Transport of Ions against Their Concentration Gradient across Cation-Exchange Membranes with Very Small Mechanical Permeabilities

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Abstract: In two sets of experiments the transport of potassium ions and of potassium and lithium ions against their concentration difference between two solutions across a cation-exchange membrane is being investigated. The driving forces of the ion transport are a concentration gradient and an electric potential gradient within the membrane separating these solutions. The membrane has a small mechanical permeability so that the contribution of convection to the ion transport can be neglected. In the stationary state of the system, an increase of the concentration of potassium or potassium and lithium ions up to a factor of 4 above the concentration of these ions in the initial state is observed in one outside solution of the membrane. In the initial state the concentrations of the alkali ions are the same in both outside solutions. During the simultaneous transport of potassium and lithium ions, there is a certain period of time between the initial and the stationary state of the system in which a partial separation of potassium and lithium ions is observed. The experimental results are discussed in terms of the equation of ion transport across membranes with narrow pores.

It is the aim of this study to investigate the transport of ions against their concentration difference between two solutions across a cation-exchange membrane separating these solutions under the simultaneous influence of a concentration gradient and a potential gradient (diffusion potential) within the membrane. We have chosen highly cross-linked membranes with small mechanical permeabilities for our investigation in order to keep the contribution of convection to the ion transport negligibly small. The ions are transported against their concentration difference between the outside solutions, but they move in the direction of their electrochemical potential difference. It is a "passive" transport not influenced by chemical reactions. The first quantitative investigations in this field have been carried out by Teorell.[1,2] Later Neihof and Sollner[3] studied transitional accumulations of electrolytes in one of the two outside solutions of cation- and anion-exchange membranes. Recently a number of papers concerning this subject have been published.[4] These investigations are directed toward the contribution of convection to the ion transport in nonisobaric systems. In connection with our studies of the influence of different driving forces on the transport of ions across porous membranes in isothermal–isobaric systems, we again have taken up Teorell's investigations.[5]

I. Description of the Transport Mechanism

We consider an isothermal–isobaric system in which two electrolyte solutions are separated by a cation-exchange membrane with strong acid groups. The experimental arrangement is shown schematically in Figure 1. The electrolyte concentrations in the outer compartments, and the concentration, potential, and pressure profiles inside the membrane can be seen in Figure 2. In order to simplify the picture, the profiles are assumed to be linear. We are interested in the transport of potassium ions against their concentration difference between the outside solutions. In the beginning of the experiment, the concentration of this ion species is the same in both compartments. We have chosen a value of 0.1 N. The electrical potential gradient and the concentration gradient of potassium inside the membrane—the driving forces of the transport of this ion—are generated by a concentration difference of a second electrolyte between the outside solutions. As the second electrolyte we have chosen hydrochloric acid. The acid concentration in the right cell compartment is 0.1 N and in the left compartment 2×10^{-2} N. During the experiment the acid concentrations in the two outside solutions and the concentration of the potassium chloride in the left compartment are kept constant. This is accomplished by adding slowly a concentrated solution of hydrochloric acid ($c_{\mathrm{HCl}}{}^{\mathrm{add}} = 5.06$ N) to the right compartment and by continuously renewing the solution in the left compartment. The addition of the concentrated acid solution is carried out with the aid of an automatic titrator (Radiometer PH 25 SE in connection with T 11).

At least phase boundaries (membrane–solution), there exist jumps of the concentrations of the mobile ions (hydrogen, potassium, and chloride), jumps of the electric potential, and jumps of the hydrostatic pressure caused by the electric charged groups of the membrane matrix. In case of a cation-exchange membrane, these charges ("fixed charges") have a negative sign and are electrically compensated by an equivalent number of mobile cations (counterions). At the left membrane boundary the counterions are almost exclusively potassium ions because the adjacent external solution contains practically only potassium chloride, but at the right phase boundary the counterions are hydrogen and potassium ions. Although the concentration of these ions in the right outside solution at first are equal, this is not necessarily the case within the membrane at the right boundary due to the selectivity of the cation-ex-

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(1) (a) T. Teorell, *Proc. Natl. Acad. Sci. U. S.*, 21, 152 (1935); (b) *J. Gen. Physiol.*, 21, 107 (1937).

(2) T. Teorell, *Progr. Biophys. Biophys. Chem.*, 3, 305 (1953).

(3) R. Neihof and K. Sollner, *J. Phys. Chem.*, 61, 159 (1957).

(4) L. F. Nims and R. E. Thurber, *Am. J. Physiol.*, 201, 995 (1961); S. Salminen, *Nature*, 200, 1069 (1963).

(5) D. Woermann and M. Spei, *Ber. Bunsenges. Physik. Chem.*, 68, 449 (1964).

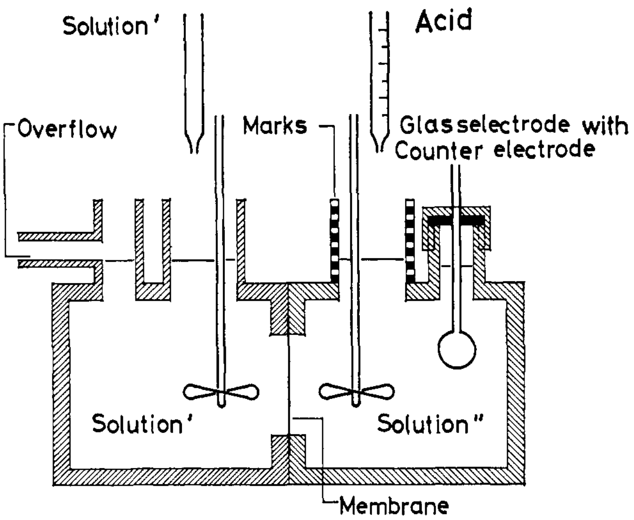

Figure 1. Experimental arrangement (schematically): solution'', 100 cm^3; membrane area, 12.5 cm^2.

change material. Ion-exchange resins usually exhibit a preference for the counterion species with the smaller volume in the hydrated state. Accordingly, the membrane shows a selectivity for potassium ions with respect to hydrogen ions.

As a consequence of this distribution of potassium and hydrogens ions at the two membrane–solution interfaces, concentration gradients for both ion species are formed inside the membrane (Figure 2), and an interdiffusion of these ions takes place. The concentration gradient of the potassium ions is directed from left to right. That of the hydrogen ions has the opposite direction. Because of the higher mobility of the hydrogen ions compared with the mobility of the potassium and chloride ions inside the membrane, a potential gradient (diffusion potential) is developed. The potential of the left inside of the membrane is positive wih respect to the potential of the right inside.

The potential gradient and the concentration gradient of the potassium ions within the membrane have the same direction in the beginning of the experiment. Under the influence of these two driving forces a transport of potassium ions from the left to the right outside solution takes place. The increase of the concentration of potassium (or potassium chloride) in the right cell compartment which can be observed as a function of time comes finally to a standstill ($dc_K''/dt = 0$). The system reaches a steady state characterized by the vanishing of the time derivative of all intensive state functions of the system (concentration of all mobile ions, pressure, and temperature). The time necessary to reach the stationary state depends on the ratio of membrane area to volume of the right cell compartment. In the stationary state the molar flux of the potassium ions across the membrane is close to zero ($\phi_K = 0$) because the volume of the right outside solution is almost constant (for details see section IIIb).

The jumps of the hydrostatic pressure at least-phase boundaries (membrane–solution) can be interpreted as an osmotic pressure caused by the concentration difference of the osmotically active mobile ions between the liquid medium within the pores and the outside solutions. If the concentrations of the mobile ions inside the membrane (at the interfaces) and in the outside solutions are known, the pressure jumps can be calculated by van't Hoff's equation.[6]

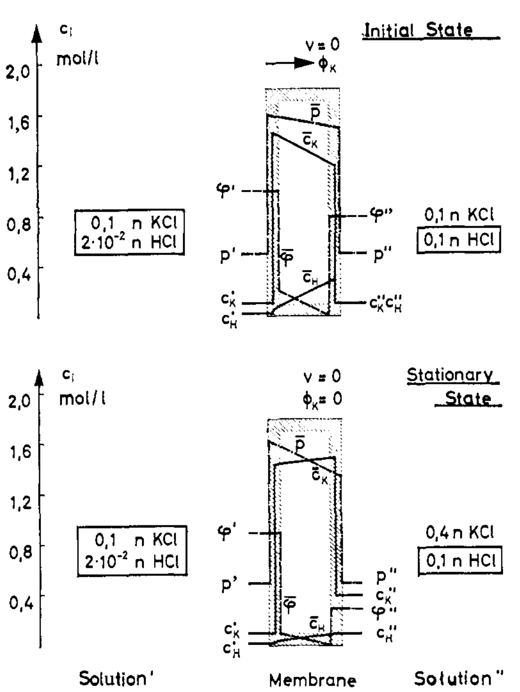

Figure 2. Concentration of the outside solutions and the linear concentration, potential (φ), and pressure (P) profiles within the membrane (schematically). The framed concentration values are kept constant during the experiment: $\bar{c}_i$ = mol l^{-1} membrane phase (membrane, Permaplex C20).

The liquid medium within the pores is always under the higher hydrostatic pressure compared with that of the outside solutions. Under our experimental conditions the pressure jump at the right-phase boundary (membrane–solution) is smaller than that at the left because of the higher electrolyte concentration in the right cell compartment. Consequently, a pressure gradient is formed within the membrane. This pressure gradient together with the diffusion potential act as driving forces for a volume flow across the membrane, but the mechanical permeability of the membrane used in this investigation is so small that no appreciable volume flow is observed.

II. Theoretical Section

The flux of ion species i across a membrane with narrow pores and vanishing small mechanical permeability (convective volume flow $v = 0$) is expressed by[7]

$$\Phi_i = -D_i(dC_i/dx + z_iC_i d\bar{\psi}/dx + C_i d \ln \bar{y}_i/dx) \quad (1)$$

$$\bar{\psi} = F/RT\bar{\varphi}$$

Φ_i = molar flux density of ion species i (mol cm^{-2} sec^{-1}); C_i = molar volume concentration of ion species i, relative to the volume unit of the solution inside the pores (mol cm^{-3}); D_i = effective diffusion coefficient of ion species i within the membrane (cm^2 sec^{-1}); x = coordinate of position (the x axis runs perpendicular to the phase boundaries of the membrane; the left

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[6] R. Schlögl, *Z. Physik. Chem.* (Frankfurt), 3, 73 (1955).

[7] R. Schlögl, "Stofftransport durch Membranen," Steinkopff-Verlag, Darmstadt, 1964.

boundary has the coordinate $x = 0$ and the right boundary $x = \delta$ where δ = thickness of the membrane); z_i = valency of ion species i including the sign; $\bar{\varphi}$ = electrical potential within the membrane; $\bar{y}_i$ = practical activity coefficient of ion species i within the membrane. F = Faraday number = 96,487 A sec mol^{-1}; R = gas constant = 8314 J grad^{-1} mol^{-1}; T = absolute temperature; $RT/F = 0.025$ V at room temperature.

The main assumptions for the validity of eq 1 are (1) the concentrations of all components of the medium within the pores are only functions of the coordinate of position x; (2) the medium within the pores and the outside solutions are considered as being dilute; (3) the exchange of momentum between the dissolved components is neglected. But the exchange of momentum between the dissolved components and the matrix to the membrane is taken into account. This effect is included in the effective diffusion coefficient D_i.

The flux of ion species i across the membrane vanishes if the driving forces (electrical field of the diffusion potential and gradient of the activity) acting on this ion species are in equilibrium. The flux of the other ion species for which there is no equilibrium of the driving forces is different from zero. The integration of eq 1, taking into account the boundary conditions

$$x = 0,\ A_i = A_i';\ x = \delta,\ A_i = A_i''$$

yields

$$z_i \Delta\bar{\psi} = \ln A_i''/A_i' \qquad (2)$$

with $A_i = \bar{y}_i C_i$ and $\Delta\bar{\psi} = \bar{\psi}' - \bar{\psi}''$. The activity of ion species i within the membrane A_i is related to the activity of the same ion species in the outside solution a_i by the Donnan equation

$$A_i = a_i \exp(-z_i \delta\psi) \qquad (3)$$

$\delta\psi = \bar{\psi} - \psi$ is the potential jump at the phase boundary membrane–solution (Donnan potential), expressed in units of RT/F. Inserting eq 3 into eq 2 one obtains

$$\Delta\psi = 1/z_i \ln (a_i''/a_i')_{\text{stat}} \qquad (4)$$

with $\Delta\psi = \psi' - \psi'' = \Delta\bar{\psi} + \delta\psi'' - \delta\psi'$. This expression, which has already been derived by Teorell[1,2] for the "diffusion effect," gives the relationship between the ratio of the activities of ion species i in the outside solution $(a_i''/a_i')_{\text{stat}}$ and the membrane potential $\Delta\psi$ in the stationary state provided the flux of this ion species across the membrane vanishes. Equation 4 can be checked experimentally if the activity of the single ions is replaced by the mean activity of the salt. It must further be assumed that the membrane potential can be identified with the potential difference between the two outside solutions measured with calomel electrodes. The calomel electrodes must make contact with the outer solutions through concentrated KCl bridges.

Let us now turn to a situation in which two cation species, for example, potassium and lithium, are transported simultaneously across a cation-exchange membrane. We will observe changes of the concentration ratio of both ion species in the outer solutions (separation effect) if the chemical flux densities χ_i of the ions to be separated differ. The chemical flux density χ_i of the ion species i in the right cell compartment is defined by

$$\chi_i'' = \frac{V''}{A} \frac{dc_i''}{c_i'' dt} \qquad (5)$$

The relation between the chemical flux density χ_i and the molar flux density ϕ_i follows from eq 10 (below) and 5 is given by

$$\chi_i'' = \frac{\phi_i}{c_i''} - v'' \qquad (6)$$

In order to obtain a general expression for the molar flux ratio of the two cation species across a membrane with vanishing small mechanical permeability for the "stationary case" (div $\phi_i = 0$), we integrate (1) with simplifying assumptions.[8] Assuming that the potential gradient within the membrane is approximately linear ($d\bar{\psi}/dx = \Delta\bar{\psi}/\delta$) and assuming further that the activity coefficient and the effective diffusion coefficient of the ions within the membrane and fixed ion concentration are constant, the integration yields the following expression for the flux ratio of potassium to lithium ions

$$\frac{\phi_K}{\phi_{Li}} = \frac{D_K[C_K' - C_K'' \exp(-z_i\Delta\bar{\psi})]}{D_{Li}[C_{Li}' - C_{Li}'' \exp(-z_i\Delta\bar{\psi})]} \qquad (7)$$

(With the last-mentioned group of assumptions, the potential gradient within the membrane is constant if the membrane contains only counterions of the same valency and no co-ions.)

Turning now to the stationary state, we see that according to eq 4 the activity ratio of lithium to potassium ions will be given by eq 8 provided the molar flux of both ion species across the membrane vanishes.

$$(a_{Li}''/a_{Li}')_{\text{stat}} = (a_K''/a_K')_{\text{stat}} \qquad (8)$$

III. Transport of Potassium Ions

a. **Results.** The experiments are carried out with a cation-exchange membrane Permaplex C20 (Permutit Comp. Ltd. London). It consists of a thermoplast in which powder of polystyrene–divinylbenzenesulfonate is imbedded.

Table I contains the main characteristics of the membrane.

Table I

Thickness, cm	5.5×10^{-2}
Density, cm^3 g^{-1}	1.14
Concn of fixed ions, mol cm^{-3}	5.0×10^{-3} (inside the pores)
Water content, wt %	36.0

The experimental results are compiled in Table II. The values in Tables I and II are obtained by standard techniques.[9] The second column of Table II refers to the composition of the solutions in the left and the right cell compartments at the beginning of the experiment. The concentration of the electrolytes which are kept constant during the experiment are noted with an asterisk. Column 3 contains the experimentally determined concentration ratio of the potassium ions in the outside solutions in the stationary state, which is attained in our experimental arrangement after about 4 days (V'' = 100 cm^3, membrane area = 12.5 cm^2). The ratio of the mean activities of potassium chloride in the stationary state is listed in column 4. These values are calculated taking into account the influence of the

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[8] R. Schlögl, *Ber. Bunsenges. Physik. Chem.*, 70, 400 (1966).

[9] F. Helfferich, "Ionenaustauscher," Verlag Chemie, Weinheim (Bergstrasse), 1959.

Table II

1 Membrane	2 Concn of the outside solutions in the beginning of the expt[a] Left cell	 Right cell	3 $[c_K''/c_K']_{stat}$	4 $[a_\pm''/a_\pm']_{stat}$	5[b] $(\Delta\varphi)_{init}$ $((\Delta\varphi)_{stat})$, mV	6 v_{stat}, cm sec^{-1}	7 $[v_{HCl}{}^{add}]_{stat}$, cm sec^{-1}
Permaplex C20	0.1 *N* KCl* 2×10^{-2} *N* HCl*	0.1 *N* KCl 0.1 *N* HCl*	4.0	3.5	22 (32)	2.2×10^{-6}	1.4×10^{-6}
Permaplex C20	0.1 *N* KCl* 4×10^{-2} *N* HCl*	0.1 *N* KCl 0.1 *N* HCl*	2.8	2.6	16 (24)	2.0×10^{-6}	0.82×10^{-6}
Permaplex C20	0.1 *N* KCl* 6×10^{-2} *N* HCl*	0.1 *N* KCl 0.1 *N* HCl*	1.9	1.8	11 (15)	1.3×10^{-6}	0.46×10^{-6}
Phenolsulfonic acid membrane, strongly cross-linked	0.1 *N* KCl* 4×10^{-2} *N* HCl*	0.1 *N* KCl 0.1 *N* HCl*	3.3	3.0	19 (28)	...	...
Permaplex C20	5×10^{-2} *N* LiCl* 5×10^{-2} *N* KCl* 2×10^{-2} *N* HCl*	5×10^{-2} *N* LiCl 5×10^{-2} *N* KCl 0.1 *N* HCl*	Li: 3.8 K: 3.8	LiCl: 3.46 KCl: 3.3	31 (stat)	2.6×10^{-6}	1.1×10^{-6}

[a] An asterisk denotes concentration kept constant. [b] Calomel electrode.

hydrochloric acid on the activity of potassium chloride.[10] The fifth column includes the potential difference between the outside solutions measured with calomel electrodes at the beginning of the experiment and in the stationary state. The increase of the membrane potential is first of all due to the decrease of the absolute value of the Donnan potential at the right phase boundary of the membrane. With increasing potassium concentration in the right outside solution, the ratio A_i''/a_i'' (i = K, H) determining the Donnan potential (see eq 3) decreases. At the same time the absolute value of the diffusion potential also decreases. Both potential changes influence the membrane potential in different directions.

The volume of the right outside solution increases continuously during the experiment. Two quantities contribute to this increase

$$v'' = v_{HCl}{}^{add} + v$$

with $v'' = (1/A)\mathrm{d}V''/\mathrm{d}t$ and

$$v_{HCl}{}^{add} = (1/A)\mathrm{d}V''_{HCl}{}^{add}/\mathrm{d}t$$

where A = membrane area, V'' = volume of the right outside solution, v = convective volume flow density across the membrane, and $v_{HCl}{}^{add}$ = volume flow density of the solution of hydrochloric acid added to the right outside solution. In order to keep constant the concentration of the hydrogen ions in the right cell compartment it is necessary to add continuously a certain volume of concentrated solution of hydrochloric acid. This contribution to the volume increase is represented by the term $v_{HCl}{}^{add}$. Values of $v_{HCl}{}^{add}$ in the stationary state are compiled in the column 7 of Table II. Furthermore, the volume of the right outside solution increases because of a small convective volume flow across the membrane. The driving forces of this volume flow are the electric field of the diffusion potential and the hydrostatic pressure gradient inside the membrane.[7] (Both forces are directed from left to right.) The mechanical permeability of the Permaplex C20 membrane is not small enough to suppress this volume flow completely. Values of v in the stationary state are listed in column 6 of Table II. It can be estimated that the contribution of the electric field of the diffusion potential to this convective volume flow is larger than that of the hydrostatic pressure gradient ($\Delta\bar{\varphi} = 1$ mV corresponds to $\Delta\bar{P} = 10$ atm for a fixed ion concentration of 1 mol/l.).

Discussion. The experimental results now will be analyzed in terms of eq 9. This expression follows from eq 4 for the case of the transport of monovalent cations ($z_i = +1$, in our example potassium ions).

$$\Delta\varphi = 2303RT/F \log (a_\pm''/a_\pm')_{stat} \qquad (9)$$

The mean activities of the salt (potassium chloride) are substituted for the single ion activities. According to eq 9 a plot of the membrane potential against the logarithm of the activity ratio $(a_\pm''/a_\pm')_{stat}$ should give a straight line running through the origin and should have a slope of 58 mV per activity ratio $(a_\pm''/a_\pm')$ of 10 (T = 300°K). Figure 3 shows such a diagram. The theoretical curve is represented by the drawn line.

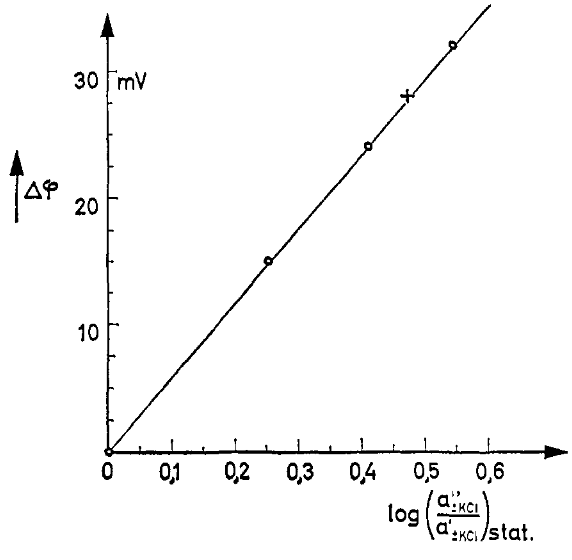

Figure 3. Membrane potential $\Delta\psi$ ($= \psi' - \psi''$) as a function of $\log (a_\pm''_{KCl}/a_\pm'_{KCl})$ stat: ○ Permaplex C20; +, phenolsulfonic acid membrane (strongly cross-linked).

The experimental data are taken from columns 4 and 5 of Table II. Equation 9 is valid only under the condition that the flux of the potassium ions across the membrane vanishes. This condition is not rigorously fulfilled in the stationary state, because there is a small but continuous volume increase of the right outside solution.

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(10) H. S. Harned, *J. Am. Chem. Soc.*, 57, 1865 (1935).

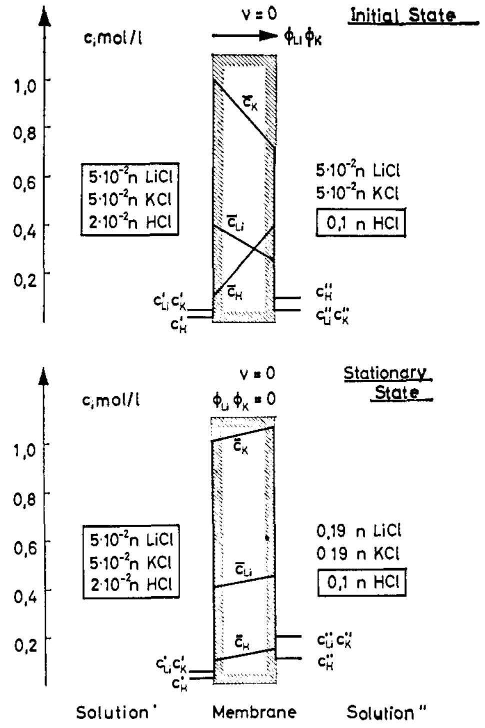

Figure 4. Concentrations of the outside solutions and the linear concentration profiles within the membrane (schematically). The framed concentration values are kept constant during the experiment: $\bar{c}_i$ = mol l^{-1} membrane phase (membrane, Permaplex C20).

The molar flux density of ion species i across the membrane is given by

$$\phi_i = \frac{1}{A}\frac{dn_i''}{dt} = \frac{1}{A}\frac{d(c_i''V'')}{dt} = \frac{V''}{A}\frac{dc_i''}{dt} + c_i''v'' \qquad (10)$$

In the stationary state the first term on the right-hand side of this equation vanishes ($dc_K''/dt = 0$), but the second term still gives a contribution. In the stationary state the volume increase is about $v_{stat}'' = 3 \times 10^{-6}$ cm sec^{-1}. This corresponds to a molar flux of potassium ions of about $(\phi_K)_{stat} = c_K''v_{stat}'' = 1 \times 10^{-9}$ mol cm^{-2} sec^{-1}.

A molar flux of this order of magnitude can still be regarded as a good approximation of $\phi_i = 0$ because we have found that our experimental results are well represented by eq 4 which was derived on condition of $\phi_i = 0$. The fourth line of Table II contains the experimental results obtained with a strongly cross-linked cation-exchange membrane prepared on the basis of phenolsulfonic acid and formaldehyde.[11] It will be noticed that the membrane potential of the phenolsulfonic acid membrane is larger than that of the Permaplex membrane with the same electrolyte concentrations in the outside solutions. Measurements of the equilibrium distribution of hydrogen and potassium ions on both membranes demonstrate that the selectivity constant of the phenolsulfonic acid membrane for hydrogen ions with respect to potassium ions $K_K{}^H$ is larger than that of the Permaplex membrane

$$K_K{}^H = \frac{C_H c_K}{C_K c_H} \sim \frac{\bar{y}_K}{\bar{y}_H}$$

when $y_H/y_K \approx 1$. For the phenolsulfonic acid membrane $K_K{}^H = 0.59$; for Permaplex, $K_K{}^H = 0.28$.

In our experimental situation the membrane potential is given by eq 11,[8,12] assuming that the membrane contains no co-ions (chloride ions) and that the activity coefficients and the mobility of the counterions within the membrane are constant.

$$\Delta\psi = \ln\frac{D_H a_H''\bar{y}_K/\bar{y}_H + D_K a_K''}{D_H a_H'\bar{y}_K/\bar{y}_H + D_K a_K'} \qquad (11)$$

According to this equation a higher selectivity for hydrogen ions should result in a higher value for the membrane potential. This prediction is confirmed by experiment.

IV. Transport of Potassium and Lithium Ions

a. **Results.** For our experiments we used the same experimental arrangement and technique as described in section I. The electrolyte concentrations in the two outside solutions and the concentration profiles within the membrane in the initial state and in the stationary state are shown in Figure 4. The potential and pressure profiles are not included. They do not differ appreciably from the profiles shown in Figure 2. The experimental results obtained by standard techniques are compiled in the last line of Table II.

b. **Discussion.** The experiments demonstrate that there is a certain period of time between the initial state and the stationary state of the system in which a separation of potassium and lithium ions ($\chi_K > \chi_{Li}$) is observed. The ratio c_K''/c_{Li}'' in the right outside compartment becomes bigger than that in the left compartment (c_K'/c_{Li}' = constant = 1).

In the beginning of the experiment the molar fluxes of both ion species are directed from left to right, and an increase of concentration of both ions is observed in the right cell compartment, but the flux of potassium ions is temporarily bigger than the flux of the lithium ions. This is caused by the transiently steeper concentration gradient and the higher mobility of the potassium ions within the membrane (see Figure 4 and eq 7). The membrane has a distinct selectivity for potassium ions with respect to lithium ions. This is in agreement with the common rule that a cation-exchange resin takes up preferably that cation species with the smaller volume in the hydrated state. The bigger molar flux of the potassium ions results in a bigger chemical flux of this ion species and causes the separation effect as long as the ratio Φ_K/c_K'' is bigger than the increase of the volume of the right cell compartment v'' (relative to the unit of membrane area). The value of the observed chemical flux ratio in the initial state is 2.4. In the stationary state the chemical flux of the lithium and potassium ions vanishes, but the chemical flux of the potassium ions becomes zero after a shorter period of time compared with that of the lithium ions because of the bigger molar flux of the potassium ions in the beginning of the experiment. The molar fluxes Φ_K and Φ_{Li} do not vanish completely in the stationary state because the volume of the right cell compartment increases continuously as already mentioned: $(\Phi_i)_{stat} = c_i v \sim 1 \times 10^{-9}$ mol cm^2 sec^{-1}. In section I we have seen that a value of Φ_i of this magnitude can be considered a good approximation

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(11) R. Schlögl and U. Schödel, *Z. Physik. Chem.* (Frankfurt), 5, 372 (1955).

(12) F. Helfferich and R. Schlögl, *Discussions Faraday Soc.*, 21, 133 (1956).

for the condition $\Phi_i = 0$. The experiments further show that in the stationary state eq 4 is obeyed by both alkali ion species if the mean activities of the salts are substitutes for the single ion activities. The ratio $(a_{\pm}{}''_{\mathrm{KCl}}/a_{\pm}{}''_{\mathrm{LiCl}})_{\mathrm{stat}}$ which will be attained in the stationary state can be calculated from the known electrolyte concentrations in the left cell compartment by eq 8. The experimentally determined and the predicted value agree within the limits of error of our concentration determination: $(a''_{\mathrm{KCl}}/a''_{\mathrm{LiCl}})_{\mathrm{stat}}$ experimentally, 0.95; calculated, 0.98. The mutual influence upon one another of the activity coefficient of the alkali ions is not taken into account in the calculation.

Acknowledgment. The author is indebted to Professor R. Schlögl for his interest in this work and many helpful discussions.

On the WKB[1a] Evaluation of Vibrational Transition Probabilities[1b]

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Contribution from the Department of Chemistry, University of Nevada, Reno, Nevada. *Received November 6, 1967*

Abstract: A complete WKB evaluation of the vibrational transition probability per collison, P, is developed by using the saddle-point method. The final expression of P is applied to several interaction systems for which the "exact" quantum mechanical solutions are known. Both results become identical in the asymptotic limit.

The probability of energy transfer between translation and vibration has been discussed theoretically by a number of authors on both classical and quantum mechanical grounds.[2-4] Although various forms of the interaction $U(r)$, where r is the distance between centers of mass of the collision partners, were assumed in the calculation, only for a few interaction potentials explicit forms of the probability have been obtained. The probability $P(E)$ that the oscillator will undergo the transition $i \rightarrow j$ because of the collision with the incident particle may be calculated by the method of distorted waves or by the method of perturbed stationary states in quantum mechanical treatments.[2,5] In either case, the probability is given by the following expression

$$P(E) = \frac{8\mu\xi_{ij}{}^2}{\hbar^2\sqrt{E(E+\Delta)}}\left[\int_0^\infty F(r)\mathcal{R}_i(E,r)\mathcal{R}_j(E+\Delta,r)\,\mathrm{d}r\right]^2 \tag{1}$$

where ξ_{ij} is the matrix element of the displacement of the oscillator from its equilibrium position taken between the unperturbed initial and final states of the oscillator, Δ (>0) is the magnitude of the change in the oscillator's energy due to the transition, μ is the reduced mass of the collision partners, $F(r)$ is the perturbing force of the oscillator, and for any positive energy E the function $\mathcal{R}_i(E,r)$ is the well-behaved solution of the radial wave equation

$$\frac{\mathrm{d}^2\mathcal{R}_i(E,r)}{\mathrm{d}r^2} + \frac{2\mu}{\hbar^2}[E - U(r)]\mathcal{R}_i(E,r) = 0$$

which is normalized so that as $r \rightarrow \infty$, $\mathcal{R}_i(E,r) \sim \cos(\sqrt{2\mu E}r/\hbar + \delta_i)$. If we include the centrifugal potential energy, then $U(r)$ should be replaced by the effective potential $U(r) + \hbar^2(l + {}^1/_2)^2/2\mu r^2$.

By recognizing the Landau principle,[6,7] Widom[8] has evaluated the integral, I, in eq 1 by using the WKB semiclassical wave functions. However, in his work and also in Landau's original work, the evaluation of the preexponential part of I has not been properly subjected to a critical examination; *i.e.*, the preexponential part of $P(E)$ has not yet been determined in the WKB treatment. This situation is largely due to the fact that a direct calculation of the perturbation integral with respect to the semiclassical wave functions presents formidable difficulties. Such difficulties arise because the wave functions are exponential, and the integrand in the integral is large whereas the integral itself is an exponentially small quantity. Rapp[9] has also attempted to evaluate the integral with the WKB wave functions; since he did not eliminate the difficulties arising from the infinities in the wave functions at the classical turning points, no result was obtained in his work. Furthermore, these works considered a one-dimensional case which is of little practical interest. In the case of motion in a central field of force the general wave equation in spherical polar coordinates permits a separation of the variables. If the radial component of the motion is designated by $\mathcal{R}(r)/r$, the function $\mathcal{R}(r)$ is then the solution of the radial equation given above. Langer[10] showed the application of the WKB analysis to the radial equation and obtained the solutions which can be used to evaluate the integral.

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