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K. J. Laidler and K. E. Shuler

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The Kinetics of Membrane Processes. II. Theoretical Pressure-Time Relationships for Permeable Membranes

K. J. LAIDLER AND K. E. SHULER

Department of Chemistry, The Catholic University of America, Washington, D. C.

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The rate equations developed in Part I for the flow of solvent and solute through a permeable membrane have been extended to the case in which the flow is measured by the rise and fall in a capillary inserted into the more concentrated solution. The differential equation obtained for this case has been integrated to give an explicit relationship between the height of rise in the capillary and the time. The equation is shown to give the height-time relationship in the form found by experiment. It is shown that the osmotic pressure obtained with a semipermeable membrane is a special case of the more general theory of diffusion through membranes permeable to both solvent and solute. The possibility of positive and negative values of P, i.e., of *initial* rise or fall respectively in the capillary, is discussed, and the significance of these cases evaluated in terms of the molar volumes and permeation constants of solvent and solute.

INTRODUCTION

IN the previous paper[1] (Part I), equations have been derived for the rates of flow of solvent and solute molecules from a solution α to a solution β separated from it by a membrane which is permeable, to different extents, to both species. For the solvent it was found that the number $n_1{}^\beta$ of molecules entering solution β in time t is given fairly accurately by the expression

$$dn_1{}^\beta/dt = \frac{Q_1 A c_t \bar{V}_1}{d'RT}(\pi - P), \qquad (1)$$

where Q_1 is the permeation constant for the solvent, A the area and d' the thickness of the membrane, c_t is the total molar concentration in the membrane, $\bar{V}_1$ the molar volume of the solvent, π the difference $(\pi^\beta - \pi^\alpha)$ between the true osmotic pressures for the two solutions, and P is the hydrostatic pressure acting on solution β, solution α being maintained at atmospheric pressure. This equation was shown to be accurate for fairly dilute solutions, whether ideal or not. For the solute a rate expression was obtained on the assumption of ideality; it was

$$dn_2{}^\beta/dt = -\frac{Q_2 A c_t \bar{V}_1}{d'RT}\pi, \qquad (2)$$

the symbols having the same meaning as before, the subscript 2 indicating that the properties of the solute are now referred to.

On the basis of these equations, kinetic laws will be derived which should be applicable to the following type of experiment. Two solutions of a non-electrolyte at different concentrations of the same solute are separated by a membrane, the pressure of one being maintained at atmospheric pressure; the pressure and volume of the other are allowed to vary, and the changes are measured by observing the level in a capillary tube. In practice it is most convenient to arrange the solutions so that the level rises rather than falls in the

[1] K. J. Laidler and K. E. Shuler, J. Chem. Phys. **17**, 851 (1949).

capillary tube, the more dilute solution usually being the one to be maintained at atmospheric pressure. Measurements are made of the level of the meniscus as a function of the time, a correction being made for capillarity within the tube.

If the membrane is semipermeable and separates a solution from the pure solvent maintained at atmospheric pressure, the level of the meniscus rises owing to the passage of pure solvent into the solution, and continues to rise until it reaches a maximum pressure, which is the osmotic pressure of the solution (somewhat diluted by the passage of the solvent); the change of pressure with time in this case is represented by curve I in Fig. 1. If, on the other hand, the solute also diffuses through the membrane, but passes through it less rapidly than the solvent, the curve will be as represented in curve II; the pressure rises to a maximum and then falls to zero. If the solute diffuses through the membrane sufficiently rapidly as compared with the solvent, the pressure falls initially, reaches a minimum, and then rises to zero (curve III); this last case is realized only infrequently. The general laws governing these types of behavior will now be derived on the basis of the equations developed in Part I for the kinetics of flow of solvent and solute through a membrane permeable to both.

PRESSURE-TIME CURVES FOR OSMOTIC FLOW

The Differential Equation

Equations (1) and (2) may now be used to relate the rates of change of volume and pressure in terms of the osmotic pressure difference π and the hydrostatic pressure P. The equations give the rate of flow from α to β, so that the rate of increase of volume of solution β due to the flow of solvent is

$$dV_1{}^\beta/dt = \frac{Q_1 A c_t \bar{V}_1{}^2}{d'RT}(\pi - P). \qquad (3)$$

Similarly the rate of increase of volume due to the flow

of solute is

$$dV_2{}^\beta/dt = -\frac{Q_2 A c_t \bar{V}_1 \bar{V}_2}{d'RT}\pi. \qquad (4)$$

The net rate of increase of volume of solution β is thus

$$dV^\beta/dt = dV_1{}^\beta/dt + dV_2{}^\beta/dt$$

$$= \frac{Q_1 A c_t \bar{V}_1{}^2}{d'RT}(\pi - P) - \frac{Q_2 A c_t \bar{V}_1 \bar{V}_2}{d'RT}\pi. \qquad (5)$$

If a is the area of cross section of the capillary tube and the pressure P is expressed as centimeters of rise in the tube,[2] the rate of increase of volume is $d(aP)/dt$, and it follows that

$$dP/dt = \frac{Q_1 A c_t \bar{V}_1{}^2}{d'RTa}(\pi - P) - \frac{Q_2 A c_t \bar{V}_1 \bar{V}_2}{d'RTa}\pi. \qquad (5)$$

This equation may be written as

$$dP/dt = \lambda_1(\pi - P) - \lambda_2\pi, \qquad (7)$$

where

$$\lambda_1 = \frac{Q_1 A c_t \bar{V}_1{}^2}{d'RTa} \qquad (8)$$

and

$$\lambda_2 = \frac{Q_2 A c_t \bar{V}_1 \bar{V}_2}{d'RTa}. \qquad (9)$$

The Rate of Change of Osmotic Pressure

In order for Eq. (7) to be solved, the variation of the osmotic pressure difference π with time must be known. The change in the concentrations of the two solutions with time is determined largely by the diffusion of the solute molecules, since this produces a much greater proportional change in concentration than does the diffusion of the solvent molecules. The rate of increase of the number of moles of solute in solution β is equal to the rate of decrease in solution α, and is given by Eq. (2). If V^β liters is the total volume of solution β the rate of decrease of the mole fraction $N_2{}^\beta$ is given to a good approximation by[3]

$$-dN_2{}^\beta/dt = -(\bar{V}_1/V^\beta)(dn_2{}^\beta/dt). \qquad (10)$$

Introducing Eq. (2) gives

$$-dN_2{}^\beta/dt = \frac{Q_2 A c_t \bar{V}_1{}^2}{V^\beta d'RT}\pi \qquad (11)$$

and similarly the rate of increase of the mole fraction of the solute in solution α of volume V^α, is

$$dN_2{}^\alpha/dt = \frac{Q_2 c_t A \bar{V}_1{}^2}{V^\alpha d'RT}\pi. \qquad (12)$$

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[2] The osmotic pressure difference π must also be in the same units, and RT must be expressed as cm^4.

[3] In dilute solutions, $n_1{}^\beta = V^\beta/\bar{V}_1$ and $N_2{}^\beta = n_2{}^\beta/n_1{}^\beta$; hence $N_2{}^\beta/n_2{}^\beta = \bar{V}_1/V^\beta$.

Since the rate of change of osmotic pressure is related to the sum of these quantities it is sufficiently accurate to introduce the osmotic pressures π^α and π^β by the approximate expressions

$$\pi^\alpha = N_2{}^\alpha(RT/\bar{V}_1) \qquad (13)$$

and

$$\pi^\beta = N_2{}^\beta(RT/\bar{V}_1). \qquad (14)$$

Substitution for $N_2{}^\alpha$ and $N_2{}^\beta$ in Eqs. (11) and (12) gives

$$-\frac{d\pi^\beta}{dt} = \frac{Q_2 A c_t \bar{V}_1}{d'V^\beta}\pi \qquad (15)$$

and

$$\frac{d\pi^\alpha}{dt} = \frac{Q_2 A c_t \bar{V}_1}{d'V^\alpha}\pi. \qquad (16)$$

The rate of change of the osmotic pressure difference π is thus given by

$$\frac{d\pi}{dt} = \frac{d(\pi^\beta - \pi^\alpha)}{dt} = -\frac{Q_2 A c_t \bar{V}_1}{d'}\pi(1/V^\beta + 1/V^\alpha). \qquad (17)$$

This may be written as

$$-d\pi/dt = \lambda_3\pi \qquad (18)$$

where

$$\lambda_3 = \frac{Q_2 A c_t \bar{V}_1}{d'}(1/V^\beta + 1/V^\alpha). \qquad (19)$$

Solution of the Equations

The equations to be solved are (7) and (18), viz.,

$$dP/dt = \lambda_1(\pi - P) - \lambda_2\pi \qquad (20)$$

and

$$-d\pi/dt = \lambda_3\pi. \qquad (21)$$

The solution of Eq. (21) subject to the boundary condition $\pi = \pi_0$, $t = 0$, where π_0 is the theoretical equilibrium value of $\pi^\beta - \pi^\alpha$ as given by the Morse equation at the beginning of the experiment, is

$$\pi = \pi_0 e^{-\lambda_3 t}. \qquad (22)$$

Substitution of this into Eq. (20) gives

$$dP/dt = \lambda_1(\pi_0 e^{-\lambda_3 t} - P) - \lambda_2\pi_0 e^{-\lambda_3 t}, \qquad (23)$$

FIG. 1. The variation of pressure with time when a solution is separated from the pure solvent by a membrane, the solvent being maintained at atmospheric pressure. For a semipermeable membrane (curve I) the pressure rises exponentially to the osmotic pressure π_0. Curves II and III are for membranes permeable to both solvent and solute; for curve II the membrane is more permeable to the solvent; for curve III to the solute.
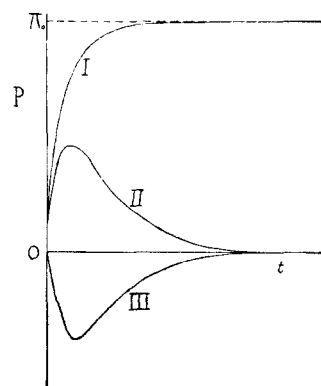
which rearranges to

$$dP/dt + P\lambda_1 = \pi_0(\lambda_1 - \lambda_2)e^{-\lambda_3 t}. \tag{24}$$

This is a linear differential equation of the first order and with the boundary condition $t=0$, $P=0$ integrates to

$$P = \pi_0 \frac{\lambda_1 - \lambda_2}{\lambda_1 - \lambda_3}(e^{-\lambda_3 t} - e^{-\lambda_1 t}). \tag{25}$$

There has thus been obtained an explicit relationship between pressure and time, involving the initial osmotic pressure difference π_0 and the three parameters λ_1, λ_2, and λ_3. The three parameters are functions of the known volumes and other dimensions of the system, and also of the two permeation constants Q_1 and Q_2. It will now be shown that Eq. (25) is of the proper form to explain curves I, II, and III in Fig. 1.

For a semipermeable membrane, for which $Q_2 = 0$, it follows that $\lambda_2 = \lambda_3 = 0$, and the equation becomes

$$P = \pi_0(1 - e^{-\lambda_1 t}). \tag{26}$$

This corresponds to an exponential rise from $P=0$ to $P=\pi_0$ (curve I).

Whatever the relative magnitudes of λ_1 and λ_3 the function $(e^{-\lambda_3 t} - e^{\lambda_1 - t})/(\lambda_1 - \lambda_3)$ is always positive. Consequently if $\lambda_1 > \lambda_2$ the curve rises initially and reaches a maximum after which it falls to zero (curve II). If $\lambda_2 > \lambda_1$ the curve falls initially and shows a minimum before returning to zero (curve III).

The expression for the maximum pressure rise in the capillary is

$$P_{\max} = \pi_0 \frac{(\lambda_1 - \lambda_2)}{\lambda_1}\left(\frac{\lambda_3}{\lambda_1}\right)^{\lambda_3/(\lambda_1 - \lambda_3)} \tag{27}$$

For a semipermeable membrane, $\lambda_2 = \lambda_3 = 0$, and the expression reduces to $P_{\max} = \pi_0$ in accordance with the definitions of these quantities, after evaluation of the indeterminate form resulting from the above substitutions.

It can furthermore be seen that if $\lambda_3 > \lambda_1$, which is usually the case, the exponential $e^{-\lambda_3 t}$ is much smaller than $e^{-\lambda_1 t}$ for sufficiently large values of t, so that Eq. (25) approximates to

$$\ln P = \ln\left\{\pi_0 \frac{(\lambda_1 - \lambda_2)}{(\lambda_3 - \lambda_1)}\right\} - \lambda_1 t. \tag{28}$$

The plot of $\ln P$ versus t should therefore be a straight line for sufficiently large values of t, the slope being $-\lambda_1$.

In testing Eq. (25) against the experimental results, the following procedure is adopted, since Eq. (25) does not readily lend itself to the usual least square method treatment. Two points P_1, t_1 near the beginning of the graph, and P_2, t_2 near the end of the graph, are chosen. Then, using Eq. (25),

$$\frac{P_1}{P_2} = \frac{(e^{-\lambda_3 t_1} - e^{-\lambda_1 t_1})}{(e^{-\lambda_3 t_2} - e^{-\lambda_1 t_2})}. \tag{29}$$

Since λ_1 is known from the slope, the above equation can be solved for λ_3, and then λ_2 can be found by substitution in (25). Doing this for several pairs of points, the proper values for λ_3 and λ_2 can readily be found. The permeation constants Q_1 and Q_2 can then be calculated from Eq. (8) and (9).

The Change of Concentration with Time

By a modification of the above procedure it is also possible to derive an expression for the concentration of the solute in solutions α and β at any time t. Equation (22) may be written as

$$\pi^\beta - \pi^\alpha = (\pi_0^\beta - \pi_0^\alpha)e^{-\lambda_3 t}, \tag{30}$$

and since by van't Hoff's law for dilute solutions, the osmotic pressures are proportional to the concentrations of the solute, it follows that

$$c_2^\beta - c_2^\alpha = ({}^0c_2^\beta - {}^0c_2^\alpha)e^{-\lambda_3 t}, \tag{31}$$

where c_2^α is the concentration of the solute in solution α at time t and ${}^0c_2^\alpha$ is the initial concentration at $t=0$. Using the auxiliary condition that at any time t

$$c_2^\alpha = n_2^\alpha/V^\alpha, \tag{32}$$

and that

$${}^0n_2^\beta + {}^0n_2^\alpha = n_2^\beta + n_2^\alpha, \tag{33}$$

it can be deduced that

$$c_2^\alpha = \frac{{}^0n_2^\beta(1 - e^{-\lambda_3 t}) + {}^0n_2^\alpha[1 + (V^\beta/V^\alpha)e^{-\lambda_3 t}]}{V^\beta + V^\alpha}, \tag{34}$$

and a similar expression for c_2^β can be obtained. The concentration of the solute in the two solutions after time t can therefore be calculated in terms of the constant λ_3, itself a function of Q_2.

The special case in which $\pi^\alpha = $ constant is of practical interest since it can easily be realized in the laboratory by using a flow system or making one volume much larger than the other. Applying the condition $\pi^\alpha = $ constant to the equations previously developed, it is found that Eq. (25) is still obeyed, but now λ_3 is given by

$$\lambda_3 = Q_2 A c_t \bar{V}_1/d' V^\beta. \tag{35}$$

The relationship between λ_2 and λ_3 is now

$$\lambda_3 = \lambda_2(RTa/\bar{V}_2 V^\beta), \tag{36}$$

and expressions in terms of concentrations may readily be obtained.

DISCUSSION

General

The treatment given has led to a general equation for the pressure and volume of a solution separated by a membrane from another solution, expressed as a function of the time. It enables these relationships to be predicted from the known dimensions of the system and from the permeation constants of solvent and

solute; conversely the permeation constants can be evaluated from the pressure-time relationships.

The theory is applicable directly to experiments in which the pressure and volume of one system are allowed to increase simultaneously by the expansion of one solution into a capillary tube; this implies a particular linear relationship between the volume and the pressure. For other types of relationships, such as will obtain in biological cells where there is an actual expansion of the cell instead of an expansion into a capillary, a different treatment is necessary.

It is to be noted that the hydrostatic pressure exerted by the column in the capillary upon the solution must be explicitly taken into account. The importance of including it is shown by Eq. (3) according to which the hydrostatic pressure P and the osmotic pressure difference π enter into the rate of flow of solvent as $\pi - P$. If π and P are of comparable magnitude, the neglect of P naturally introduces considerable error; moreover, neglect of P would lead to equations which would be at variance with the experimental pressure-time curves which will be described in Part III.

According to the theoretical treatment given in this paper a membrane is characterized with respect to the flow of the components of a binary solution by the permeation constants of the two species. Upon the values of these constants depends the general shape of the pressure-time relationship; changes in either or both of them will influence the initial pressure rise, the height of the maximum, and the rise at any arbitrary time. These quantities are also dependent upon the molar volumes, the total volumes, and the cross-sectional area of the capillary.

Maximum Height of Rise in the Capillary

Since for semipermeable membranes the height of rise, i.e., the osmotic pressure, is a linear function of the composition of the solution according to the laws of van't Hoff and Morse, it might be thought that the maximum height of rise in the type of system and experiment discussed here would also bear the same relationship, especially since the Morse law was used as one of the starting points of this treatment. However, an examination of Eq. (27) for the maximum height of rise will show that this is not the case; thus π_0 which is a linear factor of the composition is multiplied by a complicated expression involving the permeation constants of solvent and solute. This is very similar to the case of a consecutive, first-order reaction

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C \tag{37}$$

where the maximum concentration of B is given by

$$(C_B)_{\max} = a_0 (k_2/k_1)^{k_2/(k_1-k_2)}, \tag{38}$$

where a_0 is the initial concentration of A. This similarity is of course due to the fact that Eqs. (20) and (21)

are formally the rate equations for consecutive first order reactions with three instead of two rate constants.

$P_{\max}$ being a complicated function of the initial concentration and the permeation constants, it is impossible to draw any direct conclusions as to the initial concentration or the permeation constants of the system involved from its value alone; a complete analysis of the pressure-time curve obtained must be made, as described earlier in this paper, to obtain this information. For the characterization of a given membrane, the rate constants λ_1, λ_2, and λ_3, and hence Q_1 and Q_2, are therefore much more fundamental quantities than the maximum height of rise.

Initial Rise or Fall in the Capillary

When two solutions of different concentrations of the same solute are separated by a permeable membrane, and the change in the system is measured by the change in the level of a capillary inserted into the more concentrated solution, there is the possibility of either an *initial* rise or *initial* fall in the capillary (curves II and III, Fig. 1) in contrast to the case of a semipermeable membrane where there will *always* be a rise in the capillary (curve I, Fig. 1).

The explanation for this is contained in Eq. (25) which shows that the sign of P depends upon the sign of $(\lambda_1 - \lambda_2)$; this arises, as mentioned before, because the function $(e^{-\lambda_3 t} - e^{-\lambda_1 t})/(\lambda_1 - \lambda_3)$ is always positive whatever the relative values of λ_1 and λ_3. Therefore if $\lambda_1 > \lambda_2$, the value of P is always positive, while if $\lambda_1 < \lambda_2$, its value is always negative. For the case of a semipermeable membrane for which Eq. (26) applies, P is always positive, whatever the value of λ_1, the other constants not entering in the equation. Expressing λ_1 and λ_2 by means of Eqs. (8) and (9) it is seen that the condition for a positive P, i.e., an initial rise in the capillary, is given by

$$\frac{Q_1 c_i A \bar{V}_1^2}{d'RTa} > \frac{Q_2 c_i A \bar{V}_1 \bar{V}_2}{d'RTa} \tag{39}$$

which reduces to

$$Q_1 \bar{V}_1 > Q_2 \bar{V}_2. \tag{40}$$

The condition for a negative P, i.e., an initial fall in the capillary is conversely that

$$Q_1 \bar{V}_1 < Q_2 \bar{V}_2. \tag{41}$$

These simple conditions could have been arrived at intuitively, since the rates of volume increase due to solvent and solute are clearly proportional to $Q_1 \bar{V}_1$ and $Q_2 \bar{V}_2$, the product of the permeation constant of the substance and its molar volume, the mole fraction gradient at any time being the same for both solvent and solute. If $Q_2 \bar{V}_2 = Q_1 \bar{V}_1$ the concentrations of the two solutions will equalize without the development of any pressure between the two solutions.

The collodion membranes with which we have ex-

perimented so far have been much more permeable to water than to the solutes used, and for aqueous solutions it has always been found that $Q_1\bar{V}_1 > Q_2\bar{V}_2$, i.e., there was always an initial rise in the capillary inserted into the more concentrated solution. Attempts to obtain an initial fall in the capillary with aqueous solutions of non-electrolytes have failed, and this is attributed to the fact that the values of $Q_2\bar{V}_2$ do not change very much from solute to solute. A solute with a larger value of Q_2 generally has to be one of smaller molar volume $\bar{V}_2$, and in general it has been noted that Q_2 is approximately inversely proportional to $\bar{V}_2$.

It has been possible, however, to obtain an initial fall in the capillary, and thus negative values of P,

using glycerol as a solvent and urea as the solute. Since in this case $\bar{V}_1$ is of about the same order as $\bar{V}_2$, this must have been due to $Q_1 < Q_2$, where the deciding factor probably is the low diffusion coefficient for the self diffusion of glycerol. The system was picked for that reason; the experimental details and results will be given in Part III.

This discussion of the initial rise and fall in the capillary pertains directly only to solutions of non-electrolytes. For electrolytes, the electro-osmotic effect caused by the potential differences across the membrane and the zeta-potential on the membrane complicate matters; we hope to give an extension of the above treatment to electrolytes in a later paper.

The Kinetics of Membrane Processes. III. The Diffusion of Various Non-Electrolytes through Collodion Membranes

K. E. SHULER, C. A. DAMES, AND K. J. LAIDLER
Department of Chemistry, The Catholic University of America, Washington, D. C.
(Received October 15, 1948)

Measurements have been made of the rates of diffusion of various non-electrolytes, and of water, through a collodion membrane separating a dilute solution from pure water. The determinations were made by measuring the rate of rise and fall in a capillary tube in the solution, and analyzing the results using the procedure described in a previous paper. The work was done with $0.25N$ solutions of sucrose, lactose, raffinose and mannitol, and was carried out at different temperatures so that energies and entropies of activation could be determined. The energy of activation for diffusion through the membranes was found in all cases to be slightly less than for free diffusion, a result that is shown to be consistent with a positive heat of adsorption of the solute and solvent at the membrane. Analogously the entropies of activation for membrane diffusion are somewhat less than for free diffusion, since the process of adsorption brings about a decrease in entropy. The rate of diffusion of water through a membrane is shown to depend upon the nature of the solute diffusing, a result which arises from the fact that diffusion is a mutual process. An experiment is described in which there is an initial net flow from the solution into the solvent.

INTRODUCTION

IN previous papers (Parts I and II)[1,2] equations have been developed which are relevant to experiments in which a solution and the pure solvent are separated by a membrane permeable, to different degrees, to both solvent and solute, and in which the level in a capillary tube connected to the solution is measured as a function of time. An equation (Eq. (25) of Part II) was derived expressing pressure as a function of time: it involved, besides the relevant dimensions of the reaction system, the permeation constants for solvent and solute. A method was outlined for analyzing the experimental pressure-time curves so as to obtain the values of the two permeation constants.

In the present paper this procedure is applied to experimental results obtained with dilute aqueous solutions of four non-electrolytes, using collodion membranes. The object of the experiments has been the establishment of the fundamental kinetic laws obeyed

when there is simultaneous flow of two substances, the solvent and the solute; the determination of absolute values of the permeation constants, and the energies and entropies of activation, has been regarded as incidental, since they are relevant only to the particular membranes used. It has been possible, however, to show that the equations developed in the previous papers are applicable, and to arrive at some general conclusions as to the mechanism of flow through membranes of this type.

Experimental Procedure

(1) *The Membranes.* The collodion membranes used were prepared from collodion cotton, pyroxylin, manufactured by the J. T. Baker Chemical Company. The membranes used in the experiments were strong enough to hold about 60 cc of solution without tearing, but thin and porous enough to permit completion of a run within a reasonable length of time.

The membranes were prepared by standard methods. The collodion solution (about 7 percent) was prepared

[1] K. J. Laidler and K. E. Shuler, J. Chem. Phys. **17**, 851 (1949).
[2] K. J. Laidler and K. E. Shuler, J. Chem. Phys. **17**, 856 (1949).