As the efficiency of the carrier gas for energy transfer to the substrate increases, the rate should increase.

A number of other mechanisms were considered; these included several radical mechanisms, some of which involved primary fission of the C–H or C–C bonds[18] or intramolecular elimination of HCl, but consideration of the observed rate expression, products, estimated bond dissociation energies, isotope effect and influence of radical chain inhibitors indicates that the proposed mechanism is the simplest to account for these features.

Acknowledgments.—Support of this work by the U. S. Atomic Energy Commission Contract No. AT(11-1)-321 and the Michigan Memorial-Phoenix Project is gratefully acknowledged.

Ann Arbor, Michigan

---

[18] The C–H bond dissociation energy in CCl_3H is estimated to exceed by some 20 kcal. the highest reasonable value for the C–Cl bond energy, 72 kcal./mole.[3] This is presumed to be the case for C_2Cl_5H as well.

Several other products would have been formed (CCl_4, CCl_3H, CCl_2H_2, etc.), if the C–C bond had ruptured.

[Contribution from the Naval Medical Research Institute]

Transport Processes in Electrolyte Solutions[1]

By R. J. Podolsky

Received November 11, 1957

A lattice model that takes ion–solvent interaction into account is developed for aqueous electrolyte solutions. Application of absolute reaction rate theory to this model quantitatively correlates (a) the influence of an ion on the fluidity of a solution, (b) the influence of an ion on the self diffusion of the solvent, and (c) the limiting mobility of an ion. Also, the dependence of the limiting ionic mobility on temperature and on pressure is considered. Data for thirty-eight ionic species, with crystal radius less than or equal to 4 Å., are used to test the theory.

Although the theory for the change in rate of an ionic transport process with concentration is quite advanced,[2,3] the variation of rate with ionic species is only poorly understood. The hydrodynamic model, based on analogy with the motion of a macroscopic sphere through a viscous fluid, has serious shortcomings for ions of nearly the same size as the solvent molecule. This group includes most of the inorganic ions as well as the smaller organic ions. Since there is convincing evidence[4–6] that aqueous electrolyte solutions are highly structured, we thought it might be appropriate to use a lattice model for transport phenomena involving these ions. In the present paper fluidity, ionic mobility and solvent self diffusion are considered. The discussion is restricted to aqueous solutions of ions with crystal radius less than 4 Å.; however, because of their abnormal conduction mechanism,[4,7] the hydrogen and hydroxyl ions have been excluded.

Notation.—Since the connections between three different transport phenomena are considered, it is necessary to use an extensive list of symbols. For convenience, the definitions have been collected in Table I.

The Lattice Model for Transport Processes in Liquids.—The electronic distribution of the water molecule leads to formation of hydrogen bonds between adjacent molecules.[4,8] The most compelling evidence is the low density of ice and water compared with the density calculated on the basis of a close packed structure. This requires the strong directional forces that are characteristic of chemical bonds. Except at high temperatures, the liquid retains much of the crystalline character of the solid. With this high degree of coördination, the lattice model of the liquid state would be expected to be particularly relevant to water.

The lattice model has been used by Eyring and his collaborators[9] in the application of absolute reaction rate theory to transport processes in liquids. Brownian motion is considered to be a series of activated transitions between sites in a lattice structure. To make a transition a molecule must free itself of the "cage" formed by interaction with adjacent water molecules. The necessary energy is the activation energy for transition, ΔF^*_0. Transport results from superposition of a directional bias upon this random molecular motion.

In the case of self diffusion the directional bias stems from a concentration gradient of labeled molecules. It can be shown that the self diffusion coefficient D is related to the lattice spacing λ and the activation energy ΔF^*_0 by the expression[9]

$$D = \frac{RT}{Nh}\lambda^2 e^{-\Delta F^*_0/RT} \tag{1}$$

where R is the gas constant, T is the temperature, N is Avogadro's number and h is Planck's constant.

A velocity gradient generates the directional bias in the case of viscous flow. The relation between the fluidity ϕ and the lattice characteristics can be shown to be[9]

$$\phi = \frac{\lambda_2\lambda_3}{\lambda_1}\lambda^2 e^{-\Delta F^*_0/RT} \tag{2}$$

In this equation λ_1, λ_2 and λ_3 are parameters describing the lattice geometry; to a first approximation they can be set equal to λ.

---

(1) The opinions expressed herein are those of the author and are not to be construed as official or reflecting the views of the Navy Department or the Naval service at large.

(2) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolyte Solutions," Reinhold Publ. Corp., New York, N. Y., 1943.

(3) R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," Academic Press, New York, N. Y., 1955.

(4) J. D. Bernal and R. H. Fowler, *J. Chem. Phys.*, **1**, 515 (1933).

(5) H. S. Frank and M. W. Evans, *ibid.*, **13**, 507 (1945).

(6) R. W. Gurney, "Ionic Processes in Solution," McGraw-Hill Book Co., New York, N. Y., 1953.

(7) E. Hückel, *Z. Elektrochem.*, **34**, 546 (1928).

(8) C. A. Coulson, *Research*, **10**, 149 (1957).

(9) S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., New York, N. Y., 1941.

TABLE I

LIST OF SYMBOLS

c	concn., moles per liter (molarity)
e	electronic charge
f	fraction of particles participating in a transport process that are of species i
h	Planck's constant
k_π	factor in the absolute reaction rate expression for the rate of a transport process, π
k_D	RT/Nh
k_ϕ	$\lambda_2\lambda_3/\lambda_1 h$
k_u	$\mathbf{F}/Nh$
m	$r/(1 + r)v_0 = \epsilon/(\epsilon + \delta)v_0$
n_i	no. of water molecules whose activation energy for transition between lattice sites is perturbed by a solute ion of species $i = 0$
r	ϵ/δ
u	absolute mobility of an ion
v	volume
v_0	molar volume of water
x	mole fraction of the electrolyte
A	coefficient of $\sqrt{c}$ in the Jones and Dole expression for the fluidity of ionic soln.
B	coefficient of c in the Jones and Dole expression for the fluidity of ionic soln.
D	self diffusion coefficient of water
$\mathbf{F}$	faraday
F	free energy
ΔF^*	activation (free) energy for transition of particles between lattice sites
H	enthalpy
N	Avogadro's number
P	pressure
R	gas constant
S	entropy
ΔS_{sol}	entropy of soln. of ions from the gas phase
$\Delta S'$	calcd. entropy change due to (a) the decrease in volume available to an ion in solution relative to the gas phase, and (b) the interaction of the solvent with the electrostatic field of an ion
T	temperature
Δ	ionic fluidity increment
δ	perturbation of the activation energy of a water molecule interacting with an ion
ϵ	perturbation of the activation energy of an ion (considered as a modified solvent molecule) by an adjacent water molecule
θ	distribution function for activation energy
λ	distance between lattice sites
λ_i	parameters describing lattice geometry. See p. 480 of ref. 9
ν_i	no. of moles of ionic species i formed from a mole of electrolyte
ξ	either T or P
π	rate of a generalized transport process
ρ	$(u_i/\phi_0)_{\xi_2}/(u_i/\phi_0)_{\xi_1}$
ϕ	fluidity

In the case of electrolytic conduction a relation similar to eq. 1 and 2 can be derived if an ion is assumed to have the same activation energy as a solvent molecule. Then the ionic mobility u is[9]

$$u = \frac{\mathbf{F}}{Nh}\lambda^2 e^{-\Delta F^*_0/RT} \qquad (3)$$

where $\mathbf{F}$ is the faraday.

The equations for the self diffusion coefficient, the fluidity and the mobility are of the form

$$\pi = k_\pi \lambda^2 e^{-\Delta F^*_0/RT} \qquad (4)$$

where π is D, ϕ or u, and

$$k_D = RT/Nh$$
$$k_\phi = \lambda_2\lambda_3/\lambda_1 h$$
$$k_u = \mathbf{F}/Nh$$

Thus π is the rate of a generalized transport process for particles having the same activation energy. The processes of self diffusion, viscous flow and electrolytic conduction are particularized by the parameters in k_π.

The Rate Equation for Transport Processes in Solutions.—A solution corresponds to a lattice with particles of several species distributed among the sites. We shall make the reasonable assumption that eq. 4, which was derived for lattice particles characterized by a single activation energy, can be generalized for solutions if ΔF^*_0 is taken as the *average* activation energy of the particles subject to the directional bias. Also, the particles are assumed to be accommodated by a lattice with a single spacing parameter.

The activation energy of a given particle will depend on its interaction with the other particles in the lattice. There will generally be a distribution of activation energies for particles of each species. Denoting the distribution function (normalized to unity) by $\theta(\Delta F^*)$, the average activation energy for particles of species i is

$$\overline{\Delta F^*_i} = \int \Delta F^* d\theta_i \qquad (5)$$

and the extension of (4) to solutions is

$$\pi = k_\pi \lambda^2 e^{-\sum_i f_i \overline{\Delta F^*_i}/RT} \qquad (6)$$

The summation is over those species subject to the force biasing the random motion of the particles, and f_i is the fraction of particles subject to the force that are of species i. Thus if the bias is a velocity gradient, π is the fluidity of the solution, and the summation is to be made over all the species in the lattice. If the bias is the concentration gradient of labeled water, π is the self diffusion coefficient of water, and the summation refers only to the solvent. An electric gradient will influence only particles with a net charge. In this case π is the limiting ionic mobility, and the summation is over all *ionic* species.

With only two species, $i = 0$, 1 and a tetrahedral lattice, the structure corresponding to water,[10] a given particle can have five different configurations of nearest-neighbors (Table II). Since the activation energy depends primarily on nearest neighbor interactions, there can be as many as five different activation energies for each ionic species.

In dilute solution the problem is greatly simplified since the solvent is present in excess. Denoting the solvent by $i = 0$, the most probable lattice configuration can be represented by[11]

$$\begin{pmatrix} 0 & & 0 \\ & 0 & \\ 0 & & 0 \end{pmatrix}, \begin{pmatrix} 0 & & 1 \\ & 0 & \\ 0 & & 0 \end{pmatrix} \text{ and } \begin{pmatrix} 0 & & 0 \\ & 1 & \\ 0 & & 0 \end{pmatrix}$$

---

(10) J. Morgan and B. E. Warren, *J. Chem. Phys.*, **6**, 666 (1938).

(11) This notation can be extended easily to any type of lattice.

TABLE II

CONFIGURATIONS OF TWO SPECIES OF PARTICLES IN A TETRAHEDRAL LATTICE[a]

$\boxed{\begin{matrix}0&&0\\&1&\\0&&0\end{matrix}}$	$\begin{matrix}0&&1\\&1&\\0&&0\end{matrix}$	$\begin{matrix}0&&1\\&1&\\0&&1\end{matrix}$	$\begin{matrix}0&&1\\&1&\\1&&1\end{matrix}$	$\begin{matrix}1&&1\\&1&\\1&&1\end{matrix}$
$\boxed{\begin{matrix}0&&0\\&0&\\0&&0\end{matrix}}$	$\boxed{\begin{matrix}0&&1\\&0&\\0&&0\end{matrix}}$	$\begin{matrix}0&&1\\&0&\\0&&1\end{matrix}$	$\begin{matrix}0&&1\\&0&\\1&&1\end{matrix}$	$\begin{matrix}1&&1\\&0&\\1&&1\end{matrix}$

[a] The predominant configurations in dilute solutions are boxed in.

The central particle of these configurations corresponds, respectively, to a solvent molecule unperturbed by the solute, a solvent molecule perturbed by the solute and a solute molecule. In general, for dilute solutions containing several species the predominant configurations will be

$$\begin{pmatrix}0&&0\\&0&\\0&&0\end{pmatrix},\begin{pmatrix}0&&1\\&0&\\0&&0\end{pmatrix},\begin{pmatrix}0&&2\\&0&\\0&&0\end{pmatrix},\ldots,\begin{pmatrix}0&&0\\&1&\\0&&0\end{pmatrix},\begin{pmatrix}0&&0\\&2&\\0&&0\end{pmatrix},\ldots$$

The lattice spacing λ will correspond to that of the pure solvent.

The Activation Energy of the Particles in Electrolyte Solutions.—In this section the terms necessary for the application of the generalized rate equation (6) to ionic solutions will be evaluated. A perturbation method will be used to calculate the activation energies corresponding to the lattice configurations discussed in the preceding section.[12]

An ion is treated as a modified solvent molecule. The change in species results in a perturbation of the activation energy of both the "modified" particle and the "unmodified" particles with which it interacts. The magnitude of the perturbation energy will depend on the physical properties of the particular ionic species.

TABLE III

CONCENTRATIONS AND ACTIVATION ENERGIES OF THE PARTICLES IN DILUTE ELECTROLYTE SOLUTIONS

Lattice configuration	Species	Species fraction	Activation energy
$\begin{matrix}0&&0\\&1&\\0&&0\end{matrix}$	Ion 1	$\nu_1 x$	$\Delta F^*_0 - rn_1\delta_1$
$\begin{matrix}0&&0\\&2&\\0&&0\end{matrix}$	Ion 2	$\nu_2 x$	$\Delta F^*_0 - rn_2\delta_2$
$\begin{matrix}0&&1\\&0&\\0&&0\end{matrix}$	Water perturbed by ion 1	$n_1\nu_1 x$	$\Delta F^*_0 - \delta_1$
$\begin{matrix}0&&2\\&0&\\0&&0\end{matrix}$	Water perturbed by ion 2	$n_2\nu_2 x$	$\Delta F^*_0 - \delta_2$
$\begin{matrix}0&&0\\&0&\\0&&0\end{matrix}$	Unperturbed water	$1 - \sum_{i \neq 0} f_i(1 + n_i)$	ΔF^*_0

Table III schematizes the analysis for a simple electrolyte solution. An ion of species i is supposed to interact effectively with n_i solvent molecules. For these solvent molecules the activation energy is perturbed from ΔF^*_0 to $(\Delta F^*_0 - \delta_i)$. Beyond this "shell" of n_i molecules are the unperturbed solvent molecules with activation energy ΔF^*_0. Similarly, the free energy required for activation of the *ion* can be represented as ΔF^*_0 modified by a perturbation term. For reasons of symmetry, the ionic activation energy is written as $(\Delta F^*_0 - n_i\epsilon_i)$, where ϵ_i is the average difference between ion-solvent and solvent-solvent interaction, and, as before, n_i is the effective number of solvent molecules with which the ion interacts.

Theoretical evaluation of the parameters ϵ_i and δ_i would require a detailed model of the activation process. However, because of the reciprocal nature of the ion-solvent interaction, a proportionality between ϵ_i and δ_i might be expected. Then the ratio $r = \epsilon_i/\delta_i$ would not depend on the species of ion, i. It will be shown in the following sections that this argument can be supported by experimental data. This essentially empirical result will be anticipated by writing the ionic activation energy as $(\Delta F^*_0 - rn_i\delta_i)$. Thus our model of a solution with mole fraction x of an electrolyte dissociating into ν_1 ions of species 1 and ν_2 ions of species 2 is a lattice structure among whose sites are distributed the five configurations of particles in Table III. The distance between equilibrium positions in the lattice is taken to be the same for all species. We shall return to this point in the Discussion.

The Fluidity of Ionic Solutions.—The fluidity of an electrolyte solution differs from that of pure water. Two factors contributing to this difference are ion-ion interaction and ion-solvent interaction. The dependence of fluidity upon concentration is given by the Jones and Dole[13] relation[14]

$$\phi/\phi_0 = 1 + A\sqrt{c} + Bc \qquad (7)$$

The coefficients A and B depend on the solute species. The term $A\sqrt{c}$ is the contribution of the interionic electrostatic interaction and can be derived[15] from the Debye-Hückel theory. The linear term, Bc, arises from ion-solvent interaction[16] (see below, however). The constant B is highly specific and is an approximately additive property of the separate ions.

Generally, $|A| < |B|$, so that the relative magnitude of the terms in (7) depends on the concentration. For extremely dilute solutions ($c << 1$) the dominant term is $A\sqrt{c}$. When $c \approx 1$ the Debye-Hückel term is masked by the contribution of the ion-solvent interaction (except in a fortuitous circumstance of B identically 0). Thus the fluidity of a one molar solution

$$\phi(1) = \phi_0(1 + A + B) \qquad (8)$$

can generally be approximated by

$$\phi(1) \approx \phi_0(1 + B) \qquad (9)$$

---

(12) Since a perturbation method is used, it is not necessary to consider the mechanism of the transport process (however, see the Discussion). Also, the treatment does not depend on the type of lattice.

(13) G. Jones and M. Dole, THIS JOURNAL, **51**, 2950 (1929).

(14) Since we use fluidity, ϕ, rather than viscosity, $\eta = 1/\phi$, the sign of B in the present paper will be the opposite of that found in many standard works.[1,3]

(15) H. Falkenhagen, M. Dole and E. L. Vernon, *Phil. Mag.*, **14**, 537 (1932).

(16) E. C. Bingham, *J. Phys. Chem.*, **45**, 885 (1941).

The quantity ϕ (1) − ϕ_0 has been tabulated[16] for many electrolytes and is referred to as the ionic fluidity increment Δ. When ϕ (c) is not available, B can be estimated from Δ according to eq. 9

$$B \backsimeq \Delta/\phi_0 \qquad (10)$$

Table IV lists, for T = 25°, approximate values of B calculated from this equation as well as values derived from eq. 7. Since there is general agreement when the two quantities can be compared, we have used the approximation when there were insufficient data for application of eq. 7.

TABLE IV

THE JONES AND DOLE PARAMETER B AT 25°

Ion	$(\Delta/\phi) \times 10^{2}$ [a]	$B \times 10^{2}$ [b]
Li^+	−12.5	−14.7 (G)
Na^+	− 8.6	− 8.6 (G)
K^+	0.25	0.7 (G)
Rb^+	1.66	2.9 (G)
Cs^+	2.31	4.5 (G)
Ag^+	− 8.0	− 9.1 (G)
NH_4^+	0.39	0.7 (G)
$CH_3NH_3^+$	− 5.6	
$(CH_3)_2NH_2^+$	− 9.29	
$(CH_3)_3NH^+$	−30.7	
$(CH_3)_4N^+$	−12.5	
$(C_2H_5)_4N^+$	−30.6	−37.5 (LW)
Be^{++}	−40.2	
Mg^{++}	−32.6	
Ca^{++}	−28.0	
Sr^{++}	−25.4	
Ba^{++}	−22.6	−22.1 (HO)
Cu^{++}	−31.0	−33.2 (HO)
Zn^{++}	−31.8	
Co^{++}	−30.7	
La^{+++}	−46.6	−58.8 (HO)
F^-	−12.1	
Cl^-	0.25	0.7 (G)
Br^-	2.76	3.2 (G)
I^-	6.77	8.0 (G)
N_3^-	− 1.8	
NO_3^-	2.73	4.6 (G)
ClO_3^-	0.78	2.4 (G)
BrO_3^-	− 0.7	− 0.6 (G)
ClO_4^-	6.6	
HCO_3^-	−11.5	
Acetate⁻	−19.1	
Picrate⁻		−30.4 (LW)
$SO_4^=$	−18.2	−20.8 (HO)
$C_2O_4^=$	−16.0	
$CO_3^=$	−24.5	
$Fe(CN)_6^{\equiv}$	−18.9	
$Fe(CN)_6^{\equiv}$	−39.2	−39.2 (HO)

[a] Values of Δ are from Bingham[16]; the quantity ϕ_0 = 112 c.g.s. units is from Bingham and Jackson.[17] [b] (HO) Harned and Owen,[2] p. 177; (G) Gurney,[6] p. 168; (LW) Laurence and Wolfenden.[18]

The variation of B with crystal radius and ionic charge is shown in Fig. 1 for a number of ions with radial symmetry. The curve is strikingly similar to the corresponding plot of the Stokes' law radius[21] (calculated from ion mobility), suggesting an intimate connection with the fluidity increment. This long known connection[22] between the fluidity of electrolyte solutions and the mobility of the corresponding ions will find satisfactory explanation in a later section.

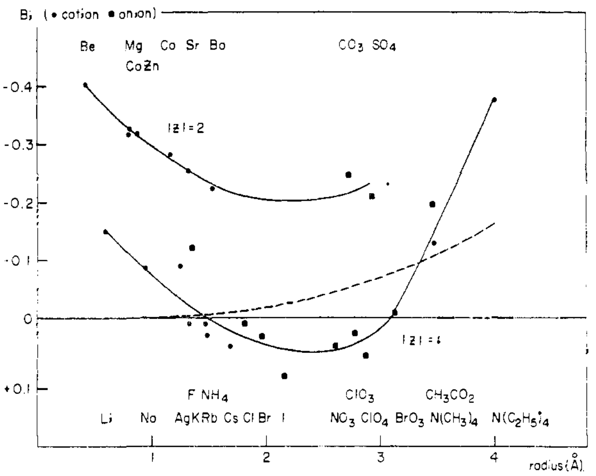

Fig. 1.—The dependence of the Jones and Dole parameter, B, on ionic crystal radius, r. The radii for the monatomic ions are the univalent crystal radii listed by Pauling,[19] p. 346. The radii for the $N(CH_3)_4$ and $N(C_2H_5)_4$ ions are from Robinson and Stokes,[3] p. 120. The radii for the remaining polyatomic ions were estimated from the structural data compiled by Wyckoff.[20] The "effective" radius was calculated from the sphere traced by the van der Waals radii of the peripheral atoms when the ion rotates about its center of mass. The van der Waals radii of oxygen (1.40 Å.) and the methyl group (2.0 Å.) are from Pauling,[19] p. 189.

There is another factor that must be considered in the measurement of B. The fluidity of a liquid is decreased by a suspension of particles largely compared with the molecules of the liquid. This is a macroscopic effect arising from distortion of the streamlines of the flowing liquid by the suspended particles. It can be calculated according to the equation derived by Einstein[23]

$$\phi = \phi_0/(1 + 2.5v) \backsimeq \phi_0(1 - 2.5v) \qquad (11)$$

where v is the volume fraction of the disperse phase. Like the contribution of the ion–solvent interaction to the fluidity, the Einstein effect is proportional to the concentration of solute. The interrupted line in Fig. 1 is an apparent B calculated from (11) with v estimated from the crystal radius. In principle, a correction to the Jones and Dole B should be made to account for this effect. In practice, we have neglected it since the applicability of (11) to solute particles with radii of the same order as the solvent is problematical. However, if (11) could be applied, the correction to B for ions with r<2 Å. would be negligible. For ions as large as $N(C_2H_5)_4$ the Einstein contribution could account for a significant fraction of the measured B.

---

(17) E. C. Bingham and R. F. Jackson, *Bull. U. S. Bur. Stand.*, **14**, 59 (1919).

(18) V. D. Laurence and J. H. Wolfenden, *J. Chem. Soc.*, 136, 1144 (1934).

(19) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1948.

(20) R. W. G. Wyckoff, "Crystal Structures," Interscience Publishers, Inc., New York, N. Y., 1951.

(21) E. Darmois, *J. chim. phys.*, **43**, 1 (1946). The relevant figure is also in A. W. Adamson, *J. Phys. Chem.*, **58**, 514 (1954).

(22) G. Bredig, *Z. physik. Chem.*, **13**, 191 (1894).

(23) A. Einstein, *Ann. physik. Lpz.*, **19**, 289 (1906); **34**, 591 (1911).

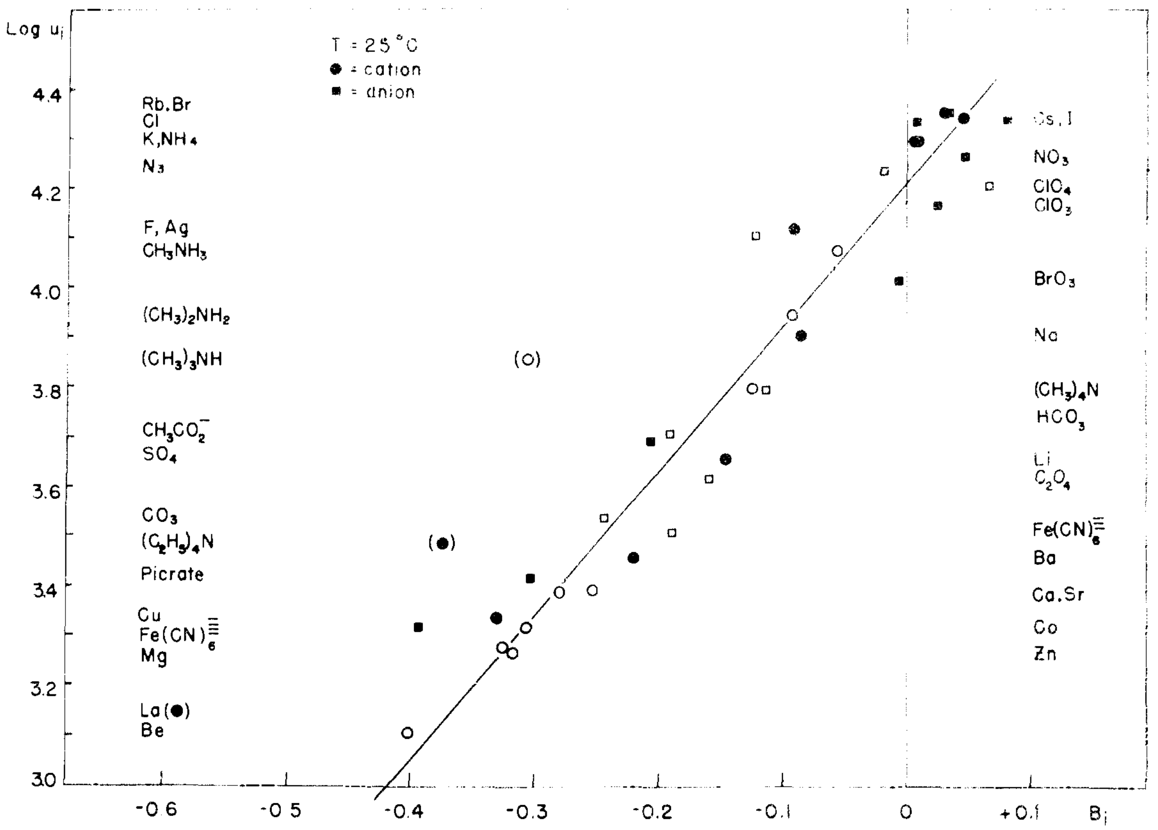

Fig. 2.—The dependence of the limiting ionic mobility, *u*, on the Jones and Dole parameter *B*. The values of *B*, from Table IV, represented by *closed* circles and squares have been derived from the Jones and Dole equation. The *open* circles and squares are approximate values of *B* calculated from eq. 10 and the ionic fluidity increments tabulated by Bingham.[16] The mobility data are from Robinson and Stokes,[3] p. 452.

Evaluation of the Perturbation Parameter $n_i\delta_i$.—For $\pi = \phi$ equation 6 is

$$\phi = k_\phi \lambda^2 e^{-[\Delta F^*_0 - x(1 + r)(\nu_1 n_1 \delta_1 + \nu_2 n_2 \delta_2)]/RT} \quad (12)$$

Since $\phi_0 = k_\phi \lambda^2 e^{-\Delta F^*_0/RT}$, we can write

$$\phi = \phi_0 e^{(1 + r)(\nu_1 n_1 \delta_1 + \nu_2 n_2 \delta_2)x/RT} \quad (13)$$

For small values of the argument this can be approximated by

$$\phi = \phi_0[1 + (1 + r)(\nu_1 n_1 \delta_1 + \nu_2 n_2 \delta_2)x/RT] \quad (14)$$

Each ion contributes independently and additively to the fluidity increment of the solution. It will be convenient to write (14) in terms of c, which, for dilute solutions, is well approximated by $\nu x/v_0$. Then

$$\phi = \phi_0[1 + (1 + r)(n_1\delta_1 + n_2\delta_2)cv_0/RT] \quad (15)$$

This equation refers to a solution without ion–ion interaction. The analogous form of the Jones and Dole relation is

$$\phi = \phi_0[1 + Bc] \quad (16)$$

Comparison with (15) leads to the desired result

$$n_i\delta_i = B_i RT/(1 + r)v_0 \quad (17)$$

Thus the Jones and Dole parameter B is proportional to the perturbation of the activation energy accompanying transformation of a lattice particle from a water molecule to an ion.

In the following it will be convenient to rewrite (17) as

$$n_i\delta_i = B_i RTm/r \quad (18)$$

where, by definition, $m = r/(1+r)v_0$.

The Limiting Ionic Mobility.—Limiting ionic mobilities are measured by an extrapolation that dissects out the influence of interionic attraction. Therefore differences in mobility reflect differences in specific ionic interaction with the solvent. This is seen by writing (6) for the rate of migration of an ion in an electric field. In this case the bias acts only on the ions and

$$u_i = k_u \lambda^2 e^{-(\Delta F^*_0 - r n_i \delta_i)/RT} \quad (19)$$

Combining (18) with the logarithm of (19)

$$\log u_i = \{-\Delta F^*_0/RT + \log k_u \lambda^2\} + mB_i \quad (20)$$

The log u_i will be a linear function of B_i with slope *m if r is the same for all ions*, since $m = r/(1+r)v_0$. This requirement is reasonably well satisfied by the available data for ions of radius up to 4.0 Å.(Fig. 2). The straight line was fitted by the method of least squares assuming the variability to be associated with B. The points in brackets, for La, $(CH_3)_3NH$ and $N(C_2H_5)_4$ ions, were excluded from the fitting procedure since the data are clearly out of line. (These values of B might include a contribution from the Einstein effect, eq. 11, since they are "too large.") The scatter about the line does not seem unreasonable, in view of the multiplicity of sources of the fluidity data, some of which are quite old. The slope of the line, m, is 2.90 ± 0.23

mole liter^{-1}. Taking $v_0 = 0.018$ liter mole^{-1}, this corresponds to a value of $r = 0.055 \pm 0.003$.

Equation 20 provides a theoretical basis for the well known correlation between fluidity and mobility.[22] Both phenomena depend on the perturbation of the water structure following accommodation of the ion by the water lattice and are measured by the same parameter, B_i.

The Self Diffusion Coefficient of Water in Ionic Solutions.—According to the present model, each molecule of electrolyte 1,2 introduced into the solvent lattice modifies the activation energy of n_1 water molecules by δ_1 and n_2 water molecules by δ_2. These perturbed water molecules as well as the remaining unperturbed waters contribute to the average self diffusion coefficient according to their relative number. These premises can be put to the test by measuring the diffusion of isotopically labeled water in electrolyte solutions.

For univalent electrolytes, the form of eq. 6 relevant to self diffusion of the solvent is

$$D = k_D\lambda^2 e^{-[\Delta F^*_0 - x(n_1\delta_1 + n_2\delta_2)]/RT} \qquad (21)$$

Noting that $D_0 = k_D\lambda^2 e^{-\Delta F^*_0/RT}$, this can be written

$$D = D_0 e^{(n_1\delta_1 + n_2\delta_2)x/RT} \qquad (22)$$

which is approximated by

$$D = D_0[1 + (n_1\delta_1 + n_2\delta_2)x/RT] \qquad (23)$$

Combining with (17), and replacing x by cv_0

$$[D - D_0]/D_0 = [B_1 + B_2]c/(1 + r) \qquad (24)$$

Whether a salt retards or accelerates the self diffusion of water will depend on the sign of $[B_1+B_2]$.

At a given concentration the quantity $[D(T,c) - D_0(T)]/D_0(T)$ should be a linear function of $[B_1(T) + B_2(T)]$, both terms being parametric functions of T. Figure 3 compares the predictions of the present theory with data reported by Wang[24] for the influence of KCl, KI and NaCl on D at both 10 and 25°. In theory, for $c = 1$ molar, the data should describe a line with slope 0.95, passing through the origin. The line fitted to Wang's data by the method of least squares has slope 0.85 $\pm$ 0.08 and intercept on the $[D - D_0]/D_0$ axis of 0.015 $\pm$ 0.008. This excellent agreement between theory and experiment is especially significant since eq. 24 describes the data without benefit of adjustable parameters.

Since the theoretical slope is an insensitive function of r when $r << 1$, the self-diffusion data do not test our assumption that r is the same for each ion. However, they do support our model for the influence of ions on the activation energy of adjacent water molecules.

The Influence of Temperature and Pressure on Ionic Mobility.—According to the hydrodynamic model for transport processes, an increase in mobility with T or P merely mirrors an increase in the fluidity of the solvent, so that the ratio of mobility to fluidity, u_i/ϕ_0, should be independent of both T and P. However, facts do not support such expectations. The values of u_i/ϕ_0 depend on both T and P in ways that follow naturally from the model developed above.

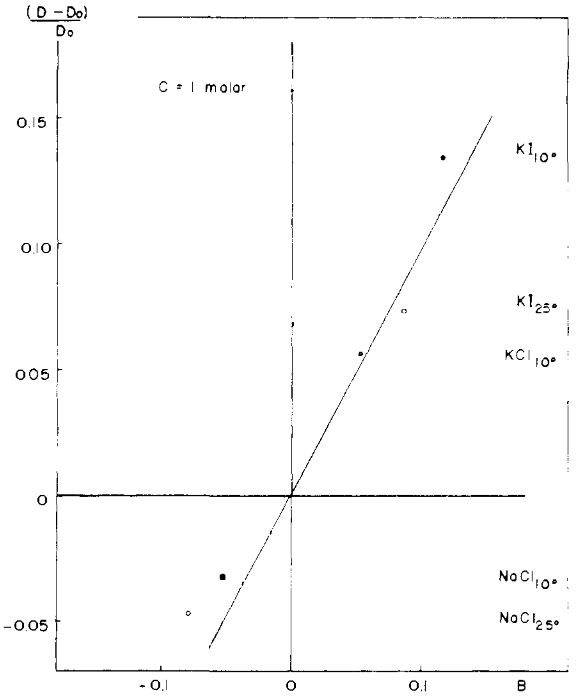

Fig. 3.—The dependence of D, the self diffusion coefficient of water in electrolyte solutions, on B, the Jones and Dole parameter of the solute. The *closed* circles are data at 10° and the *open* circles are for 25°. The self diffusion coefficients are from Wang.[24] Values of B at 25° are from Table IV; values for 10° were estimated from the temperature coefficients listed by Gurney,[6] p. 163. The line is from eq. 24.

Equation 4, written for $\pi = \phi_0$, is

$$\phi_0 = k_\phi\lambda^2 e^{-\Delta F^*_0/RT} \qquad (25)$$

Combining this with (19)

$$u_i/\phi_0 = (k_u/k_\phi)e^{rn_i\delta_i/RT} \qquad (26)$$

With (18) this becomes

$$u_i/\phi_0 = (k_u/k_\phi)e^{mB_i} \qquad (27)$$

Differentiating the logarithm of (27)

$$\frac{\partial}{\partial\xi}(\log u_i/\phi_0) = \frac{\partial}{\partial\xi}(\log k_u/k_\phi) + m\frac{\partial B_i}{\partial\xi} \qquad (28)$$

where ξ can be either T or P. For small differences in ξ this is approximated by

$$\rho_\xi = 1 + (\xi_2 - \xi_1)\left[\frac{\partial}{\partial\xi}(\log k_u/k_\phi) + m\frac{\partial B_i}{\partial\xi}\right] \qquad (29)$$

where ρ_ξ represents the ratio $(\mu_i/\phi_0)_{\xi_2}/(\mu_1/\phi_0)_{\xi_1}$. The quantity k_u/k_ϕ depends on ξ implicitly through the geometric lattice parameters. Since these parameters are much weaker functions of ξ than B_i

$$\rho_\xi \backsimeq 1 + m(\xi_2 - \xi_1)\partial B_i/\partial\xi \qquad (30)$$

Thus $\rho_\xi = 1$, as required by the hydrodynamic model, only when $\partial B_i/\partial\xi$ vanishes. The frequent deviation of ρ_T from unity prompted Cox and Wolfenden[25] to call it the "anomaly coefficient."

---

[24] J. H. Wang, *J. Phys. Chem.*, **58**, 686 (1954). The tracer H_2O^{18} was used so that diffusion required transition of the water molecule as a unit. See A. W. Adamson and R. R. Irani, THIS JOURNAL, **79**, 2967 (1957), for the dependence of the apparent self diffusion constant on the isotope used to label the water.

[25] W. M. Cox and J. H. Wolfenden, *Proc. Roy. Soc.* (*London*), **145A**, 475 (1934).

Extremely accurate measurements are required for the evaluation of $\partial B/\partial \xi$ since it is essentially a second-order correction to the fluidity of water, the first correction being due to the presence of the electrolyte and the second resulting from variation in ξ. Although there are insufficient data in the literature to test eq. 30 exhaustively, the calculations that can be made tend to support it.

(I) $\xi = T$.—Figure 4 illustrates the temperature dependence of the ratio of ionic mobility to the fluidity of water, μ_i/ϕ_0. The corresponding increase in the fluidity of water is given by the interrupted curve. The following generalizations[26] have been drawn from such data: (a) with increase in temperature the mobility of most ions increases less rapidly than the fluidity of the solvent, *i.e.*, $\rho_T < 1$. (b) There is a correlation between ρ_T and u_i. The more mobile ions have the greatest deviation of ρ_T from unity; for the less mobile ions $\rho_T \approx 1$. Since u is a function of B (eq. 20) a correlation can also be made between ρ_T and B. Both (a) and (b) can be derived from eq. 30 and the properties of $\partial B/\partial T$.

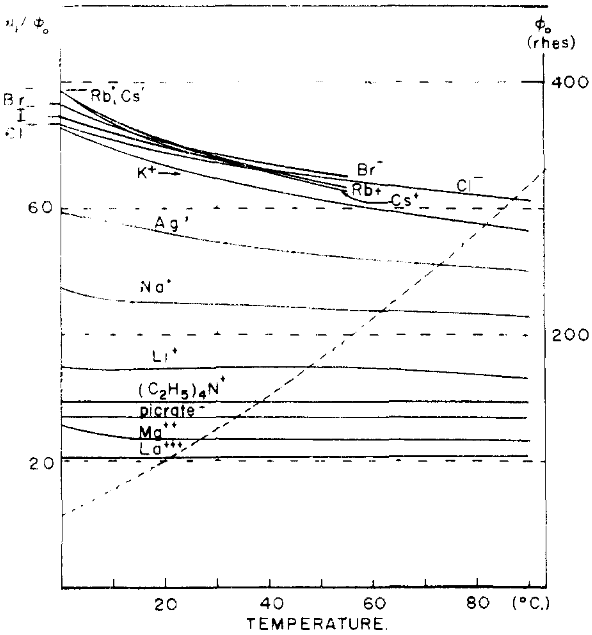

Fig. 4.—The temperature dependence of the ratio of limiting ionic mobility to the fluidity of water, u_i/ϕ_0. Data are from Robinson and Stokes,[3] p. 454, and Harned and Owen,[3] p. 185.

In the interval 0 to 40°, the coefficient B is generally a decreasing function of T.[6] Thus $\partial B/\partial T < 1$ and, from (30), it follows that $\rho_T < 1$.

The correlation between ρ_T and B, and consequently between ρ_T and u, stems from the fact that $\partial B/\partial T$ is a function of B. In particular, for the alkali ions, $\partial B/\partial T$ is well represented by a linear function of B (Fig. 5a). Differentiation of (30), written for $\xi = T$

$$\frac{\partial \rho_T}{\partial B} = m\Delta T\,\frac{\partial^2 B}{\partial B\,\partial T} \qquad (31)$$

shows that the slope of this line, $\partial^2 B/\partial B \partial T$, can be used to calculate the slope, $\partial \rho_T/\partial B$, of the observed relation between ρ_T and B (Fig. 5b).

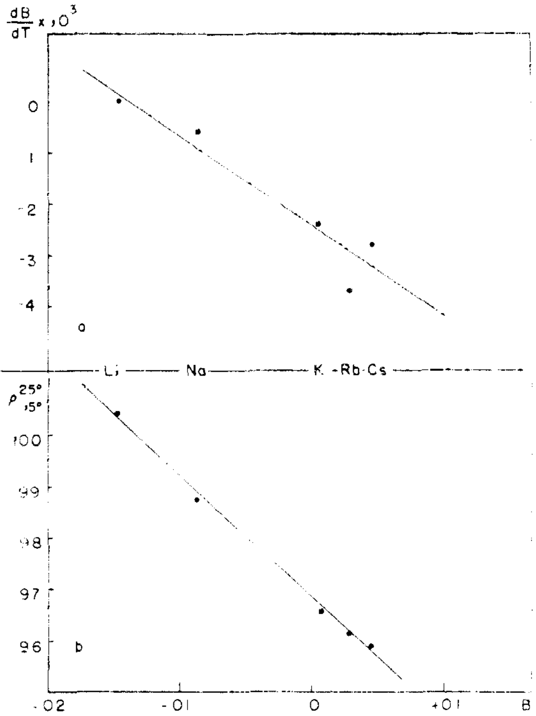

Fig. 5.—The dependence of $\partial B/\partial T$ and ρ_T on B for the alkali ions. Ordinates in (a) are $[B(25°) - B(18°)]/7$; values for $B(25°)$ and $B(18°)$ are from Cox and Wolfenden.[25] Ordinates in (b) are from Fig. 4.

The terms involved in (31) have been collected in Table V. Other than the possibility of experimental error in the difficultly measured values of $\partial B/\partial T$, we have no explanation of the discrepancy of 2.5 times the standard error in the calculated value of $\partial \rho_T/\partial B$.

TABLE V

CALCULATION OF $\partial \rho_T/\partial B$

		Ref.
m	2.90 ± 0.23	Fig. 2
ΔT	10.00	
$\partial^2 B/\partial B \partial T$	$-(1.8 \pm 0.3) \times 10^{-2}$	Fig. 5a
$\partial \rho_T/\partial B$		
Calcd.	-0.52 ± 0.11	Eq. 31
Obsd.	-0.24	Fig. 5b

For ions with $\rho_T = 1.00$, eq. 30 requires that $\partial B/\partial T = 0$. This seems to be the case for ions with large negative values of B, such as tetraethylammonium and picrate.[18,25]

(II) $\xi = P$.—The conductivity change in alkali halide solutions subjected to hydrostatic pressure is an additive property of the separate ions.[27] Analysis of the data indicates that more is involved than the change in fluidity of the solvent with pressure.[28,29] These additional factors are reflected in the dependence of ρ_P on ionic species.[27] For ex-

---

(26) R. W. Gurney's book, "Ionic Processes in Solution,"[8] contains an excellent qualitative discussion of these results.

(27) F. Korber, *Z. physik. Chem.*, **67**, 212 (1909).

(28) W. A. Zisman, *Phys. Rev.*, **39**, 151 (1932).

(29) P. W. Bridgman, "The Physics of High Pressure," G. Bell and Sons, London, 1952, p. 360.

ample, at 20° the values of ρ_P are in the sequence Li>K>Na for cations and Cl>Br>I for anions. Of the salts LiCl, KCl, NaCl, KBr, NaBr, KI, NaI, only $\rho_P(\text{KCl}) = 1.00$. With the exception of LiCl, ρ_P for the others is less than unity. On the basis of the present analysis this is not unexpected, for, as in the analogous case of the variable T, $\rho_P = 1.00$ only when $\partial B/\partial P$ vanishes. It is noteworthy that the sequence of cations is different from the order of crystal radii, which is the sequence found in a large number of phenomena. This implies that $\partial B/\partial P$ can be either positive or negative.

The simplest way of extracting $\partial B/\partial P$ from experimental data, $\phi(c,p)$, is to consider eq. 7 in the concentration range $A\sqrt{c} << Bc << 1$. Then

$$\phi(c,P) = \phi_0(P) + c\phi_0(P)B(P) \tag{32}$$

Differentiating with respect to concentration and pressure

$$\frac{\partial^2\phi(c,P)}{\partial P\partial c} = B\frac{\partial\phi_0}{\partial P} + \phi_0\frac{\partial B}{\partial P} \tag{33}$$

so that

$$\frac{\partial B}{\partial P} = \frac{1}{\phi_0}\left[\frac{\partial^2\phi(c,P)}{\partial P\partial c} - B\frac{\partial\phi_0}{\partial P}\right] \tag{34}$$

This procedure generally can be used with c of the order of unity.

Consider the case of KCl solutions. According to data of Sergeivich, Zhuse and Chestnov,[30] $\phi(P, 1\text{ molar}) = \phi(P, 2\text{ molar}) \approx \phi(P, 3\text{ molar})$ for pressures up to 400 atm., so that $\partial\phi(c,P)/\partial c \approx 0$. Also, $B(\text{KCl}) \approx 0$ (Fig. 1). Therefore, from (34) $\partial B/\partial P = 0$, and the observation that $\rho_P(\text{KCl}) = 1.00$ is confirmation of eq. 30.

For solutions of NaCl, eq. 30 and 34 lead to a value of ρ_P in fair agreement with the observed value (Table VI).

TABLE VI

CALCULATION OF ρ_P FOR NaCl

$T = 20°$

		Ref.
ϕ_0	1.0×10^2 rhe	17
$\partial^2\phi/\partial P\partial c$[a]	-8×10^{-4} rhe l. atm.$^{-1}$ mole^{-1}	31
B	-7.5×10^{-2} l. mole^{-1}	32
$\partial\phi_0/\partial P$	3×10^{-3} rhe atm.$^{-1}$	31
$\partial B/\partial P$	-6×10^{-6} l. mole^{-1} atm.$^{-1}$	Eq. 34
$(1 - \rho_1^{500\text{ atm}}) \times 10^3$		
Calcd.	9	Eq. 30
Obsd.[b]	4.4	27

[a] We have used the earlier data of Cohen[31] rather than that of Sergeivich, *et al.*,[30] because the former has a greater degree of internal consistency. Both sets of data, however, are qualitatively similar. [b] $T = 19.18°$. The datum is $[u'_{\text{NaCl}}\text{ (500 atm.)} - u'_{\text{KCl}}\text{ (500 atm.)}]/500$, where u' is the conductance after correction for the change in electrolyte concentration resulting from compression of the solution. This procedure rests on the assumption that at this temperature the conductance of a 0.01 M solution of KCl reflects the change with pressure of the viscosity of water.

Since no other suitable pressure–viscosity studies of ionic solutions were found in the literature, further tests of (30) with P as the variable must be deferred. The available data, however, seem to support the present model.

Discussion

Our treatment of transport processes in ionic solution is equivalent to assigning different activation energies to sets of particles distributed simultaneously among lattice sites of equal spacing. We have assumed that (a) perturbed water molecules and ions use the same mechanisms as unperturbed water molecules for migration through the lattice, and (b) the distance between equilibrium positions in the lattice λ is virtually independent of the activation energy required for transition of the particle. These assumptions require comment because some of the ions considered, such as the alkyl substituted ammonium series, are much larger than the water molecule.

The Mechanism of Lattice Migration.—There are many possible mechanisms for migration of particles among lattice sites. For example, particles might exchange positions in the lattice (O X Y O → O Y X O). Or transition between lattice sites might require an unoccupied site adjacent to the migration particle (OX O → O XO), a mechanism equivalent to replacement of Y, in the latter, by a "hole."[33] In a physical system many such mechanisms probably contribute to the transport process.

Since we used a perturbation method for the analysis of transport processes, it was not necessary to consider the mechanism of migration explicitly. However, this procedure implies that the mechanisms are the *same for each particle in the lattice*. Perturbed water molecules and ions are supposed to use the same mechanisms as unperturbed water for their motion among the lattice sites. This is difficult to visualize when the ionic diameters range from 0.4 to 2.7 times the diameter of the water molecule.

The question of whether the ion migrates alone or with a number of attached water molecules is related to this problem. For simplicity we treated the ion as though it moved among the lattice sites without attached water molecules. However, there would be no substantial difference in the results of the theory if water molecules were attached to the ion during its Brownian movement. Beyond this shell of molecules "frozen" to the ion would be the n_i water molecules with activation energy $\Delta F^*_0 - \delta$ rather than ΔF^*_0. There would be no kinematic constraint associated with the perturbed activation energy. This picture is similar to that used by Frank and Evans[5] to calculate the entropy of ionic solution.

One characteristic of Fig. 1, the dependence of B_i on ionic crystal radius, is of interest in this connection. The width of the U-shaped curve for the univalent ions is of the same order as the diameter of the water molecule (2.8 Å.). If B_i depends largely on the charge and size of the lattice kinetic unit, this would support the classical view[34] that the large ions forming the right arm of the U migrate as the naked ion, while the small ions on the left arm move with a single layer of electro-

---

(30) V. I. Sergeivich, T. P. Zhuse and A. I. Chestnov, *Isvest. Akad. Nauk S.S.S.R., Otdel. Tekh. Nauk*, 896 (1953).

(31) R. Cohen, *Ann. Physik. Chem.*, **46**, 666 (1892).

(32) G. Jones and S. M. Christian, THIS JOURNAL, **59**, 484 (1937).

(33) J. Frenkel, "Kinetic Theory of Liquids," Oxford University Press, London, 1946, p. 174.

(34) Reviewed by B. E. Conway and J. O. Bockris in J. O. Bockris, "Modern Aspects of Electrochemistry," Academic Press, New York, N. Y., 1954.

statically bound water molecules. The sizes of the charged units corresponding to different ionic species would then be more similar than indicated by the range of crystal radii. Furthermore, if water were to migrate through the lattice as a tetrahedrally coördinated group of five molecules rather than singly, the water unit of migration would be nearly the same size as the charged unit, regardless of ionic species. This would overcome the steric objection to particles of widely different radii moving through the lattice by the same mechanisms.

It would not be profitable to speculate further on the mechanism of lattice migration on the basis of the present theory since, as mentioned above, it was purposely constructed to sidestep this difficult question.

The Relative Influence of Geometric and Energetic Factors in Transport Processes.—Suppose the perturbation of the activation energy of a lattice particle is associated with a change in the lattice spacing, $d\lambda$. To evaluate the relative contributions of $d\lambda$ and $d\Delta F^*$ to the rate of a transport process, we differentiate eq. 4

$$d\pi/\pi = 2d\lambda/\lambda - d\Delta F^*/RT \qquad (35)$$

The quantities $2d\lambda/\lambda$ and $d\Delta F^*/RT$ can be considered as the geometric and the energetic contributions to the perturbation process.

Consider the geometric contribution. Since coördination in liquid water stems from hydrogen bonds between water molecules, the lattice properties will depend ultimately on characteristics of this bond. Flexibility in the length of the hydrogen bond permits a greater number of coördination schemes than the almost constant internuclear distance in the normal covalent bond. Thus ions with diameter less than or equal to 3.0 Å. can fit into the lattice substitutionally[35]; with larger solutes, there is evidence of a change in the coördination of water resulting in structures with suitably spacious "holes."[36,37]

An upper limit to the value of $d\lambda/\lambda$ can be estimated from the range of $O \cdots O$ distances compatible with the $O-H \cdots O$ bond. The reported distances for various substances are between 2.44 and 3.36 Å.[8] Since the $O \cdots O$ distance in water at 20° is 2.90 Å., the value of $d\lambda/\lambda$ is almost certainly less than 1/6.

The second term in eq. 35, $d\Delta F^*/RT$, is $rn_i\delta_i/RT$ for an ion and δ_i/RT for a perturbed water molecule (Table III). Considering (17), these quantities are $rB_i/(1+r)v_0$ and $B_i/n_i(1+r)v_0$, respectively. Since $r = 0.055$ and $v_0 = 0.018$ liter mole^{-1}, the ionic perturbation energy is $2.9B_i$. The perturbation energy for a water molecule, however, depends on n_i, the number of water molecules that interact with the ion of species i. If the value of n_i is less than 18, the perturbation energy for the water molecule will be equal to or greater than that of the corresponding ion. This is not an unreasonable range for n_i, since 20 is the number of nearest plus next-nearest neighbors in a tetrahedral lattice. Assuming, then, that $n_i < 18$, the activation energy will almost certainly be a greater factor in the transport process rate than perturbation of the lattice spacing if

$$|B_i| > 1/(3)(2.9) = 0.115 \qquad (36)$$

This condition is clearly satisfied for ions that might be expected to upset the lattice geometry, that is, the multivalent and the very small (like Li) and very large (like $N(C_2H_5)_4$) univalent species (Fig. 1). Since the derivation of (36) was biased to maximize the geometric contribution, it probably is correct to conclude that this factor safely can be neglected.

The Relation between B and the Entropy of Solution.—Several authors[5,6] have called attention to the correlation that can be made between the Jones and Dole parameter B and the entropy of solution of the corresponding ion from the gas phase (Fig. 6). The graphical representation of the activation energy for a rate process (Fig. 7) brings out the connection between this observation and the present theory.

The free energy of the system is F_1 when a particle is at a lattice site. Before the particle can move to another site, the system must pass through an intermediate configuration of greater free energy F_2. The free energy of the intermediate configuration relative to the initial state $F_2 - F_1$ is the activation energy, ΔF^*_0.

Suppose F_1 and F_2 refer to unperturbed water. The change in activation energy δ for water perturbed by an ion results from F_1 and F_2 shifting to $F_1 + dF_1$ and $F_2 + dF_2$, respectively. Clearly, $\delta = dF_1 - dF_2$. The equilibrium properties of a system are unaffected by changes in F_2; however, they do reflect changes in F_1. Since dF_1 will depend on the characteristics of the perturbing ion and since δ is proportional to B (eq. 18), correlations between B and the thermodynamic properties of electrolyte solutions should not be unexpected.

The analysis by Frank and Evans[5] of the entropy of solution of ions from the gas phase, ΔS_{sol}, is relevant to this subject. These authors divide ΔS_{sol} into three qualitatively different components. The first is the entropy change due to the decrease in volume available to the ion in solution relative to the gas phase. The second arises from the electrostatic interaction of the solvent with the field of the ion. The sum of these two contributions will be denoted by $\Delta S'$. The third contribution is attributed to the specific influence of the ion on the structure of the water. This last component, the difference between the measured ΔS_{sol} and the calculated $\Delta S'$, can be identified with dS_1, the entropy term in dF_1.

If $\Delta S'$ is relatively constant for a series of ions, which seems to be the case for the univalent ions considered by Frank and Evans, the quantity ΔS_{sol} will be a measure of the dependence of dS_1 on ionic species. However, B depends on dF_2 and dH_1 (the enthalpy term in dF_1) as well as dS_1. The connection between ΔS_{sol} and B cannot be taken further without knowing the magnitudes of both dF_2 and dH_1 relative to dS_1. For example, the linear relation between ΔS_{sol} and B for univalent ions (Fig. 6) would follow from the model of Frank and Evans if $|dF_2|, |dH_1| << |dS_1|$, but it is

---

(35) G. W. Brady and J. T. Krause, *J. Chem. Phys.*, **27**, 304 (1957).

(36) W. F. Claussen, *ibid.*, **19**, 259, 662, 1425 (1951).

(37) W. F. Claussen and M. F. Polglase, THIS JOURNAL, **74**, 4817 (1952).

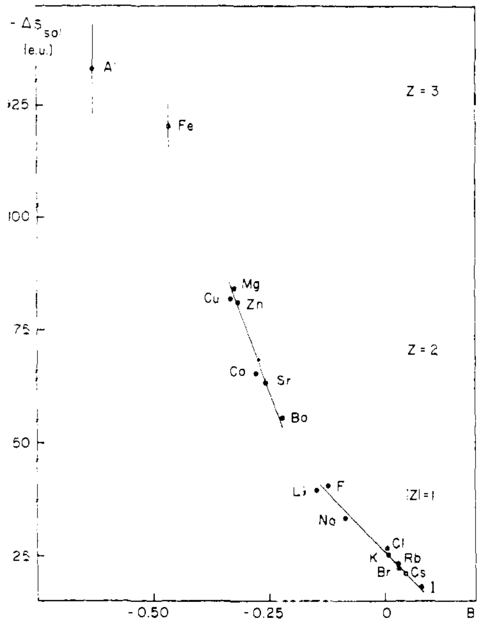

Fig. 6.—The dependence of the ionic entropy of solution from the gas phase, ΔS_{sol}, on the Jones and Dole parameter, B. The entropy data are from Frank and Evans.[5]

difficult to justify this condition. To develop the quantitative relation between the Jones and Dole coefficient and the entropy of solution would require a considerably more elaborate analysis of electrolyte solutions than the present treatment.

Conclusions.—The principal result of the present argument is that electrolyte solutions can be described as perturbations of the water lattice. The perturbation is characterized by two parameters, δ_i and r. The value of δ_i depends on ionic species, while r is essentially constant for all the ions considered.

A formula for δ_i as a function of the Jones and Dole parameter, B_i, was derived from consideration of the viscosity of electrolyte solutions. Analysis of electrolytic conduction uncovered an exponential relation between B_i and the mobility of the corresponding ion. This relation supported our initial assumption that r is independent of ionic species, and led to a numerical value of r. The quantitative

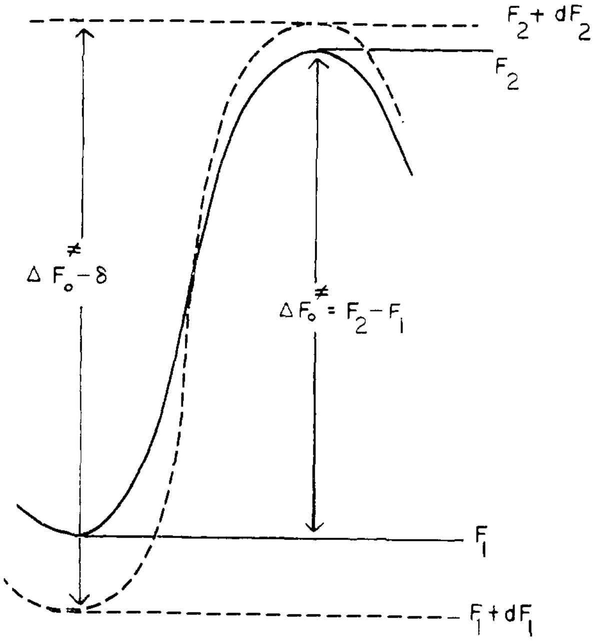

Fig. 7.—Graphical representation of the activation energy for a rate process. See text for definition of symbols.

effect of electrolytes on the self diffusion coefficient of water was calculated without the introduction of additional parameters. Finally, the dependence of ionic mobility on temperature and pressure was calculated from the corresponding values of $\partial B_i/\partial T$ and $\partial B_i/\partial P$.

The analysis is essentially a marriage of the theory of absolute reaction rates with the ideas in the classical paper of Bernal and Fowler[4] on the structure of water and electrolyte solutions. These authors' "structural temperature," the "icebergs" of Frank and Evans,[5] and the "cospheres" of Gurney[6] correspond to the "perturbed water" in the present theory. By developing the absolute reaction rate treatment of transport processes into a form applicable to electrolyte solutions, these qualitative ideas concerning the influence of ions on the structure of water find corroboration in quantitative analysis.

BETHESDA 14, MARYLAND