

# Conductimetric determination of thermodynamic pairing constants for symmetrical electrolytes

(ion pairs/association constants/conductance theory)

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Contributed by Raymond M. Fuoss, November 5, 1979

**ABSTRACT** Earlier theories of electrolytic conductance are reviewed; all of these, with the exception of the Arrhenius–Ostwald theory, are based on physical models. Their theory failed to describe the conductance of strong electrolytes because it did not include the effects (then unsuspected) of long-range forces on mobility. Thermodynamic derivations are independent of model; applied to the postulated equilibrium  $A^+ + B^- \rightleftharpoons A^+B^-$  between free ions and nonconducting paired ions, the thermodynamic pairing constant  $K_a$  equals  $a_p/(a_{\pm})^2$ , and  $\Delta G$ , the difference in free energy between paired ions (activity =  $a_p$ ) and free ions (activity =  $a_{\pm}$ ), equals  $(-RT \ln K_a)$ . Converting to the molarity scale,  $K_a = (1000 \rho/M) [(1-\gamma)/c\gamma^2(y_{\pm})^2]$ . Here  $\rho$  is the density of the solvent of molecular weight  $M$ ,  $c$  is stoichiometric concentration of electrolyte (mol/liter),  $\gamma$  is the fraction of solute present as unpaired ions, and  $y_{\pm}$  is their activity coefficient. The corresponding conductance function  $\Lambda = \Lambda(c; \Lambda_0, R, \Delta G)$  involves three parameters:  $\Lambda_0$ , the limiting equivalent conductance;  $R$ , the sum of the radii of the cospheres of the ions; and  $\Delta G$ . Conductance data for cesium bromide and for lithium chloride in water/dioxane mixtures and for the alkali halides in water are analyzed to determine these parameters. Correlations between the values found for  $R$  and  $\Delta G$  and properties characteristic of salt and solvent are then discussed.

The purpose of this contribution is to discuss the dependence of equivalent conductance  $\Lambda$  on concentration  $c$  and the information concerning ion–ion and ion–solvent interactions that is derivable from conductivity data. By definition,  $\Lambda(c)$  is  $1000 s/c$ ;  $s$  is the observed specific conductance of the solution (corrected for solvent conductance). For all electrolytic solutions,  $s$  approaches zero as  $c$  goes to zero, in such a way that the ratio (which increases with increasing dilution) approaches a constant  $\Lambda_0 = \Lambda(0)$ .

Arrhenius was the first to propose a theoretical explanation of the observed results: neutral molecules of an electrolyte  $AB$  dissociate into current-carrying ions  $A^+$  and  $B^-$ , the equilibrium  $AB \rightleftharpoons A^+ + B^-$  shifting more and more to the right as dilution increases, in accordance with the law of mass action. This hypothesis led to the Ostwald dilution equation; for weak electrolytes, the data were reproduced by the 2-parameter equation  $\Lambda^{-1} = \Lambda_0^{-1} + c\Lambda/K_d\Lambda_0^2$  where  $K_d$  is the dissociation constant.

The Arrhenius hypothesis that the ratio,  $\gamma = [A^+]/c = [B^-]/c$ , of the concentration of free ions to stoichiometric concentration equals the ratio  $\Lambda/\Lambda_0$  leads, however, to a linear law for low concentrations:  $\Lambda = \Lambda_0 - c\Lambda_0/K_d$ . Kohlrausch found that, for typical strong electrolytes, the equivalent conductance approached  $\Lambda_0$  according to the empirical equation  $\Lambda = \Lambda_0 - Sc^{1/2}$ . This so-called “anomaly of strong electrolytes” finally found its explanation in the Debye–Hückel–Onsager theory (DHO theory).

The specific conductance of the dissolved electrolyte is the ratio of current density to field strength  $X$ ; current density equals  $\sum_i n_i e_i v_i$  esu/cm<sup>2</sup>sec; here,  $n_i$  is the number of conducting ions of species  $i$ , with charge  $e_i$  and average velocity

$v_i$ . Single-ion conductance  $\lambda_i$  equals  $\mathcal{F}v_i/X$ . ( $\mathcal{F}$  is the Faraday equivalent.) Therefore,  $\Lambda = A \sum_i (n_i/c)(v_i/X)$ . Arrhenius assumed that the mobility  $u_i = v_i/X$  of the ions was independent of concentration and that  $\Lambda$  changed with concentration solely because the ratio  $(n_i/c)$  was concentration dependent. Debye, on the other hand, assumed that the electrolyte was completely dissociated into ions in solution and that the mobility of the ions was concentration-dependent, as a consequence of the long-range electrostatic forces between ions. For very low concentrations, the DHO hypothesis leads to the equation

$$\Lambda = \Lambda_0(1 - \alpha_0 c^{1/2}) - \beta_0 c^{1/2} = \Lambda_0(1 + \Delta X/X) + \Delta \Lambda_e \quad [1]$$

for the limiting tangent to the conductance curve, in complete agreement with the empirical findings of Kohlrausch. The coefficients  $\alpha_0$  and  $\beta_0$  are predicted by the DHO theory of the relaxation term  $\Delta X/X$  and the electrophoretic term  $\Delta \Lambda_e$  and are independent of model.

The theory of conductance around 1930 presented a disturbing dichotomy: weak electrolytes were adequately described by the Arrhenius–Ostwald equations, and the limiting behavior of strong electrolytes was exactly predicted by the DHO theory. MacInnes and Shedlovsky (1) suggested that both theoretical approaches should be applied: that is, the fraction of solute that contributes to conductance depends on concentration, and also the mobility of the ions is concentration-dependent. Their value for the dissociation constant of acetic acid in water agreed exactly with the Harned and Ehlers value (2) which had been derived by thermodynamic analysis of electromotive force data. Long before 1930, Kraus had shown that the conductance curves for typical salts such as sodium chloride in liquid ammonia ( $D = 22$  at  $-33^\circ\text{C}$ ) were quite similar to the curve for acetic acid in water, although  $\Lambda(c)$  for sodium chloride in water conformed to the DHO theory. Sodium chloride is a weak electrolyte in ammonia and a strong electrolyte in water? The dilemma was (to first approximation) resolved by Fuoss and Kraus (equation 7 in ref. 3); they proposed that, for electrolytes in general,  $\Lambda(c)$  decreases as concentration increases, both because the fraction of solute that contributes to conductance decreases with increasing concentration and because the mobility of the ions decreases on account of increasing effects of interionic forces. For strong electrolytes, the ion pair [proposed by Bjerrum (4)] assumed the role of the Arrhenius neutral molecule. Their model was the same as the DHO model (rigid charged spheres of diameter  $a$  in a continuum, the “primitive model”). For the association equilibrium  $A^+ + B^- \rightleftharpoons A^+B^-$ , their conductance equation is  $\Lambda = \gamma(\Lambda_0 - Sc^{1/2}\gamma^{1/2})$ , where  $\gamma = [A^+]/c = [B^-]/c$  and the association constant is  $K_A = (1 - \gamma)/c\gamma^2 y_{\pm}^2$ . Here  $y_{\pm}$  is the activity coefficient on the molarity scale (mol/liter).

This equation [or the Shedlovsky modification (equation 8 in ref. 5; ref. 6)] was used for about two decades; for electrolytes

Abbreviation: DHO, Debye–Hückel–Onsager.

whose conductance curves approach the limiting tangent (Eq. 1) from below, it reproduced the observed values within about  $\pm 0.1\%$ . But the equation could not describe conductance curves that approach the tangent from above because  $0 < \gamma < 1$ . An explanation for the latter type was found in the "higher terms" of the relaxation field and the electrophoretic velocity. Eq. 1 is a first approximation obtained by mathematical approximations that drop all terms in the fundamental differential equations (7) that would lead to terms of order higher than  $c^{1/2}$  in  $\Lambda(c)$ . Integrations (8, 9) to second approximation gave a conductance equation of the form

$$\Lambda = \Lambda_0 - Sc^{1/2} + Ec \ln c + Jc - J'c^{3/2} + HT \quad [2]$$

where  $HT$  represents terms of order higher than  $c^{3/2}$  in concentration. For strong electrolytes, the positive term  $Jc$  is numerically greater than the negative terms ( $Ec \ln c$ ,  $c < 1$ , so  $\ln c < 0$ ) and ( $-J'c^{3/2}$ ); therefore, theoretical function 2 lies above the limiting tangent. Instead of the above series expansion, which reproduces observed conductance curves for 1-1 electrolytes in water only up to about 0.01 eq/liter, retention of the higher terms by explicit integrations (10) led to a conductance equation that fitted the data up to about 0.1 eq/liter in water. Symbolically, the equation is  $\Lambda = \gamma[\Lambda_0(1 + \Delta X/X) + \Delta \Lambda_e]$  where  $\Delta X/X$  and  $\Delta \Lambda_e$  are explicit functions of concentration. Removing (mathematically) the paired ions from the ionic population permits use of the linearized Poisson-Boltzmann equation as the starting point in the derivation of  $\Delta X$  and  $\Delta \Lambda_e$ . Of course, there is an upper limit beyond which the pairing device may no longer be used; this is  $c_{\max} < 3.2 \times 10^{-7} (D_{25})^3$ , where the effects of short range three-ion interactions may no longer be neglected (equation 12 in ref. 11).

Until 1978, nearly all theoretical work on conductivity was based on the primitive model. One consequence of this approach was the isodielectric rule: a given electrolyte ( $a$  fixed) should have the same association constant in *chemically different* solvents that have the same dielectric constant (12). Numerous violations of the isodielectric rule were discovered (13, 14); the only possible deduction was that the association constant is not simply a function dependent only on contact distance and dielectric constant but, rather, it depends also on short range ion-solvent interactions which are system-specific. A new model was proposed (15) in which solvent-separated pairs were introduced as an intermediate transition state between unpaired ions and contact pairs; for this model,  $K_A = K_R(1 + K_s)$ , where  $K_R$  describes the diffusion controlled step  $A^+ + B^- \rightleftharpoons (A^+ \dots B^-)$  and  $K_s$  describes the formation of contact pairs by a series of interchanges of sites between solvent molecules and ions. The latter depend of course on short-range ion-solvent interactions and are different for structurally different solvents. The conductance function derived for the paired-ion model is a three-parameter equation  $\Lambda = \Lambda(c; \Lambda_0, R, E_s)$  where  $R$  is the diameter of the Gurney cosphere and  $E_s$  is the difference in free energy between solvent-separated pairs and contact pairs. The equation reproduces observed conductances within experimental error, and some correlations between the parameters  $R$  and  $E_s$  and molecular parameters characteristic of ions and solvent molecules have been found (15-17). This theory, however, is a theory developed for a particular model; it would be preferable to have a conductance theory that is independent of model.

Thermodynamics is independent of model; it was the approach used by Arrhenius and, as pointed out above, this theory failed to achieve generality only because it neglected to consider the effects (then unsuspected) of long-range Coulomb forces between ions on the mobility and on the postulated equilibrium between free conducting ions and nonconducting dipolar pairs.

Let us now return to first principles by applying Gibbs thermodynamics to the postulated pairing process [ $A^+ + B^- \rightleftharpoons A^+B^-$ ], for which  $K_a = a_p/(a_{\pm})^2$ ;  $a_p$  represents the activity of the pairs and  $a_{\pm}$  that of the free ions. The activity  $a_j$  of the  $j$ th component of a system equals  $f_j N_j$ ;  $f_j$  is the rational activity coefficient introduced by G. N. Lewis and  $N_j$  is the mole fraction of that component. Because conductance is a volume property, concentrations are conventionally expressed in terms of  $c$  mol/liter rather than as mole fractions. The activity is

$$a_j = c_j y_j (M/1000\rho) \quad [3]$$

where  $y_j$  is the activity coefficient on the molarity scale (18),  $M$  is the molecular weight of the solvent, and  $\rho$  is its density ( $\text{g}/\text{cm}^3$ ). For a mixture of two solvents of molecular weights  $M_1$  and  $M_2$  and weight fractions  $w_1$  and  $w_2$ ,  $M$  is replaced by the mole-fraction average molecular weight  $M_{av} = M_1 M_2 / (w_1 M_2 + w_2 M_1)$ . If we neglect the long-range effects of ion-dipole interactions,  $y_p = 1$ . Substituting  $c(1 - \gamma)$  for the concentration of pairs, and  $c\gamma$  for that of the free ions,

$$K_a = (1000\rho/M)[(1 - \gamma)/c\gamma^2 y_{\pm}^2] \quad [4]$$

where  $y_{\pm}$  equals  $\exp[-\tau/(1 + \kappa R)]$ . Here  $\tau = \beta\kappa/2$ ,  $\kappa^{-1}$  is the Debye distance,  $\beta = e^2/DkT$ , and  $R$  is the distance parameter derivable from conductance data. For free ions,  $r_{ij} > R$ ; for them, the long-range effects  $\Delta X/X$  and  $\Delta \Lambda_e$  are calculable by continuum theory. The factor in brackets in Eq. 4 is the conventional conductimetric pairing constant  $K_A = (1 - \gamma)/c\gamma^2 y_{\pm}^2$ . For the pairing equilibrium,

$$-RT \ln K_a = \Delta G = \Delta H - T\Delta S \quad [5]$$

( $R$  is the gas constant.) Summarizing at this point: given the conductimetric pairing constant  $K_A$ , the free energy change for the postulated equilibrium can be determined. This opens the way to a search for correlations between  $\Delta G$ ,  $\Delta H$ , and  $\Delta S$  on the one hand and basic properties of solutes and solvents on the other.

We now consider the conductance function  $\Lambda(c)$  from which the parameters  $\Lambda_0$ ,  $R$ , and  $\Delta G$  are to be derived by giving to the computer a set of conductance data ( $c_j$ ,  $\Lambda_j$ ;  $j = 1, 2, \dots, N$ ) for  $N$  data points and the explicit function  $\Lambda(c)$ , together with programs\* designed to find the values of these parameters which minimize  $\Sigma = \Sigma_j [\Lambda_j(\text{calc.}) - \Lambda_j(\text{obs.})]^2$ . For reasons that will be explained below, the symbolic conductance equation is expanded into

$$\Lambda = \gamma[\Lambda_0(1 + \Delta X_E/X) + \Delta \Lambda_v + \Delta \Lambda_H + \Delta \Lambda_e] \quad [6]$$

In Eq. 6,  $\Delta X_E$  is the part of the relaxation field generated by purely electrostatic interactions between free ions;  $\Delta \Lambda_v = \Lambda_0(\Delta X_v/X)$  is the part of the relaxation field term due to the perturbation of that field by the electrophoretic flow and is equal, by the Onsager reciprocal relations, to the change in electrophoretic current caused by the perturbation potential; this term is included in the numerical calculation with  $\Delta \Lambda_e$ , which is proportional to the electrophoretic current (both  $\Lambda_0 \Delta X_v/X$  and  $\Delta \Lambda_e$  have the same coefficients,  $\beta_0 c^{1/2} \gamma^{1/2}$ );  $\Delta \Lambda_H$  is a hydrodynamic-hydrodynamic interaction term derived by Sändig and Feistel (19). For convenience in programming, the terms of Eq. 6 are regrouped as follows:

$$\Lambda = \gamma[\Lambda_0(1 + \Delta X_E/X) + HXV + HY] \quad [7]$$

\* Listings of the FORTRAN programs and examples of their use are available on the writer's receipt of a postal money order (\$2.00 from USA or Canada; \$4.00 from abroad) payable to Department of Chemistry, Yale University (New Haven, CT 06520), to cover postage and reproduction costs.

where  $HXV = \Lambda_0(\Delta X_v/X) = -\beta_0 c^{1/2} \gamma^{1/2} [1 + F_1(\tau, \kappa R)]$  (i.e., independent of  $\Lambda_0$ ) and  $HY = \Delta \Lambda_e + \Delta \Lambda_H$ . The relevant equations for the computer programs are given in the *Appendix*.

Calculation of  $\Delta X_E/X$ ,  $\Delta X_v$ ,  $\Delta \Lambda_e$  has already been presented (20). Briefly summarized, the equation of continuity was solved for the perturbation  $f'_\mu$  in the pair-wise distribution function  $f_\mu = n_j n_\mu = n_j n_i \exp(-e_i \psi_j/kT)$ , subject to the boundary conditions  $f'_\mu(\infty) = 0$ ,  $f'_\mu(R) = 0$ ; the result was then substituted in the Poisson equation to obtain  $\psi'$ , the perturbation of the potential due to the asymmetry of the ionic atmosphere generated by the external field  $X$ , subject to the boundary conditions  $\nabla \psi'(\infty) = 0$ ,  $(r \partial \psi' / \partial r - \psi')_R = 0$ . The electrostatic term  $\Delta \Lambda_e$  was obtained by integration of the Navier-Stokes equation using the Oseen hydrodynamic tensor to calculate velocities. In the 1978 derivation, the 1932 approximation  $\text{div}[\mathbf{V}_2(\mathbf{r}_2)] = 0$  was used.<sup>†</sup> Sändig and Feistel (19) calculated the leading term of the thereby neglected  $c \ln c$  term in  $\Lambda(c)$ ; their value is  $(+0.5 \beta_0 \beta_0 / 16 c^{1/2}) c \ln c$ ; this of course comes from a term proportional to the negative exponential integral  $E_n(x) = -0.577216 - \ln x + x + \dots$ ,  $x = \kappa R$ . The term  $\Delta \Lambda_H$  in the revised Eq. 7 includes these previously neglected terms; some small terms of order  $c$  and  $c^{3/2}$  have been dropped, but the significant part of  $\Delta \Lambda_H$  is now included. (Other terms of order  $c$ ,  $c^{3/2}$ , and higher have also been neglected: see section 5 of ref. 20.)

I next present the results obtained by analysis of conductance data for cesium bromide and for lithium-7 chloride in water/dioxane mixtures (21). Table 1 gives values of the parameters  $\Lambda_0$ ,  $K_A$ ,  $G_S = \Delta G/RT$ , and  $10^3 R$  (cm) for these salts in mixtures identified by their dielectric constants  $D$  listed in the first column. The average value of  $\sigma$  (standard deviation expressed as percentage of  $\Lambda_0$ ) is 0.02%; for 9 of the 28 systems, the data are reproduced by Eq. 7 to 0.010% or better. Values of the parameters were obtained by the 3-PARAMETER program for CsBr in the first five systems listed and for the first two listed for LiCl. The data for all the systems were also analyzed by program SCAN. The  $\sigma$ - $R$  curves showed minima that were quite sharp for some and rather shallow for others. For these curves, there are, of course, two values  $R_1$  and  $R_2$  ( $R_1 < R_{min} < R_2$ ) which correspond to the same value of  $\sigma$ ; the precision,  $P_R$ , with which  $R$  can be determined is given by  $(\sigma_{1,2} - \sigma_{min})\% / (R_2 - R_1)$ , shown in the last column of Table 1. The sharpest minima were obtained for the solutions in water ( $D = 78.35$ ), for which many data points from replicate runs, covering a wide range of concentration, were available. For these solutions (and for the five others for which the 3-parameter program converged), the values of  $\Lambda_0$  and  $K$  calculated by using the value of  $R$  corresponding to  $\sigma$  (*min*) agreed exactly with the values obtained by the 3-parameter program. The data for the mixtures were from single runs of five to eight points; as the  $P_R$  values show, the minima in the  $\sigma$ - $R$  curves for these systems are much less sharp; the consequence is, of course, that the uncertainty in  $R$  is rather large.

For CsBr in water,  $R$  is 3.86 Å; the sum of the Pauling radii for the ions is 3.85. For these large ions, the field strength at the surface evidently is so low that it has little effect on the solvent. For LiCl,  $R = 5.50$ ; the sum of the Pauling radii for this salt is 2.41. The difference, 3.09, is slightly greater than 2.76, the diameter of a water molecule; this result suggests that the lithium ion is hydrated in solution, all nearest neighbors being water

Table 1. Parameters for salts in dioxane-water mixtures

$D$	$\Lambda_0$	$K_A$	$G_S$	$10^3 R$	$\sigma, \%$	$10^3 P_R$
Cesium bromide						
78.35	155.37	0.60	-3.50	3.86	0.003	10.2
74.75	142.82	0.59	-3.49	3.69	0.004	3.9
71.90	133.42	0.54	-3.35	3.43	0.002	1.0
70.28	128.45	0.67	-3.54	3.83	0.010	2.8
59.91	102.00	1.13	-3.97	3.89	0.002	4.0
55.58	93.20	1.21	-3.99	3.59	0.006	0.3
46.37	77.23	3.48	-4.94	4.12	0.018	0.5
45.91	76.58	3.14	-4.83	3.84	0.028	1.6
43.70	73.39	4.32	-5.12	4.19	0.014	1.1
41.74	70.68	5.00	-5.24	4.20	0.018	0.5
38.59	66.90	6.85	-5.51	4.25	0.014	1.6
30.48	58.01	22.7	-6.58	5.22	0.006	0.5
24.17	52.18	76.2	-7.68	6.50	0.019	0.3
20.11	48.64	169	-8.38	6.76	0.021	0.4
16.73	45.81	482	-9.36	8.15	0.073	1.4
16.54	45.89	537	-9.46	8.88	0.061	0.8
14.08	43.31	1250	-10.24	10.65	0.017	0.2
13.83	43.41	1430	-10.37	9.60	0.017	0.3
13.43	42.71	1615	-10.47	8.80	0.041	1.0
Lithium-7 chloride						
78.35	115.03	0.87	-3.87	5.50	0.006	25.9
62.25	81.49	1.62	-4.34	5.64	0.006	12.1
49.99	64.66	2.16	-4.50	4.65	0.013	1.4
41.37	55.58	6.58	-5.50	6.38	0.035	1.4
27.18	44.40	30.0	-6.80	5.83	0.030	6.0
21.97	40.98	52.5	-7.26	7.00	0.047	2.3
18.13	38.84	206	-8.54	8.20	0.023	1.5
18.07	38.81	205	-8.53	7.15	0.026	2.3
16.23	37.83	372	-9.10	9.15	0.012	1.1

molecules. The ion pair for this salt is a solvent-separated pair. As the dielectric constant of the solvent decreases,  $R$  increases systematically. This behavior suggests that  $R$  is the sum of the radii of the Gurney cospheres of the two ions; the lower the dielectric constant, the farther will the charge on a given ion affect the properties of the solvent. This definition of  $R$  confirms the use of  $R$  as the lower limit in the boundary conditions for calculating long-range interactions (16).

The free energy for all the systems is negative and becomes more negative as  $D$  decreases. The free energy is the sum of two terms,  $\Delta H$  and  $-T\Delta S$ . Because the enthalpy contains the work done in separating a contact pair to "infinity," this part of the enthalpy is negative and increases numerically as  $D$  decreases. The enthalpy also contains a positive term due to the replacement of a nearest-neighbor solvent molecule by the partner ion in the last step in the formation of a contact pair. Because two unpaired ions can be represented by many configurations, whereas a contact pair corresponds to a small number of configurations (the partner ion must occupy one of the  $z$  nearest-neighbor sites), the entropy decreases so  $-T\Delta S$  is positive. Because Table 1 shows that  $R$  depends on  $D$ ,  $\Delta S$  does also. For these systems, a plot of  $\Delta G/RT$  (or of  $\log K_A$ ) against  $1/D$  is linear in the range  $D < 35$ ; from the slope, the distance parameter for the equivalent primitive model (for which  $\Delta H = -e^2/aDkT$  and  $\Delta S = 0$ ) is 6.2 Å.

Table 2 gives the values of the parameters for the alkali halides (except for potassium fluoride for which no data could be found). For sodium and potassium chlorides and for cesium bromide and iodide, precision data covering a wide concentration range are available in the literature; for these four salts, the 3-parameter program converged. For the 15 other systems, the available data covered a rather short range of concentra-

<sup>†</sup> In ref. 7,  $\mathbf{V}(\mathbf{r}_2)$  was defined as the bulk velocity at the point located by vector  $\mathbf{r}_2$ . Footnote 2 on p. 2700 of ref. 7 stated that "we here neglect the hydrodynamic motion of the fluid at  $dV_2$  caused by the presence of a moving  $j$ -ion at  $dV_1$ . This approximation amounts to dropping terms of the order  $c \log c$  in the final results."

Table 2. Parameters for the alkali halides

Salt	$\Lambda_0$	$K_A$	$G_S$	$10^8 R$	$\sigma, \%$	Ref.
LiF	94.12	1.97	-4.69	4.72	0.020	22
LiCl	115.12	0.75	-3.72	5.17	0.011	21
LiBr	116.89	0.71	-3.55	5.31	0.010	22, 23
LiI	116.03	0.54	-3.39	5.52	0.015	21
NaF	105.49	0.85	-3.85	5.07	0.008	24
NaCl	126.53	0.82	-3.82	5.52	0.015	25
NaBr	128.41	0.73	-3.70	5.66	0.023	24
NaI	127.17	0.60	-3.50	5.87	0.012	22
KCl	149.90	0.53	-3.37	4.52	0.011	25
KBr	151.74	0.44	-3.20	4.66	0.021	24
KI	150.61	0.40	-3.10	4.87	0.016	26
RbF*	132.78	0.30	-2.21	3.8	0.005	22
RbCl	153.64	0.24	-2.57	3.29	0.009	27
RbBr	155.45	0.23	-2.53	3.43	0.004	28
RbI	154.01	0.24	-2.58	3.64	0.004	29
CsF*	132.79	0.49	-3.30	4.8	0.008	22
CsCl	153.05	0.62	-3.54	3.50	0.012	30
CsBr	155.39	0.54	-3.39	3.64	0.006	31
CsI	154.18	0.50	-3.32	3.85	0.003	31

\* Values obtained by the scanning program.

tions, and the highest concentrations were for the most part considerably lower than  $10^{-7}D^3$ . It can be shown (32) that  $\Lambda' = \Lambda_0 + A\tau^2 + B\tau^3$ , where  $\Lambda'$  is defined by

$$\Lambda' = [\Lambda(\text{obs}) + \beta_0 c^{1/2}(1 + 0.5\tau \ln 2\tau)] / [1 - \alpha_0 c^{1/2} + (\tau^2/3) \ln(2\tau)] \quad [8]$$

In Eq. 8,  $\tau^2$  is proportional to concentration. The values of  $R$  and  $K_A$  are determined in principle by the difference ( $\Lambda' - \Lambda_0$ ); obviously, if the concentration is small, this difference is small and the precision in determining  $R$  and  $K_A$  from such data is poor. For most of the 15 systems mentioned above, the  $\sigma$ - $R$  curves were practically horizontal (i.e., a wide range of  $R$  values fitted the data equally well). Above, I noted that the  $R$  value for CsBr matched the sum of the Pauling radii of the two ions, and that the  $R$  value for LiCl was nearly equal to the sum of the Pauling radii plus the diameter of a water molecule. In order to obtain values of  $\Lambda_0$  and  $K_A$  from the data for systems that showed a very shallow minimum on the  $\sigma$ - $R$  plots, values of  $R$  were preset at the sum of the Pauling radii for the cesium and rubidium salts, at  $(a^+ + a^- + 2.76)$  for the lithium and sodium salts, and at  $(a^+ + a^- + 1.38)$  for the potassium salts. This is equivalent to assuming that the cesium and rubidium pairs are contact pairs, that the lithium and sodium pairs are solvent separated, and that, on average, half of the  $KX$  pairs are solvent separated. This choice is supported by the values of the single ion conductances, which at 25°C are  $\lambda(\text{Li}^+) = 38.7$ ,  $\lambda(\text{Na}^+) = 50.1$ ,  $\lambda(\text{K}^+) = 73.5$ ,  $\lambda(\text{Rb}^+) = 77.8$ , and  $\lambda(\text{Cs}^+) = 77.3$  (33).

The pairing constants and the values of  $\Delta G/RT$  for cesium chloride, bromide, and iodide are practically identical; the difference in the conductance curves is due to the difference in limiting conductances and to different values of  $\Delta X/X$  and  $\Delta \Lambda_e$  at a given concentration (these terms depend on  $\kappa R$ , and  $R$  is different for different salts). The rubidium halides are less associated than the cesium halides; the values of  $K_A$  are nearly the same for these salts. The values of  $\Delta G/RT$  for the potassium and sodium halides become less negative in the sequence fluoride, chloride, bromide, iodide; this is the expected sequence because the electrostatic part of the enthalpy term should decrease as the halide ion becomes larger. For the lithium halides, the fluoride has the greatest value of  $K_A$  among the alkali halides;  $K_A$  decreases as the halide ion becomes larger. The rate of increase of  $K_A$  with decreasing size of the anion is much more rapid than for the sodium and potassium halides. For a given

halide ion,  $K_A$  increases in the sequence  $K_A(\text{Li}^+) > K_A(\text{Na}^+) > K_A(\text{Cs}^+) > K_A(\text{K}^+) > K_A(\text{Rb}^+)$ . Excluding the anomalous position of the cesium salts, the order corresponds to the order of increasing size of the cation, again as expected, due to the decrease in  $\Delta H$ . The cesium ion has the greatest polarizability of the alkali ions. The enhanced pairing of the cesium halides, compared to that of the potassium and rubidium halides, may well be the consequence of the attractive force between the dipole induced by the halide ion in the cesium ion and the halide ion.

## APPENDIX

The conductance equation is

$$\Lambda = \gamma[\Lambda_0(1 + RXE) + HXV + HY].$$

Expressed as functions of  $t = \kappa R$ ,  $\beta = e^2/DkT$ ,  $q^2 = 1/2$ ,

$$RXE = -\beta\kappa/6(1 + q)(1 + t)(1 + qt) + \beta^2\kappa^2[(\ln t)/12 + FH2 + \beta\kappa(FH3)]$$

$$HXV = -\beta_0 c^{1/2} \gamma^{1/2} \beta \kappa [(H2)/16 - 0.125 \ln t]$$

$$HY = -\beta_0 c^{1/2} \gamma^{1/2} \{1/(1 + t) + \beta\kappa[(\ln t)/16 + (H1)/2 - 0.03608 + t/16]\}.$$

Interpolating polynomials for the functions  $H1$ ,  $H2$ ,  $FH2$ , and  $FH3$ , valid over the range  $0 < t < 0.8$ , are given in the appendix of ref. 15.

- MacInnes, D. A. & Shedlovsky, T. (1932) *J. Am. Chem. Soc.* **54**, 1429-1438.
- Harned, H. S. & Ehlers, R. W. (1932) *J. Am. Chem. Soc.* **54**, 1350-1357.
- Fuoss, R. M. & Kraus, C. A. (1933) *J. Am. Chem. Soc.* **55**, 476-488.
- Bjerrum, N. (1926) *K. Dan. Vidensk. Selsk.* **7**, 1-48.
- Shedlovsky, T. (1938) *J. Franklin Inst.* **225**, 739-743.
- Fuoss, R. M. & Shedlovsky, T. (1949) *J. Am. Chem. Soc.*, **71**, 1496-1497.
- Onsager, L. & Fuoss, R. M. (1932) *J. Phys. Chem.* **36**, 2689-2778.
- Pitts, E. (1953) *Proc. R. Soc. Edinburgh Sect. A.* **217**, 43-70.
- Fuoss, R. M. & Onsager, L. (1955) *Proc. Natl. Acad. Sci. USA* **41**, 274-283.
- Fuoss, R. M. & Hsia, K. L. (1967) *Proc. Natl. Acad. Sci. USA* **57**, 1550-1557; correction, *ibid*, p. 1818.
- Fuoss, R. M. (1935) *J. Am. Chem. Soc.* **57**, 2604-2607.
- Fuoss, R. M. (1958) *J. Am. Chem. Soc.* **80**, 5059-5061.
- D'Aprano, A. & Fuoss, R. M. (1969) *J. Am. Chem. Soc.* **91**, 211-212.
- D'Aprano, A., Komiyama, J. & Fuoss, R. M. (1976) *J. Solution Chem.* **5**, 279-295.
- Fuoss, R. M. (1978) *Proc. Natl. Acad. Sci. USA* **75**, 16-20.
- Fuoss, R. M. (1978) *J. Am. Chem. Soc.* **100**, 5576-5578.
- Schiavo, S., Fuoss, R. M., Marrosu, G. & Guida, G. (1979) *J. Solution Chem.* **8**, 557-571.
- Harned, H. S. & Owen, B. B. (1958) *The Physical Chemistry of Electrolytic Solutions* (Reinhold, New York), 3rd Ed., Eq. (1-8-11).
- Sändig, R. & Feistel, R. (1979) *J. Solution Chem.* **8**, 411-426.
- Fuoss, R. M. (1978) *J. Phys. Chem.* **82**, 2427-2440.
- Mattina, C. F. & Fuoss, R. M. (1975) *J. Phys. Chem.* **79**, 1604-1610.
- Pethybridge, A. D. & Spiers, O. J. (1977) *J. Chem. Soc. Faraday Trans.* **73**, 768-775.
- Broadwater, T. L. & Kay, R. L. (1970) *J. Phys. Chem.* **74**, 3802-3812.
- Reynolds, A. F. (1966) Dissertation (Yale University, New Haven, CT).

25. Chiu, Y. C. & Fuoss, R. M. (1968) *J. Phys. Chem.* **72**, 4123–4129.
26. Chambers, J. F. (1958) *J. Phys. Chem.* **62**, 1136–1138.
27. Kunze, R. W. & Fuoss, R. M. (1963) *J. Phys. Chem.* **67**, 914–916.
28. Lind, J. E., Jr. & Fuoss, R. M. (1962) *J. Phys. Chem.* **66**, 1727–1729.
29. Fabry, T. L. & Fuoss, R. M. (1964) *J. Phys. Chem.* **68**, 974–976.
30. Justice, J. C. & Fuoss, R. M. (1963) *J. Phys. Chem.* **67**, 1707–1708.
31. Hsia, K. L. & Fuoss, R. M. (1968) *J. Am. Chem. Soc.* **90**, 3055–3060.
32. Schiavo, S., Fuoss, R. M. & Marrosu, G. (1980) *J. Solution Chem.* **9**, in press.
33. Stokes, R. H. & Robinson, R. A. (1959) *Electrolyte Solutions* (Academic, New York), 2nd Ed., p. 463.