcheon and Lucke⁶ the surface increases during the experiment. If the water is assumed to diffuse through the membrane, the thickness of the membrane being constant, then $S \propto v^{\frac{2}{3}}$; or if the volume of the membrane remains constant $\frac{S}{h} \propto v^{\frac{4}{3}}$. If the water is supposed to flow through pores in the membrane and the increase in surface is due to enlarging the size of the pores, the thickness remaining constant, then $r^2 \propto S \propto v^{\frac{2}{3}}$ and $r^4 \propto v^{\frac{4}{3}}$. According to the first assumption the velocity should be very slightly slower than that predicted by the monomolecular formula and according to the second or third assumption it should be very

⁶ McCutcheon, M., and Lucke, B., *J. Gen. Physiol.*, 1925-26, ix, 697.

slightly faster. In either case the deviation from the monomolecular formula would be noticed only in very accurate experiments.

SUMMARY.

It is shown that by combining the osmotic pressure and rate of diffusion laws an equation can be derived for the kinetics of osmosis.

The equation has been found to agree with experiments on the rate of osmosis for egg albumin and gelatin solutions with collodion membranes.