The Kinetics of Membrane Processes. I. The Mechanism and the Kinetic Laws for Diffusion through Membranes

K. J. Laidler and K. E. Shuler

Additional information on J. Chem. Phys.

TABLE III. Constants for interatomic potential energy.

	Neon[a]	Argon[a]	Krypton[b]
r_0 (A)	3.08	3.83	4.06
ϕ_0 (10^{15} erg)	4.89	16.5	22.6

[a] R. H. Fowler and E. A. Guggenheim, *Statistical Thermodynamics* (Cambridge University Press, London, 1939), p. 285.
[b] T. Kihara and M. Kotani, Proc. Phys. Math. Soc. Japan 25, 602 (1943).

exact magnitude of those repulsive forces, when atoms are so close together, has not yet been published so far as we know. But it seems likely that the corresponding extrapolation of interatomic forces of neon, argon, and krypton empirically obtained from interatomic distances, heats of sublimation, second virial coefficients and other methods gives the right order of magnitude as the values of F_{FF}', F_{FF}, F_{ClCl}', F_{ClCl}, F_{BrBr}', and F_{BrBr}.

The interatomic potential energy of neon etc., is expressed by Lennard-Jones as

$$U(q) = \phi_0 [(r_0/q)^{12} - 2(r_0/q)^6], \qquad (8)$$

where r_0 is the value of interatomic distance q at which $U(q)$ has a minimum value equal to $-\phi_0$. The values of ϕ_0 and r_0 used are tabulated in Table III. From this equation F' and F defined in Eq. (1) are expressed by

$$F' = \left(\frac{1}{q}\frac{dU}{dq}\right)_{q=q_0} = \frac{12\phi_0}{q_0^2}\left[-\left(\frac{r_0}{q_0}\right)^{12} + \left(\frac{r_0}{q_0}\right)^6\right], \qquad (9)$$

$$F = \left(\frac{d^2U}{dq^2}\right)_{q=q_0} = \frac{12\phi_0}{q_0^2}\left[13\left(\frac{r_0}{q_0}\right)^{12} - 7\left(\frac{r_0}{q_0}\right)^6\right]. \qquad (10)$$

TABLE IV. Force constants, F' and F, and interatomic forces (10^5 dynes/cm).

	F	F'		F	F'
F...F (CF4)	1.35	−0.30	F...F (SiF4)	0.43	−0.31
Ne...Ne (2.22A)	0.75	−0.05	Ne...Ne (2.51A)	0.12	−0.01
Cl...Cl (CCl4)	0.65	−0.10	Cl...Cl (SiCl4)	0.30	−0.06
Ar...Ar (2.87A)	0.91	−0.06	Ar...Ar (3.30A)	0.11	−0.01
Br...Br (CBr4)	0.50	−0.10	Br...Br (SiBr4)	0.23	−0.04
Kr...Kr (3.12A)	0.75	−0.05	Kr...Kr (3.50A)	0.13	−0.01

We can calculate from these equations the values of F' and F when the two neon (argon, krypton) atoms are so close together as the two fluorine (chlorine, bromine) atoms are in CF_4 (CCl_4, CBr_4) and in SiF_4 ($SiCl_4$, $SiBr_4$). The calculated values are compared with the repulsive force constants obtained from normal coordinate treatment in Table IV. The agreement of these two kinds of values seems to be of significant. That the repulsive force constants for CF_4 molecule are large as compared with those of others is to be attributed partly to the shortness of the CF bond length and partly to the ionic nature of CF bond. In view of these facts it is not a good approximation to neglect interactions between two CF_3- groups in the normal coordinate treatment of CF_3-CF_3 molecule.

The author wishes to express his sincere thanks to Professor S. Mizushima for many helpful discussions.

Note added in proof.—Since some revisions have been made in proof, the calculated frequencies of C_2Cl_6 molecule given in Table II are somewhat different from those reported in the article by Mizushima, Morino, Simanouti, and Kuratani, J. Chem. Phys. 17, 838 (1949). The conclusion of our previous paper, however, is not affected by this revision.

The Kinetics of Membrane Processes. I. The Mechanism and the Kinetic Laws for Diffusion through Membranes*

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The equations for diffusion in binary systems are extended to the case of diffusion through a membrane. Three elementary rate processes are considered at a solution-membrane interface: (1) adsorption of the diffusing species, (2) desorption back into the solution, and (3) diffusion into the membrane, and an expression for the rate constant of the over-all process of surface penetration is developed in terms of three specific rate constants. Various special cases are considered and discussed with reference to the experimental data. A general expression for the rate of diffusion of a species through a membrane under steady-state conditions is derived, the rate being expressed as a function of activities. It is shown that the application of this expression to the case of a solvent passing through a membrane which is impermeable to the solute leads to the thermodynamically exact equation for the osmotic pressure. Expressions are given for the rate of flow of solvent and solute through a membrane as a function of the osmotic and hydrostatic pressures across the membrane.

INTRODUCTION

IN a paper on the diffusion laws in liquid systems[1] it has been shown on both statistical and thermo-

* Parts I, II, and III of this series have been accepted as the dissertation of Kurt E. Shuler, submitted to the Faculty of the Graduate School of Arts and Sciences of the Catholic University of America in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry.
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[1] K. E. Shuler and K. J. Laidler (to be published).

dynamical grounds that the proper composition unit to be used is the mole fraction activity Nf, and that more constant diffusion coefficients are found if the equations are formulated on this basis. In the present paper this treatment is extended to the case in which phase boundary processes occur in addition to diffusion, i.e., to the permeation of a solid by molecules in solution. The kinetic laws for the penetration of membranes, in the steady state of flow, are derived, and

equations for various special cases of interest are developed.

DIFFUSION INTO A SOLID

When a molecular species in solution penetrates a solid it can generally be assumed, especially if the solution be well stirred, that the rate of diffusion in the liquid is sufficiently rapid so that it need not be taken into consideration; if this is the case the elementary processes occurring at the interface are

(1) Adsorption on the interface
(2) Desorption at the interface back into the solution
(3) Diffusion into the solid.

For convenience it will be assumed that the molecules undergoing these processes are solute molecules, but the treatment can, as will be seen, be applied equally well to the solvent. As a result of the three elementary processes occurring above, a certain concentration of solute molecules will be maintained at the interface, the amount being controlled by the relative magnitudes of the three rates.

The rates of the adsorption and desorption processes may be formulated by a modification of the procedure used previously for gas-solid interfaces,[2] the change being that mole fractions will here be used instead of concentrations; that mole fractions should be used in formulating the kinetic laws for liquid systems has already been noted by G. Scatchard.[3] For convenience of representation, mole fractions, N, will be used instead of mole fraction activities, Nf, but the application to non-ideal solutions can easily be made.

The process of adsorption may be regarded as a bimolecular reaction between solute molecules in solution of mole fraction N and bare sites; if the mole fraction of adsorbed solute molecules on the surface is N', that of the bare sites is $1-N'$. The rate of adsorption, v_1, is therefore given by

$$v_1 = k_1 N (1 - N'),\qquad (1)$$

where k_1 is a specific rate constant for the process; its value can, in principle, be calculated using the theory of absolute reaction rates,[2] although the procedure would be difficult for a liquid system. The process of desorption can be regarded as a unimolecular dissociation; since the mole fraction of the adsorbed molecules is N', the rate of the process is

$$v_{-1} = k_{-1} N',\qquad (2)$$

where k_{-1} is the specific rate constant for desorption.

The rate, v_2, of the diffusion into the solid is obtained by integrating the diffusion equation

$$(\partial N / \partial t)_x = D_N (\partial^2 N / \partial x^2)_t,\qquad (3)$$

subject to the correct boundary conditions. Explicit

solutions are not required for the present purposes, but have been collected by R. M. Barrer[4] who uses the concentration law. It is sufficient to note here that the rate of disappearance from the surface by the process of diffusion is proportional to the first power of the mole fraction of the solute molecules, i.e.,

$$v_2 = k_2 N',\qquad (4)$$

where k_2 is a function of the diffusion coefficient D.

The rate of entry into the solid will be much greater than the rate of change of concentration of adsorbed molecules, so that steady-state conditions may be assumed, i.e.,

$$k_1 N (1 - N') - k_{-1} N' - k_2 N' = 0.\qquad (5)$$

This gives

$$N' = k_1 N / (k_1 N + k_{-1} + k_2),\qquad (6)$$

so that the rate of entry into the solid, $k_2 N'$, is

$$v = k_1 k_2 N / (k_1 N + k_{-1} + k_2).\qquad (7)$$

An equation of similar form, involving concentrations instead of mole fractions, has been shown[5] to account for the rate of uptake of gases by surfaces into which penetration will occur.

Two special cases of Eq. (7) are of interest:

Case I—If $k_1 N \gg k_{-1} + k_2$, the rate is given approximately by

$$v = k_2,\qquad (8)$$

which means that the diffusion in the solid is rate controlling; the adsorption rate is sufficiently rapid to maintain a fully covered surface, so that the rate of uptake is independent of the composition of the liquid phase. For gas-solid systems this type of law is usually obeyed in corrosion processes.

Case II—If $k_{-1} + k_2 \gg k_1 N$, the rate is given by

$$v = (k_1 k_2 / k_{-1} + k_2) N,\qquad (9)$$

i.e., it is now proportional to the first power of the mole fraction. In this case the rate of entry is in general determined by the three specific rate constants k_1, k_{-1}, and k_2. If, in addition, $k_{-1} \gg k_2$, the rate is given by

$$v = (k_1 / k_{-1}) k_2 N,\qquad (10)$$

so that the rate is determined by the diffusion rate and the adsorption equilibrium constant k_1 / k_{-1}. If on the other hand $k_2 \gg k_{-1}$ the rate is given by

$$v = k_1 N,\qquad (11)$$

and the rate of adsorption controls the over-all rate. In gas-solid systems this linear rate of uptake is obeyed for example in the uptake of hydrogen gas by palladium.

[2] Laidler, Glasstone, and Eyring, J. Chem. Phys. **8**, 659 (1940); Glasstone, Laidler, and Eyring, *The Theory of Rate Processes* (McGraw-Hill Book Company, Inc., New York, 1941) Chapter VII.

[3] G. Scatchard, J. Chem. Phys. **7**, 657 (1939).

[4] R. M. Barrer, *Diffusion in and through Solids* (Cambridge University Press, London, 1941), Chapter I.

[5] K. J. Laidler, J. Phys. Colloid Chem. **53**, 712 (1949); K. J. Laidler, *Symposium on Reactions in the Solid State* (Paris, 1948).

STEADY FLOW THROUGH MEMBRANES

When two solutions, which may be designated α and β, are separated by a membrane which is initially free of the solute, the solute molecules enter the membrane at both interfaces, the rates of uptake obeying the law represented by Eq. (7) or one of its special cases. Under these circumstances the concentration of solute builds up within the membrane and there is at first no steady state, except (to a good approximation) at the two interfaces. After a certain time, however, a steady state is established at all points within the membrane, and there is a net flow of solute from the more concentrated to the more dilute solution. For a steady state it follows that $(\partial N/\partial t)_x = 0$ at all points on the membrane, so that according to Eq. (3)

$$(\partial^2 N/\partial x^2)_t = 0 \tag{12}$$

or

$$(\partial N/\partial x)_t = \text{const.}, \tag{13}$$

i.e., the mole fraction gradient is a constant. If the mole fraction in the membrane at the interface with solution α be denoted N'^α and that at solution β as N'^β, as represented in Fig. 1, the mole fraction gradient within the membrane is given by

$$(\partial N/\partial x)_t = (N'^\beta - N'^\alpha)/d', \tag{14}$$

where d' is the thickness of the membrane. The integrated form of Eq. (3) is[1]

$$dn^\beta/dt = -D_N A c_t (dN/dx), \tag{15}$$

where dn^β is the number of moles passing from α into β through a cross-sectional area A in time dt, and c_t is the total concentration of all species present, which is essentially constant. The net rate of flow through the membrane is therefore

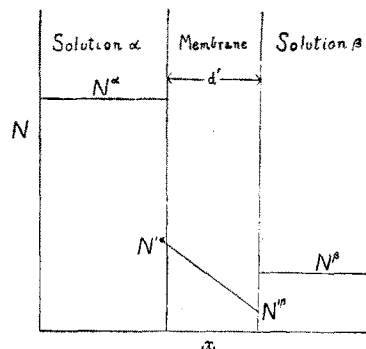$$dn^\beta/dt = -D_N A c_t (N'^\beta - N'^\alpha)/d', \tag{16}$$

FIG. 1. The variation of the mole fraction of a species in two solutions α and β separated by a membrane. The species is less soluble in the membrane than in the solvent ($k_1/k_{-1} < 1$), and the mole fraction gradient within the membrane is $(N'^\alpha - N'^\beta)/d'$ which is less than $(N^\alpha - N^\beta)/d'$, the reduction factor being k_1/k_{-1}.

in which N'^β and N'^α have still to be expressed in terms of the mole fractions in the two solutions, N^β and N^α. Equation (16) may be written in the form

$$dn^\beta/dt = -k_2(N'^\beta - N'^\alpha), \tag{17}$$

where k_2 is equal to $D_N A c_t/d'$.

The rate of flow may be expressed in terms of the mole fractions N^α and N^β by obtaining the steady-state expression at the two interfaces. At the interface α the rates of adsorption, desorption, and diffusion are

$$v_1 = k_1 N^\alpha (1 - N'^\alpha), \tag{18}$$

$$v_{-1} = k_{-1} N'^\alpha, \tag{19}$$

$$v_2 = -k_2(N'^\beta - N'^\alpha), \tag{20}$$

and the steady-state expression is therefore

$$k_1 N^\alpha (1 - N'^\alpha) - k_{-1} N'^\alpha + k_2(N'^\beta - N'^\alpha) = 0. \tag{21}$$

Similarly, at interface β the expression is

$$k_1 N^\beta (1 - N'^\beta) - k_{-1} N'^\beta - k_2(N'^\beta - N'^\alpha) = 0. \tag{22}$$

Solution of these two simultaneous equations gives

$$N'^\beta - N'^\alpha = \frac{N^\beta - N^\alpha}{(2k_2 + k_{-1})/k_1 + [(k_2/k_{-1}) + 1](N^\beta + N^\alpha) + (k_1/k_{-1})N^\alpha N^\beta}. \tag{23}$$

In the case that $k_2 \ll k_{-1} \gg k_1$, i.e., the rates of diffusion in the membrane and of adsorption are small compared with the rate of desorption, Eq. (23) reduces to

$$N'^\beta - N'^\alpha = (k_1/k_{-1})(N^\beta - N^\alpha), \tag{24}$$

and the rate of flow from α to β is given by

$$dn^\beta/dt = k_1 k_2/k_{-1}(N^\alpha - N^\beta). \tag{25}$$

The rate is therefore proportional to the difference between the mole fractions in the two solutions, and examination of Eq. (23) shows that this result will only arise if $k_2 \ll k_{-1} \gg k_1$. Since the ratio k_1/k_{-1} is the equi-

librium constant for the adsorption process, Eq. (25) corresponds to the slow step being diffusion through the membrane; this can therefore be inferred if the results show that the rate of flow is proportional to $N^\alpha - N^\beta$. It is to be noted that the ratio k_1/k_{-1} is required by the above conditions to be small; the distribution coefficient of the diffusing species between the membrane and the solution must therefore be small for the above result to be obtained.

Equation (25) may be written as

$$\frac{dn^\beta}{dt} = \frac{k_1}{k_{-1}} \frac{D_N A c_t}{d'} (N^\alpha - N^\beta), \tag{26}$$

which it is convenient to write as

$$dn^\beta/dt = (QAc_t/d')(N^\alpha - N^\beta), \quad (27)$$

where Q, equal to $(k_1/k_{-1}) D_N$, may be called the permeation coefficient of the species with respect to the membrane; it is seen to have the dimensions L^2T^{-1} (like the Fick's law diffusion coefficient), and will be expressed in the units cm^2 sec.$^{-1}$. For a non-ideal solution the rate of flow is

$$dn^\beta/dt = (QAc_t/d')(N^\alpha f^\alpha - N^\beta f^\beta). \quad (28)$$

The permeation constant Q defined above differs from the permeability constant P used by Barrer;[4] Q is the product of the diffusion coefficient and the ratio of the concentrations, i.e., solubilities, in the membrane and in the solvent, while P is the product of the diffusion coefficient and the solubility of the diffusing species in the membrane. Whereas Q has the same dimensions as D, P involves the concentration; the use of Q thus has a distinct advantage in comparing permeation with free diffusion.

Rates of Flow of Solvent and Solute: Influence of Pressure

Expressions will now be deduced for the rates of flow of solvent and solute molecules through a membrane separating two solutions. The solutions are designated α and β, the solvent and solute 1 and 2 respectively, and the permeation constants of solvent and solute as Q_1 and Q_2 respectively. The influence of hydrostatic pressure on the rates of flow will be taken into account, and it will be supposed that the hydrostatic pressure on solution β exceeds that on solution α by an amount P.

The hydrostatic pressure influences the rates by modifying the activities of the species in solution β. The change in partial vapor pressure (dp_i) of a species i brought about by the imposition of the hydrostatic pressure dP is[6]

$$dp_i/p_i = (\bar{V}_i/RT) \cdot dP \quad (29)$$

where $\bar{V}_i$ is the molar volume of the species i; this integrates to

$$p_i = p_i^0 \exp(P\bar{V}_i/RT) \quad (30)$$

where p_i^0 is the partial vapor pressure corresponding to zero hydrostatic pressure (relative to atmospheric). The activity coefficient at pressure P of a component which at zero pressure has an activity coefficient of f_i^0 is therefore $f_i^0 \exp(P\bar{V}_i/RT)$, and the activity is $N_i f_i^0 \exp(P\bar{V}_i/RT)$. The activity of the solvent in solution β is therefore $N_1 f_1^0 \exp(P\bar{V}_1/RT)$, and that of the solute is $N_2 f_2^0 \exp(P\bar{V}_2/RT)$, where f_1^0 and f_2^0 are the activity coefficients at atmospheric pressure.

The activity differences $N^\beta f^\beta - N^\alpha f^\alpha$ may now be written down; for the solvent we have

$$N_1^\beta f_1^\beta - N_1^\alpha f_1^\alpha = N_1^\beta f_1^{0\beta} \exp(P\bar{V}_1/RT) - N_1^\alpha f_1^{0\alpha} \quad (31)$$

and for the solute

$$N_2^\beta f_2^\beta - N_2^\alpha f_2^\alpha = N_2^\beta f_2^{0\beta} \exp(P\bar{V}_2/RT) - N_2^\alpha f_2^{0\alpha}. \quad (32)$$

According to Eq. (28) the rates of flow from α to β are thus: For the solvent

$$dn_1^\beta/dt = (Q_1 Ac_t/d')\{N_1^\alpha f_1^{0\alpha} - N_1^\beta f_1^{0\beta} \exp(P\bar{V}_1/RT)\}; \quad (33)$$

and for the solute

$$dn_2^\beta/dt = (Q_2 Ac_t/d')\{N_2^\alpha f_2^{0\alpha} - N_2^\beta f_2^{0\beta} \exp(P\bar{V}_2/RT)\}. \quad (34)$$

The Osmotic Pressure

Since it is convenient to express the rates of flow as functions of the osmotic pressures π^α and π^β of the two solutions, equations for these quantities will be derived. The pressure π^β is the pressure developed at equilibrium when α is pure solvent $(N_1^\alpha f_1^{0\alpha} = 1)$ and when there is no diffusion of the solute, i.e., when $Q_2 = 0$, so that $dn_2^\beta/dt = 0$. The condition for equilibrium is defined by $dn_1^\beta/dt = 0$, from which, using Eq. (33), it follows that

$$1 - N_1^\beta f_1^{0\beta} \exp(\pi^\beta \bar{V}_1/RT) = 0 \quad (35)$$

since $(Q_1 Ac_t/d') \neq 0$; this rearranges to

$$\pi^\beta = (RT/\bar{V}_1) \ln(1/N_1^\beta f_1^{0\beta}) \quad (36)$$

which is the exact thermodynamic relationship between osmotic pressure and mole fraction.[7] At low concentrations for which $f_1^{0\beta} = 1$ it becomes[1] $\pi^\beta V_1 = n_2^\beta RT$ (Morse's equation) where V_1 is the total volume of solvent associated with n_2^β moles of solute. Similarly the osmotic pressure of solution α is given by

$$\pi^\alpha = (RT/\bar{V}_1) \ln(1/N_1^\alpha f_1^{0\alpha}). \quad (37)$$

Equations analogous to (36) and (37) could also be written down for the solute, the osmotic pressure now being that which would be developed if the membrane were impermeable to the solvent and permeable to the solute, the distinction between solute and solvent being completely arbitrary. Such equations will not, however, be used here since it is more convenient to relate the mole fraction of the solute molecules to the osmotic pressures of Eqs. (36) and (37); this will be done in deriving the rate of flow of the solute molecules.

Rate of Flow as Functions of Osmotic and Hydrostatic Pressures

The rates of flow will now be expressed in terms of osmotic pressures instead of in mole fractions as in

[6] Cf. E. A. Guggenheim, *Modern Thermodynamics by the Methods of Willard Gibbs* (Methuen and Company, Ltd., London, 1933), p. 63.

[7] F. G. Donnan and E. A. Guggenheim, Zeits. f. physik. Chemie **A162**, 346 (1932).

Eqs. (33) and (34). From Eq. (37) it follows that

$$N_1{}^\alpha f_1{}^{0\alpha} = \exp(-\pi^\alpha \bar{V}_1/RT), \qquad (38)$$

and from Eq. (36) that

$$N_1{}^\beta f_1{}^{0\beta} = \exp(-\pi^\beta \bar{V}_1/RT). \qquad (39)$$

Substitution of these expressions into Eq. (33) gives, for the net rate of flow of the solvent from α to β,

$$dn_1{}^\beta/dt = (Q_1 A c_t/d')\{\exp(-\pi^\alpha \bar{V}_1/RT) - \exp((P-\pi^\beta)\bar{V}_1/RT)\}. \qquad (40)$$

If the solutions are sufficiently dilute so that $\pi^\alpha \bar{V}_1/RT \ll 1$ and $(\pi^\beta - P)\bar{V}_1/RT \ll 1$ the exponentials can be expanded with the neglect of terms beyond the first; the error introduced by expanding the exponentials and taking the first term only is very slight for all solutions in which one would be interested. Even for a three-normal $(3N)$ sucrose solution in water, the error is only 0.5 percent. Expansion of the exponentials then gives

$$dn_1{}^\beta/dt = (Q_1 A c_t/d')(\bar{V}_1/RT)(\pi^\beta - \pi^\alpha - P). \qquad (41)$$

This may be written as

$$dn_1{}^\beta/dt = (Q_1 A c_t \bar{V}_1/d'RT)(\pi - P), \qquad (42)$$

where $\pi = \pi^\beta - \pi^\alpha$ is the difference between the osmotic pressures of the two solutions. Apart from the restriction, introduced by the inequalities, that the solutions be fairly dilute, this rate equation is exact and does not require that the solution be ideal.

A similar treatment for the rate of flow of solute leads to expressions of great complexity; to simplify the treatment the assumption will be made that the solution is sufficiently dilute so as to be ideal. Then, the rate of flow in terms of mole fractions will be (cf. Eq. (34))

$$dn_2{}^\beta/dt = (Q_2 A c_t/d')\{N_2{}^\alpha - N_2{}^\beta \exp(P\bar{V}_2/RT)\}. \qquad (43)$$

The mole fraction $N_2{}^\alpha$ is given by

$$N_2{}^\alpha = 1 - N_1{}^\alpha = 1 - \exp(-\pi^\alpha \bar{V}_1/RT), \qquad (44)$$

using Eq. (38), and similarly, using Eq. (39)

$$N_2{}^\beta = 1 - \exp(-\pi^\beta \bar{V}_1/RT). \qquad (45)$$

The rate of flow is, therefore,

$$\frac{dn_2{}^\beta}{dt} = \frac{Q_2 A c_t}{d'}\{1 - \exp(-\pi^\alpha \bar{V}_1/RT) - (1 - \exp(-\pi^\beta \bar{V}_1/RT)\exp(P\bar{V}_2/RT)\}. \qquad (46)$$

Expansion of these exponentials gives

$$\frac{dn_2{}^\beta}{dt} = \frac{Q_2 A c_t}{d'}\left\{\frac{\pi^\alpha \bar{V}_1}{RT} - \frac{\pi^\beta \bar{V}_1}{RT}\left(1 + \frac{P\bar{V}_2}{RT}\right)\right\} \qquad (47)$$

$$\frac{dn_2{}^\beta}{dt} = \frac{Q_2 A c_t \bar{V}_1}{d'RT}(\pi^\alpha - \pi^\beta) \qquad (48)$$

$$\frac{dn_2{}^\beta}{dt} = -\frac{Q_2 A c_t \bar{V}_1}{d'RT}\pi. \qquad (49)$$

In going from Eq. (47) to Eq. (48), the small term $\pi^\beta P\bar{V}_1\bar{V}_2/(RT)^2$ has been neglected. This approximation introduces only a very small error in the usual type of membrane experiments with fairly dilute solutions in which the hydrostatic pressure P is only a few hundred mm of solution; thus for a rise of 500 mm occurring with a sucrose solution, $1 + P\bar{V}_2/RT$ differs from unity by only 0.04 percent. In Eq. (41), however, P must not be neglected since it may be of comparable magnitude with π, however small it may be. It is to be noted that according to Eq. (49) the hydrostatic pressure P does not influence the rate of flow of the solute in a dilute solution.

Equations similar to (42) and (49), but without explicit coefficients, were proposed in 1911 by A. von Antropoff[8] on intuitive grounds. The application of our equations to osmotic experiments with membranes permeable to both solvent and solute will be considered in subsequent papers..

[8] A. von Antropoff, Zeits. f. physik. Chemie 76, 721 (1911).