and temperatures for the freezing point curves were measured by means of a G-2 Mueller bridge and a platinum resistance thermometer. In each case, the freezing point cell was first charged with carefully purified benzene, the freezing point determined, a sample of the addition compound added, the mixture stirred until complete solution had been obtained, and the freezing point of the solution determined. An atmosphere of dry nitrogen was maintained in the cell at all times. Results of a series of four determinations in the concentration range of 0.0168 to 0.0375 *m* gave values of 313, 320, 324 and 355 for the molecular weight. Since the theoretical value for the formula $TiCl_4{\cdot}2C_5H_{10}O$ is 314.09, these results indicate that this is the molecular formula for the compound.

Discussion and Conclusions

The addition compounds of titanium tetrachloride with the ethers studied appear to have decreasing stabilities in the order: dioxane > (tetrahydrofuran, tetrahydropyran) > anisole > diisopropyl ether. Titanium tetrachloride reacts vigorously with these ethers to form crystalline solids which hydrolyze rapidly at room temperature. Though it is possible that an addition compound is first formed with diisopropyl ether, only the substitution product $TiCl_3(OCH(CH_3)_2)$ was isolated. Both this compound and the addition compound $TiCl_4{\cdot}CH_3OC_6H_5$ gradually decompose at room temperature. At higher temperatures the compound $TiCl_4{\cdot}C_5H_{10}O$ breaks down to yield the compound $TiCl_4{\cdot}2C_5H_{10}O$ and titanium tetrachloride. Failure of the compound $TiCl_4{\cdot}C_4H_8O$ to react in a similar manner can possibly be attributed to the lower decomposition temperature of the compound $TiCl_4{\cdot}2C_4H_8O$. However, it is difficult to explain the apparent reversals of the decomposition temperatures of the tetrahydrofuran and tetrahydropyran addition compounds.

The fact, demonstrated by this research, that titanium tetrachloride forms stable addition compounds with a variety of ethers whereas germanium tetrachloride does not, is undoubtedly at least partially the result of the somewhat larger size of the titanium atom. However, it is quite likely that the "transitional" character of the electronic configuration of the titanium atom which enables it to form very stable octahedral orbitals (d^2sp^3 type) also contributes to this phenomenon; *i.e.*, the very strong bond forming character of d^2sp^3 orbitals may promote bond formation in spite of a certain amount of steric interference.

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Ion Exchanger Electrodes

BY GEORGE SCATCHARD

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The equations for the electromotive force of ion exchanger electrodes are developed from the general equation for the electromotive force of a cell with transference. The most important difference from earlier results is in the effect of the transfer of water or other solvent, which gives the largest of the deviations from ideal electrode behavior. The discussion includes also: hydrolysis, the transition layers between membrane and solutions, diffusion, hydrolytic diffusion and biionic potentials.

The electromotive force of a galvanic cell containing a membrane with a fixed ionic charge was calculated independently by Teorell[1] and by Meyer and Sievers[2] for membranes in which the ions behave as ideal solutes and through which no water or other non-electrolyte is transferred by the electrical current. Neither of these conditions is satisfied in a high capacity ion exchanger. The differential equation for the electromotive force at such a membrane[3] may be obtained from the general thermodynamic equation for the electromotive force of a voltaic cell with the assumption that the laws of reversible thermodynamics apply in terms of the instantaneous values of the concentrations and activities, even though these values are changing due to the irreversible process of diffusion. This assumption is common to all thermodynamic treatments of voltaic cells, and will be made here without discussion. The integrated equation requires the assumption that the changes in activity in the transition layers between membranes and solutions are negligible relative to the changes within the membrane. This assumption will be discussed later.

Voltaic Cells in General.—The electromotive force, E, of a voltaic cell may be expressed as

$$E\mathfrak{F}/RT = E_{0\alpha}\mathfrak{F}/RT - \Sigma_i \nu_{i\alpha} \ln a_{i\alpha} - \int_\alpha^\omega \Sigma_i t_i \mathrm{d} \ln a_i - \Sigma_i \nu_{i\omega} \ln a_i - E_{0\omega}\mathfrak{F}/RT \qquad (1)$$

in which $\mathfrak{F}$ is the faraday, R and T have their usual significance, $E_{0\alpha}$ and $E_{0\omega}$ are the standard potentials of the two electrodes, $\nu_{i\alpha}$ and $\nu_{i\omega}$ are the numbers of moles of species i formed at the respective electrodes when one faraday of electricity goes through the cell from left to right, t_i is the number of moles of species i transferred in the direction of positive current for one faraday,[4] and a_i is the activity of species i. The transference number of an anion is therefore negative. It is also convenient to take the mobility, u_i, and the valence, z_i, as negative for an anion. The fraction of the current carried by the species i, its transport number, T_i, is $t_i z_i$, which is positive. The transference num-

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[1] T. Teorell, *Proc. Soc. Exp. Biol. Med.*, **33**, 282 (1935); *Proc. Nat. Acad. Sci. Wash.*, **21**, 152 (1935); *J. Biol. Chem.*, **113**, 735 (1936).

[2] K. H. Meyer and J. V. Sievers, *Helv. Chem. Acta*, **19**, 649 (1936).

[3] Although the electromotive force can be measured only for the whole cell, the associated change of state can be located, and it is sometimes convenient to talk of the electromotive force of a part of the cell in this sense, even though it involves single ion activities which cannot be determined.

[4] G. Scatchard in Cohn and Edsall, "Proteins, Amino Acids and Peptides," Reinhold Publ. Corp., New York, N. Y., 1943.

ber, t_i, of a neutral species, like the amount formed at an electrode, ν_i, cannot be neglected. It may be positive or negative. The transport number of a neutral species, T_i, like its valence, z_i, is zero. It has been customary to use the names transference number and transport number and the symbols t_i and T_i interchangeably for the transport number T_i. Since it is more important to know which way a species travels than how fast, and particularly since the transference of neutral species cannot be neglected, the transference number, t_i, is the more important quantity.

Staverman[5] calls "electrical transport number" what I have called "transport number," and "reduced electrical transport number" what I have called "transference number." He also emphasizes the need to consider the transference of non-electrolytes. His equation for the liquid junction potential may be obtained from ours by integrating for α to ω with each transference number constant, even through the transition layers. His conclusion that the transference of solvent can be taken into account by using Hittorf transference numbers should be restricted to this special case.

Equation 1 is valid, at constant temperature and pressure, provided that the transfer of non-electrolytes is properly taken into account, for a liquid junction between any mixtures of solutes and solvents, with or without a membrane, or for any combination of such junctions in series.

Cation Exchanger and One Uni-univalent Salt.—Let us consider the case of an aqueous solution of a univalent cation A^+ and two univalent anions X^- and R^-. The integrand of equation 1 is

$$\Sigma_i t_i \,\mathrm{d}\ln a_i = t_A \,\mathrm{d}\ln a_A + t_X \,\mathrm{d}\ln a_X + t_R \,\mathrm{d}\ln a_R + t_W \,\mathrm{d}\ln a_W \quad (2)$$

If all the ions are mobile it is customary to measure the transference relative to the water, that is, to take $t_W = 0$. This gives

$$\Sigma_i t_i \,\mathrm{d}\ln a_i = t_A \,\mathrm{d}\ln_A + t_X \,\mathrm{d}\ln a_X + t_R \,\mathrm{d}\ln a_R \quad (3)$$

If the R^- ions are fixed on a resin lattice, however, it is very much more convenient to consider that they are stationary, that is, to take $t_R = 0$. In this case the transference of water cannot be neglected, and equation 2 becomes

$$\begin{aligned}\Sigma_i t_i \,\mathrm{d}\ln a_i &= t_A \,\mathrm{d}\ln a_A + t_X \,\mathrm{d}\ln a_X + t_W \mathrm{d}\ln a_W \\ &= \mathrm{d}\ln a_A + t_X \mathrm{d}\ln a_A a_X + t_W \mathrm{d}\ln a_W \quad (4)\end{aligned}$$

The first term of equation 4, d ln a_A integrates to ln $a_{A\omega}$ − ln $a_{A\alpha}$, which gives an electromotive force equal to that of two similar electrodes reversible to the A ion, one in solution α and one in solution ω.[6] It is for this reason that we speak of ion exchanger electrodes, even though there are no free electrons involved and there is no oxidation or reduction. Ion exchangers are electrodes in the same sense as a glass electrode, but they are not so specific. A combination of a cation exchanger and an anion exchanger permits measurements of mean activities in solutions of ions for which there are no reproducible electrodes or which are destroyed at true electrodes.

The deviations from perfect electrode behavior are given by the second and third terms of equation 4. To estimate the magnitude of these terms we utilize the relations

$$t_i = u_i m_i / \Sigma_j z_j u_j m_j \quad (5)$$

$$m_A m_X = (m_R + m_X) m_X = a_{AX}^2/\gamma_{AX}^2 = m_X'^{\,2}(\gamma_{AX}'/\gamma_{AX})^2 \quad (6)$$

In equation 6, m_A is the molality of A^+ in the resin, a_{AX} is the mean activity of A^+ and X^- ($a_{AX}^2 = a_A a_X$), γ_{AX} their mean activity coefficient, and m'_{AX} and γ'_{AX} are the molality and the mean activity coefficient in the solution where m_R is zero. In equation 5, m_j may be the molality in the resin, in the aqueous solution, or in a transition layer. The mobility of the water when the resin is fixed must be the negative of the mobility of the resin when the water is fixed, which should be somewhat, but not much, less than the mobility of the univalent resin unit. The molality of the water is, of course, 1/0.018.

Each surface of the membrane is in equilibrium with an aqueous solution with respect to the transfer of either AX or of water. Each intermediate portion of the resin would be in equilibrium with a solution of intermediate composition with respect to AX, and would be in equilibrium with a solution of intermediate composition with respect to water. If these two intermediate solutions are the same, we may relate d ln a_W to d ln a_{AX} by the Gibbs–Duhem equation

$$\mathrm{d}\ln a_W = -0.018\, m'_{AX} \,\mathrm{d}\ln a_{AX}^2 \quad (7)$$

to give, with equation 4

$$\Sigma_i t_i \mathrm{d}\ln a_i - \mathrm{d}\ln a_A = \frac{u_X m_X - u_W m'_{AX}}{u_A m_R + (u_A - u_X) m_X} \,\mathrm{d}\ln a_{AX}^2 \quad (8)$$

$$= \frac{u_X m_X - u_W(\gamma_{AX}/\gamma'_{AX})\sqrt{m_X(m_R + m_X)}}{u_A m_R + (u_A - u_X) m_X} \,\mathrm{d}\ln a_{AX}^2 \quad (9)$$

$$= \frac{\frac{u_X}{u_A}\left(\sqrt{1 + \left(\frac{2a_{AX}}{\gamma_{AX} m_R}\right)^2} - 1\right) - \frac{u_W \gamma_{AX}}{u_A \gamma'_{AX}}\left(\frac{2a_{AX}}{\gamma_{AX} m_R}\right)}{2 + \left(1 - \frac{u_X}{u_A}\right)\left(\sqrt{1 + \left(\frac{2a_{AX}}{\gamma_{AX} m_R}\right)^2} - 1\right)} \,\mathrm{d}\ln a_{AX}^2 \quad (10)$$

$$\cong \left[\frac{u_X}{u_A}\left(\frac{a_X}{\gamma_{AX} m_R}\right)^2 - \frac{u_W \gamma_{AX}}{u_A \gamma'_{AX}}\left(\frac{a_{AX}}{\gamma_{AX} m_R}\right)\right] \mathrm{d}\ln a_{AX}^2 \quad (11)$$

when

$$(2a_{AX}/\gamma_{AX} m_R)^2 \ll 1, \text{ and}$$

$$\cong \frac{u_X - u_W \gamma_{AX}/\gamma'_{AX}}{u_A - u_X} \,\mathrm{d}\ln a_{AX}^2 \quad (12)$$

when

$$(2a_{AX}/\gamma_{AX} m_R)^2 \gg 1$$

The actual distribution probably does not differ enough from that assumed above to make any important difference in these relations.

In a cation exchanger the mobility of water is positive, so that each term of these equations reduces the potential. Since Meyer and Sievers[2] it is customary to ignore the second term which arises from the water transfer, and to calculate the two remaining parameters u_X/u_A and $\gamma_{AX}^2 m_R^2$ from the curve of dE/d ln a_{AX}^2 *vs.* ln a_{AX}^2, with the further assumption that these parameters are constant. The failure for real solutions of the assumption of

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[5] A. J. Staverman, *Trans. Faraday Soc.*, **48**, 176 (1952).

[6] Combination of these terms with the respective electrode expressions in equation 1, leaving the rest of equation 4 as an integral, eliminates single ion activities from that equation.

constancy probably leads to minor discrepancies, but the neglect of the transfer of water must lead to major errors. Equation 12 shows that for large values of the activities the ratio of the second term to the first is $-u_\mathrm{W}/u_\mathrm{X}$, which is not negligibly small. Equation 11 shows that for small activities the effect of water transfer is proportional to the mean activity, while the effect of the transfer of X^- ion is proportional to the square of the mean activity. The Meyer–Sievers plot does not bring out the difference but a plot of $\mathrm{d}E/\mathrm{d}\ln a_\mathrm{AX} - RT\mathfrak{F}$ against a_AX indicates a finite initial slope, and with negative curvature. The neglect of water transfer leads to too small values of $\gamma_\mathrm{AX}m_\mathrm{R}$ and too large values of $u_\mathrm{X}/u_\mathrm{A}$.

From equation 10 or 11 we see that the best chance to improve the exchanger electrode is to increase m_R. Probably the most effective way of doing this without increasing $u_\mathrm{W}/u_\mathrm{A}$ is that of Wyllie and Patnode[7] by keeping the exchange resin under pressure. This gain is at the cost of high resistance. Different resin types may differ appreciably in $u_\mathrm{W}/u_\mathrm{A}$ or in $u_\mathrm{X}/u_\mathrm{A}\gamma_\mathrm{AX}{}^2$.

Hydrolysis.—In aqueous solutions there are always hydrogen and hydroxyl ions. The most direct effect of hydrolysis is the replacement of cations in a cation exchanger by hydrogen ions, or the replacement of anions in an anion exchanger by hydroxyl ions. To take the hydrogen ion into account we will treat the more general case in which there are several univalent cations and, as before, one mobile univalent anion, X^-, one fixed univalent anion, R^-, and water. We will represent a sum over the cations by Σ^+, and we will represent a standard cation as the S^+ ion. Then

$$\Sigma_\mathrm{i}t_\mathrm{i}\mathrm{d}\ln a_\mathrm{i} = \Sigma_\mathrm{i}{}^+t_\mathrm{i}\,\mathrm{d}\ln a_\mathrm{i} + t_\mathrm{X}\mathrm{d}\ln a_\mathrm{X} + t_\mathrm{W}\mathrm{d}\ln a_\mathrm{W}$$

$$= \mathrm{d}\ln\Sigma_\mathrm{i}{}^+a_\mathrm{i}(u_\mathrm{i}\gamma_\mathrm{S}/u_\mathrm{S}\gamma_\mathrm{i}) - \frac{\Sigma_\mathrm{i}{}^+u_\mathrm{i}m_\mathrm{i}\mathrm{d}\ln(u_\mathrm{i}\gamma_\mathrm{S}/u_\mathrm{S}\gamma_\mathrm{i})}{\Sigma_\mathrm{j}{}^+u_\mathrm{j}m_\mathrm{j}} \quad (13)$$

$$+ \frac{(u_\mathrm{X}m_\mathrm{X})(\Sigma_\mathrm{i}{}^+u_\mathrm{i}m_\mathrm{i}\mathrm{d}\ln a_\mathrm{i}\,a_\mathrm{X})}{(\Sigma_\mathrm{j}{}^+u_\mathrm{j}m_\mathrm{j})(\Sigma_\mathrm{j}{}^+u_\mathrm{j}m_\mathrm{j} - u_\mathrm{X}m_\mathrm{X})} + t_\mathrm{W}\mathrm{d}\ln a_\mathrm{W} \quad (14)$$

As before the last two terms are deviation terms which decrease with decreasing salt concentration. The second term is another deviation term which may be very small. If there are two cations, A^+ and H^+, the first term may be written

$$\mathrm{d}\ln\Sigma_\mathrm{i}a_\mathrm{i}(u_\mathrm{i}\gamma_\mathrm{S}/u_\mathrm{S}\gamma_\mathrm{i}) = \mathrm{d}\ln a_\mathrm{A} + \mathrm{d}\ln\left(1 + \frac{a_\mathrm{H}u_\mathrm{H}\gamma_\mathrm{A}}{a_\mathrm{A}u_\mathrm{A}\gamma_\mathrm{H}}\right) \quad (15)$$

The first term is the same as the first term in equation 4, the second gives the most important correction for hydrolysis. The relative mobility of the hydrogen ion is large, but its relative activity coefficient in the exchanger is also large. The factor $u_\mathrm{H}\gamma_\mathrm{A}/u_\mathrm{A}\gamma_\mathrm{H}$ may be greater than unity, but is probably not greater than ten. For concentrations at which hydrolysis may become important the ratio of the activity coefficients of two univalent cations in aqueous solutions is so near unity that the concentrations in the solutions without R^- may replace the activities in equation 15.

Transition Layers.—At each surface of the exchanger membrane there is a transition layer from the aqueous phase, in which the concentrations of the mobile ions A^+ and X^- are equal and their transference numbers are at least of the same order of magnitude, to the exchanger phase, in which the ratios $m_\mathrm{X}/m_\mathrm{A}$ and $t_\mathrm{X}/t_\mathrm{A}$ are extremely small. It is usual to assume that the change in mean activity in these transition layers is negligibly small compared to the change within the exchanger.[8] To check this assumption we examine the diffusion. For any species we may write

$$\frac{\mathrm{d}n_\mathrm{i}}{\mathrm{d}t} = -Am_\mathrm{i}\left[D_\mathrm{i}\frac{\mathrm{d}\ln a_\mathrm{i}}{\mathrm{d}x} + u_\mathrm{i}\frac{\mathrm{d}E}{\mathrm{d}x}\right] \quad (16)$$

in which $\mathrm{d}n_\mathrm{i}/\mathrm{d}t$ is the number of moles of species i which pass per unit time in the direction of increasing x through a plane of area A perpendicular to x, D_i is the diffusion coefficient, a_i the activity and u_i the mobility of species i. This is equivalent to

$$\frac{\mathrm{d}\ln a_\mathrm{i}}{\mathrm{d}x} = -\frac{1}{AD_\mathrm{i}m_\mathrm{i}}\frac{\mathrm{d}n_\mathrm{i}}{\mathrm{d}t} - \frac{u_\mathrm{i}}{D_\mathrm{i}}\frac{\mathrm{d}E}{\mathrm{d}x} \quad (17)$$

For the ions A^+ and X^- ($z_\mathrm{A} = +1$, $z_\mathrm{X} = -1$)

$$\frac{\mathrm{d}\ln a_\mathrm{AX}{}^2}{\mathrm{d}x} = -\frac{1}{A}\left(\frac{1}{D_\mathrm{A}m_\mathrm{A}}\frac{\mathrm{d}n_\mathrm{A}}{d_t} + \frac{1}{D_\mathrm{X}m_\mathrm{X}}\frac{\mathrm{d}n_\mathrm{X}}{\mathrm{d}t}\right) - \left(\frac{u_\mathrm{A}}{D_\mathrm{A}} + \frac{u_\mathrm{X}}{D_\mathrm{X}}\frac{\mathrm{d}E}{\mathrm{d}x}\right) \quad (18)$$

In the ideal case

$$u_\mathrm{i}/D_\mathrm{t} = \mathfrak{F}z_\mathrm{i}/RT \quad (19)$$

In real solutions there are deviations from this behavior because the mobility is different when the ion atmosphere is moving with the central ion due to concentration gradients and when the atmosphere is moving in the opposite direction due to an imposed electromotive force, but the sum $(u_\mathrm{A}/D_\mathrm{A} + u_\mathrm{X}/D_\mathrm{X})$ may be assumed to be very nearly zero. In the absence of current $\mathrm{d}n_\mathrm{X}/\mathrm{d}t = \mathrm{d}n_\mathrm{A}/\mathrm{d}t = \mathrm{d}n/\mathrm{d}t$. So

$$\frac{\mathrm{d}\ln a_\mathrm{AX}{}^2}{\mathrm{d}x} = -\frac{1}{A}\left(\frac{1}{D_\mathrm{A}m_\mathrm{A}} + \frac{1}{D_\mathrm{X}m_\mathrm{X}}\right)\frac{\mathrm{d}n}{\mathrm{d}t} \quad (20)$$

In the steady state $\mathrm{d}n/\mathrm{d}t$ is the same for every plane. The area is usually not greater in the exchanger than in the transition layers, and the diffusion constants are smaller. These tend to make $\mathrm{d}(\ln a_\mathrm{AX}{}^2)/\mathrm{d}x$ larger in the exchanger. However, the big difference in $\mathrm{d}(\ln a_\mathrm{AX}{}^2)/\mathrm{d}x$ is caused by m_X being very much smaller within the exchanger when m_R is much greater than m'_AX. Moreover, the total thickness of the transition layers is small compared to the thickness of an exchanger membrane. For crosslinked polystyrene or phenol–formaldehyde resins, the linear distance between sulfonate neighbors is about 10 Å. so that there are 10^6 sulfonates per mm. An essentially complete transition should require between ten and a thousand sulfonates, or 10^{-5} to 10^{-3} mm. Since the effect per unit length and the length are both small, the neglect of the potential change in the transition layers appears to be justified.

Diffusion through Membrane.—Every ion exchanger electrode must offer a compromise between ion mobility high enough to give a useful conductivity but low enough not to give excessive diffusion. We may include the case of hydrolytic diffusion in our first treatment without too much complication

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(7) M. R. J. Wyllie and H. W. Patnode, *J. Phys. Colloid Chem.*, **54**, 204 (1950).

(8) In the ideal solute treatment this assumption is usually expressed as the potential at such a surface being the Donnan potential.

if we treat three univalent ions A^+, H^+ and X^- in an exchanger R^-, recalling that in the absence of current $dn_X = dn_A + dn_H$. Then algebraic manipulation of equation 18 for $d \ln a_{AX}^2/dx$ and $d \ln a_{HX}^2/dx$, with $(u_A/D_A + u_X/D_X)$ and $(u_H/D_H + u_X/D_X)$ assumed zero, yields

$$\frac{dn_A}{dt} = \frac{-AD_Am_A\left[(D_Hm_H + D_Xm_X)\frac{d \ln a_{AX}^2}{dx} - D_Hm_H\frac{d \ln a_{HX}^2}{dx}\right]}{D_Am_A + D_Hm_H + D_Xm_X} \tag{21}$$

$$\frac{dn_X}{dt} = \frac{-AD_Xm_X\left[D_Am_A\frac{d \ln a_{AX}^2}{dx} + D_Hm_H\frac{d \ln a_{HX}^2}{dx}\right]}{D_Am_A + D_Hm_H + D_Xm_X} \tag{22}$$

The expression for dn_H/dt may be obtained by interchanging the subscripts A and H in equation 21.

We may obtain a first approximation of the salt diffusion from the limiting case $D_Hm_H \ll D_Xm_X \ll D_Am_A$, for which equation 20 yields

$$\frac{dn_A}{dt} \leqq -AD_Xm_X\frac{d \ln a_{AX}^2}{dx} \leqq \frac{-AD_X}{\gamma^2 m_R} d\, a_{AX}^2 \tag{23}$$

This means that, at constant ratio of the activities at the two sides of the membrane, the relative rate of change of the activity is proportional to the mean activity, so that the disturbance from salt diffusion should decrease as the activity decreases.

We may obtain a first approximation of hydrolytic diffusion from the limiting case $D_Xm_X \ll D_Hm_H \ll D_Am_A$ for which equation 21 yields

$$\frac{dn_A}{dt} \leqq -AD_Hm_H\frac{d \ln a_A/a_H}{dx} \leqq AD_H\, d\, m_H/dx \tag{24}$$

$$\leqq AD_H(\gamma_A/\gamma_H)m_R\frac{d(a_H/a_A)}{dx}$$

in which (γ_A/γ_H) is the equilibrium constant and m_R the capacity of the resin.

The hydrolytic diffusion may become particularly important when there are two exchangers, one cationic and the other anionic. The diffusion of hydrogen ion through one and of hydroxyl ion through the other keeps the intermediate solution essentially neutral, so there is no slowing up by reduction of the activity of H^+ or OH^-.

At constant activity of H^+, the relative rate of change of the activity of A^+ is inversely proportional to the square of the activity of A^+, and so it becomes very important in dilute solutions. The effect is proportional to the capacity of the exchanger.

The effect of either salt diffusion or hydrolytic diffusion on the electromotive force comes through the changes in concentrations of the solutions next to the membrane, particularly that of the more dilute solution, which increase the thickness of the transition layers. Lack of sufficient stirring may seriously decrease the electromotive force by making much of the change in activity outside the membrane.

Biionic Potentials.—A biionic potential is the electrical potential difference due to the separation by an ion exchanger of solutions of two different counter-ions. If the counter-ions are univalent cations we may apply equation 14 directly, recalling that the last three terms are relatively small corrections. Integration of the first term, which corresponds to $(u_i\gamma_S/u_S\gamma_i)$ being constant, gives

$$\int_\alpha^\omega d \ln \Sigma_i{}^+ a_iu_i\gamma_S/u_S\gamma_i = \frac{(\Sigma_ia_iu_i\gamma_S/u_S\gamma_i)_\omega}{(\Sigma_ia_iu_i\gamma_S/u_S\gamma_i)_\alpha} \tag{25}$$

If the only cation in solution α is S^+ and the only cation in solution ω is I^+

$$\ln\frac{(\Sigma_ia_iu_i\gamma_S/u_S\gamma_i)}{(\Sigma_ia_iu_i\gamma_S/u_S\gamma_i)_\alpha} = \ln (a_I)_\omega/(a_S)_\alpha + \ln (u_I\gamma_S/u_S\gamma_I) \tag{26}$$

which corresponds to a normal electrode potential difference

$$(E_{0I} - E_{0S})\mathfrak{F}/RT = \ln (u_I\gamma_S/u_S\gamma_I) \tag{27}$$

A more accurate expression is given by including the first correcting term

$$(E_{0I} - E_{0S})\mathfrak{F}/RT = \ln (u_I\gamma_S/u_S\gamma_I)_\omega - \int_\alpha^\omega\frac{u_Im_I d \ln (u_I\gamma_S/u_S\gamma_I)}{u_Sm_S + u_Im_I} \tag{28}$$

Equation 25 applies equally to any mixture of univalent cations.

Ions of Any Valence Types.—All of the equations which have been derived for univalent ions and a cation exchanger hold for univalent ions and an anion exchanger if the plus and minus signs and the subscripts A and X are interchanged, and OH replaces H as subscript.

The equations for any other valence types may be derived as we have derived those for univalent ions from equations 1 and 5 and the generalizations of equation 6

$$\Sigma_im_iz_i + m_Rz_R = 0 \tag{29}$$

in which $z_R = \pm 1$, and

$$m_i\gamma_i/a_i = (m_S\gamma_S/a_S)^{z_i/z_S} \tag{30}$$

However, particularly for mixtures of different valence types, the results will not generally be so simple as for only univalent ions.

The general equation which corresponds to equations 4, 15 and 26 is

$$\int_\alpha^\omega \Sigma_it_i d \ln a_i = \frac{1}{z_S}\ln\frac{a_{S\beta}}{a_{S\alpha}} + \frac{1}{z_I}\ln\frac{a_{I\omega}}{a_{I\beta}} + \int_\alpha^\beta\frac{\Sigma_iu_im_i(d \ln a_i - \frac{z_i}{z_S}d \ln a_S)}{\Sigma_jz_ju_jm_j} + \int_\beta^\omega\frac{\Sigma_iu_im_i(d \ln a_i - \frac{z_i}{z_I}d \ln a_I)}{\Sigma z_ju_jm_j} \tag{31}$$

For the case of biionic potentials, I will not be the same as S, and it will be convenient to choose β so that $a_{S\beta}$ and $a_{I\beta}$ are of the same order of magnitude, and probably convenient to replace $a_{S\beta}$ by $m_{S\beta}\gamma_{S\beta}$ and $a_{I\beta}$ by $m_{I\beta}\gamma_{I\beta}$. In the simpler case where I is identical with S, equation 31 reduces to

$$\int_\alpha^\omega \Sigma_it_i\, d \ln a_i = \frac{1}{z_S}\ln\frac{a_{S\omega}}{a_{S\alpha}} + \int_\alpha^\omega\frac{\Sigma_iu_im_i\left(d \ln a_i - \frac{z_i}{z_S}d \ln a_S\right)}{\Sigma_iz_ju_jm_j} \tag{32}$$

Integration.—Equation 31 and its simpler special cases are so arranged that for ion exchanger membranes the important parts are integrated directly. For the integration of the correcting terms, it is necessary to have detailed information about the membranes. Since these are relatively small terms, however, this information does not need to be very exact. For the effect of water transfer, for example

$$\int_\alpha^\beta t_W \left(\mathrm{d}\ln a_W - \frac{z_W}{z_S}\,\mathrm{d}\ln a_S\right) = \int_\alpha^\beta \frac{u_W}{0.018\,\Sigma_j z_j u_j m_j}\,\mathrm{d}\ln a_W \quad (33)$$

The ratio $u_W/0.018$ will usually be nearly constant. The sum $\Sigma_j z_j u_j m_j$ is $1/\mathfrak{F}$ times the conductance of the membrane, which ordinarily is a monotone function of ln a_w, so the value of the integral lies between

$$\left(\frac{u_W}{0.018\,\Sigma_j z_j u_j m_j}\right)_\alpha \ln \frac{a_{W\beta}}{a_{W\alpha}} \text{ and } \left(\frac{u_W}{0.018\,\Sigma_j z_j u_j m_j}\right)_\beta \ln \frac{a_{W\beta}}{a_{W\alpha}}$$

and is probably not far from their average.

Similarly, in the expression for an ion

$$\int_\alpha^\beta t_i \left(\mathrm{d}\ln a_i - \frac{z_i}{z_S}\,\mathrm{d}\ln a_S\right) = \frac{u_i m_i}{\Sigma_j z_j u_j m_j}\left(\mathrm{d}\ln a_i - \frac{z_i}{z_S}\,\mathrm{d}\ln a_S\right) \quad (34)$$

u_i is nearly constant and $\Sigma_j z_j u_j m_j$ is $1/\mathfrak{F}$ times the conductance of the membrane. For ions of the same sign as the membrane, m_i will usually be small. Except for the case of biionic potential, the standard S may usually be chosen so that every other m_i is small. The correcting term vanishes, of course for S itself.

The Teorell–Meyer and Sievers method of splitting the potential into two Donnan potentials and a Henderson liquid function potential loses the advantage of separating the potential into a main term and deviation terms. The simplifying assumptions which they make would, however, lead to their result by this method also. This is not true of the later treatments involving activity coefficients. Obviously a membrane potential is like an electrode potential in that it cannot be expressed completely in terms of mean activities. However, the important error in these earlier treatments arises from the neglect of water transfer.

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The Preparation of Monosilicic Acid

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Monosilicic acid has been prepared as a 0.1 M solution at pH 3 by the reaction of crystalline sodium metasilicate with a slurry of the hydrogen form of a cation-exchange resin at about 0°. Polymerization occurs at this temperature, even at this optimum pH. Based on the degree of polymerization of the silicic acid formed, it has been concluded that silicate ions are monomeric in crystalline hydrated metasilicate, but are partially polymerized in an aqueous solution of this salt. In a solution of sodium orthosilicate, the silicate ions are essentially monomeric.

The preparation of monosilicic acid by the hydrolysis of silicon tetrachloride in the presence of silver oxide has been previously reported by Willstätter.[1] Moreover, monosilicic acid has been prepared by Kraut[2] by dissolving sodium metasilicate, $Na_2SiO_3 \cdot 6H_2O$, in various acid solutions. These authors have shown that monosilicic acid is most stable in dilute acidic solutions of about pH 2–3.

Based on this background, a new method of preparing a relatively pure solution of this unstable compound has been devised: pulverized, hydrated, crystalline sodium metasilicate is treated with an aqueous slurry of a cation-exchange resin in the hydrogen form at 0°.[3] The liberated monosilicic acid is stabilized at pH 3 by a trace of acid in the solution. This method has the advantages that the procedure is simple, and there is obtained a solution of the monomer free from electrolytes, except for the small amount of acid required as a stabilizer.

Experimental

Materials used were as follows: J. T. Baker C.P. sodium metasilicate, $Na_2SiO_3 \cdot 9H_2O$ (SiO_2, 19.67 ± 0.06%; Na_2O, 20.27 ± 0.05%, fluoride, less than 1 p.p.m.); the hydrogen form of the cation-exchange resin "Nalcite" HCR (National Aluminate Corp.) was prepared by regenerating the sodium form of the resin with 5% sulfuric acid, followed by thorough washing with distilled water, air drying, and screening to obtain a fraction between 16 and 24 mesh.

Determination of Molecular Weight.—The cryoscopic method was used to determine the degree of polymerization, D.P., of silicic acid solutions, using a Heyden–Hahn cryoscopic thermometer, and an apparatus similar to that used by Adams[4] and Robertson and LaMer.[5] Briefly, the procedure consisted of measuring the freezing point depression of a silicic acid solution, and calculating the D.P. from

$$\text{D.P.} = \frac{(1.86)M}{x}$$

where x is the freezing point depression due to the silicic acid in C°, and M is the molality of silicic acid in the solution.

The apparatus used to measure freezing point depression consisted of a box 14" square and 21" high, lined with 3" of insulation, and containing an inner steel box 8" square and 16" high. Centered upright in the bottom of this inner box was a stainless steel cylinder 10" deep and 3.25" diameter, open at the top, serving as a housing for a thermos flask. The section of the inner block above the cylinder was fitted with a tray 8" square and 6" deep, through which ran 3 stainless steel pipes, permitting entry of the thermometer, the inlet and sampling tube, and the stirring handle.

To determine the zero reading (or blank), the tray and and space around the thermos housing were filled with cracked ice and ice-water. The thermos was partially filled with 200 g. of cracked ice (prepared from distilled water) and 220 ml. of distilled water previously cooled to 0 ± 0.2°. The ice-water mixture was occasionally stirred with an 8" stainless steel rod, having a loop in the lower end. When equilibrium had been reached (about half an hour), the zero reading was taken. The freezing point depression

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[1] Richard Willstätter, *et al.*, *Ber.*, **62**, 2027 (1929).

[2] Heinrich Kraut, *ibid.*, **64**, 1709 (1931).

[3] R. K. Iler, U. S. Patent 2,588,389, assigned to E. I. du Pont de Nemours & Co., Inc.

[4] Leason H. Adams, This Journal, **37**, 481 (1915).

[5] Campbell Robertson and Victor K. LaMer, *J. Phys. Chem.*, **35**, 1954 (1931).