

Table I. Scope of Independent Variables

Concentration dependent data	
Temperatures, °C	
3, 5, 10, 15, 20, 25, 35, 45, 55	
Pressures, atm (typical, NaCl at 15°C)	
1, 207, 410, 621, 814, 1000, 1264, 1475, 1748, 1994, 2240	
Solution concentrations, mM	
LiCl	3.60 6.42 10.00 14.40
NH ₄ Cl	3.59 6.43 9.98 14.41 19.63
NaCl	3.61 6.41 9.99 14.43 19.57
KCl	1.62 3.62 6.42 10.00 19.61
RbCl	3.61 6.41 9.99 14.42 19.59
(Et) ₄ NCl	3.61 6.40 10.00 14.40
3 mM data	
Temperatures, °C	
3, 5, 10, 15, 20, 25, 35, 45, 55	
Pressures, atm (all salts)	
1, 200, 400, 600, 1000, 1250, 1500, 1750, 2000, 2250	

close to the compressibility of the Pt metal and involved a correction at 2000 atm, just small enough to be ignored.

The data were taken at rounded temperatures (Table I) measured with Hg-in-glass thermometers accurate to within 0.05°C (NBS). Pressures were measured with a Bourdon tube gauge (Heise Co., Newton, Conn.), and are accurate to 0.1% of full scale (3 atm). Other details of the apparatus and techniques used were described elsewhere (1, 2, 4, 8, 9).

After all of the factors already mentioned were taken into account, the accuracy attained in the high pressure coefficients of conductance of dilute aqueous solutions (≥ 2 mM) of strong electrolytes is about 0.1% which is believed to be the most reliable information obtained to date.

Scope of Data Investigation. Six strong 1,1 electrolytes, LiCl, NH₄Cl, NaCl, KCl, RbCl, and (Et)₄NCl, were studied over the range 3–55°C, and the approximate ranges 1–2250 atm and 3–15 mM. The actual way in which the ranges were covered is shown in Table I. This investigation, with the exception of the (Et)₄NCl data, established the reproducibility of the data and the appropriate applicability of the pressure-dependent Debye-Hückel-Onsager limiting conductance equation

$$\kappa_p/\kappa_1 = (\kappa_p/\kappa_1)^\circ \left[1 + \left\{ \frac{S_1}{\Lambda_1^\circ} - \frac{S_p}{\Lambda_p^\circ} \left(\frac{\rho_p}{\rho_1} \right)^{1/2} \right\} (c_1)^{1/2} \right] \quad (1)$$

$S \equiv \alpha\Lambda^\circ + \beta$, where α and β are the usual constants (13). ρ is, strictly speaking, the density of the solution; water densities were used and are sufficiently accurate.

A full description of the applicability of this equation was given elsewhere (9). κ_p/κ_1 data increased linearly with $(c_1)^{1/2}$ up to ~ 20 mM, to within 0.1% in κ_p/κ_1 . Without benefit of the equation, somewhat lower slopes were usually drawn through the data points owing to what are now recognized as negative deviations from limiting law (0.1% at 2000 atm and 20 mM).

Thereafter, it was sufficient to study only one appropriate solution concentration (~ 3 mM) for each salt, and to determine infinite dilution values using the theoretical limiting slopes. This practice greatly accelerates the acquisition of data. The five strong 1,1 electrolytes studied at ~ 3 mM only were CsCl, KF, KBr, KI, and KNO₃. The temperature and pressure ranges were essentially the same as those mentioned earlier. All five salts were studied simultaneously in the same pressure vessel. Thus, the actual temperatures and pressures shown in Table I apply to all five systems.

The measured cell resistances corresponding to the above

Table II. Representative Original Data of LiCl System at 25°C

P, atm	Cell resistance, ohms			
	c, mM			
	3.60	6.42	10.0	14.4
1	1474.1 ^a	8646.5	5595.1	3935.1
200	1446.0	8483.7	5489.3	3860.2
400	1421.6	8340.8	5306.2	3794.4
800	1384.2	8122.0	5253.8	3693.3
1000	1369.4	8037.2	5198.7	3654.0
1500	1344.6	7890.8	5102.9	3585.8
1750	1336.4	7842.6	5071.4	3563.4
2000	1330.8	7809.0	5049.4	3547.5
2250	1327.8	7792.8	5038.7	3539.6
1287	1354.4	7944.0	5138.0	3610.4
600	1403.7	8224.6	5322.1	3740.2
1	1476.9	8650.8	5599.3	3935.9

^a Rod-ring electrode design, requiring no correction for the pressure coefficient of the cell constant. All others are capillary cells, where corrections have been made, approximately equal to the compressibility of borosilicate glass.

variety of conditions comprise some 2700 data points (2) too numerous to be included here. For illustration typical original data for the LiCl system are given in Table II.

Treatment of Data. The first step in data reduction is the division of each measured resistance at pressure P into the corresponding value at 1 atm which gives the ratio R_1/R_p ($\equiv \kappa_p/\kappa_1$ after correction for cell constant variation with P). The κ_p/κ_1 ratio is then plotted against $c^{1/2}$, and extrapolation to infinite dilution is made with the help of the theoretical limiting law (Equation 1) adapted for variation in pressures (9).

For the LiCl, NH₄Cl, KCl, NaCl, and RbCl systems, where data were collected as a function of salt concentration, $(\kappa_p/\kappa_1)^\circ$ was found by direct graphical extrapolation with the aid of the theoretical limiting slope. This treatment, applied to the (Et)₄NCl data, was not entirely satisfactory. Tentatively, only the raw data for this system are reported (2). For the five remaining salt systems, Equation 1 was solved explicitly for $(\kappa_p/\kappa_1)^\circ$ (this ratio is implicit in the slope term), and the latter was then calculated directly from the 3 mM data.

$(\kappa_p/\kappa_1)^\circ$ values were fitted to the third-order polynomial expression

$$\ln (\kappa_p/\kappa_1)^\circ = \sum_{N=0}^3 D(N)P^N \quad (2)$$

by the method of least squares. P designates the gauge pressure in the experiment. At each temperature, pressure ratios are adequately represented by four entries per salt system— $D(0)$, $D(1)$, $D(2)$, and $D(3)$. These coefficients are given in Table III.

That the polynomial expression accurately represents the data is illustrated in Table IV. Typical differences between measured 3 mM data in conjunction with the theoretical slope) and calculated values of $(\kappa_p/\kappa_1)^\circ$, shown for the CsCl system, are well within the 0.1% experimental accuracy. Also given are similar results for the KI system, the least satisfactory of the entire series and whose fit is still within experimental error.

Reliability of Infinite Dilution Data. The accuracy of the conductance ratios at infinite dilution is influenced by the accuracy of the concentration-dependent data points as well as their degree of scatter.

Important factors are the constancy of temperature over the pressure cycles which start and end at 1 atm and attainment of thermal equilibrium after each pressure increment. The accuracy of the pressure coefficient is not a strong function of the absolute temperature as long as the temperature is