Table III. Polynomial Coefficients in Expression $\ln (\kappa_p/\kappa_1)^\circ = \sum_{N=0}^{3} D(N)P^N$

	Temperatures, °C								
LiCl	3	5	10	15	20	25	35	45	55
$D(0) \times 10^4$	3.215	−1.657	−1.376	−1.741	−1.027	−0.6098	−0.1705	−0.4221	0.1116
$D(1) \times 10^4$	1.958	1.851	1.592	1.363	1.159	1.018	0.7664	0.5796	0.4430
$D(2) \times 10^8$	−6.755	−6.406	−5.538	−4.591	−3.670	−3.354	−2.465	−1.903	−1.519
$D(3) \times 10^{12}$	7.979	7.631	6.896	5.285	3.635	3.731	2.444	1.737	1.262
NH_4Cl									
$D(0) \times 10^4$	0.7839	0.3419	−2.503	−0.2943	0.3560	−0.7373	0.5812	−1.221	−1.581
$D(1) \times 10^4$	1.775	1.656	1.417	1.205	1.049	0.8977	0.6736	0.5258	0.3864
$D(2) \times 10^8$	−6.965	−6.281	−5.394	−4.541	−3.970	−3.314	−2.473	−2.223	−1.647
$D(3) \times 10^{12}$	9.099	7.624	6.543	5.346	4.630	3.491	2.215	2.505	1.416
NaCl									
$D(0) \times 10^4$	−0.2432	2.946	−1.463	−1.513	−2.031	−0.9871	−2.715	0.2682	−0.3163
$D(1) \times 10^4$	1.663	1.532	1.321	1.140	0.9589	0.8182	0.6113	0.4326	0.3305
$D(2) \times 10^8$	−6.412	−5.719	−4.927	−4.329	−3.481	−2.959	−2.354	−1.622	−1.520
$D(3) \times 10^{12}$	8.166	6.653	5.708	5.143	3.728	2.881	2.260	1.232	1.681
KCl									
$D(0) \times 10^4$	8.019	−1.855	−0.3459	−1.707	−1.382	−0.0859	−0.8493	−1.237	3.864
$D(1) \times 10^4$	1.655	1.536	1.318	1.125	0.9751	0.8293	0.6314	0.4739	0.3012
$D(2) \times 10^8$	−6.312	−5.513	−4.811	−4.038	−3.496	−2.945	−2.338	−1.813	−0.7245
$D(3) \times 10^{12}$	8.261	6.147	5.661	4.450	3.759	2.930	2.313	1.583	−1.499
RbCl									
$D(0) \times 10^4$	−1.560	−3.063	−0.1641	−1.564	−0.1306	−1.837	−0.9944	−0.3806	0.2574
$D(1) \times 10^4$	1.609	1.482	1.265	1.071	0.9195	0.7893	0.5729	0.4060	0.2953
$D(2) \times 10^8$	−6.440	−5.695	−4.938	−4.105	−3.499	−3.048	−2.109	−1.645	−1.398
$D(3) \times 10^{12}$	8.622	6.795	6.168	4.827	3.838	3.240	1.490	1.309	1.445
CsCl									
$D(0) \times 10^4$	0.8316	−2.164	−1.274	−1.107	−1.185	−1.234	−0.0944	−0.8013	0.2515
$D(1) \times 10^4$	1.502	1.391	1.169	0.9742	0.8283	0.7107	0.5097	0.3491	0.2429
$D(2) \times 10^8$	−6.317	−5.685	−4.725	−3.931	−3.368	−2.947	−2.359	−1.718	−1.603
$D(3) \times 10^{12}$	8.524	7.097	5.576	4.473	3.604	3.210	2.679	1.594	2.224
KF									
$D(0) \times 10^4$	2.209	−0.0308	−0.4858	0.7505	0.0156	−1.172	0.8747	−3.262	1.282
$D(1) \times 10^4$	1.618	1.496	1.289	1.107	0.9507	0.8162	0.6186	0.4859	0.3401
$D(2) \times 10^8$	−6.059	−5.300	−4.541	−3.965	−3.228	−2.676	−2.086	−2.096	−1.211
$D(3) \times 10^{12}$	8.575	6.692	5.748	5.350	3.807	2.865	2.251	3.735	1.203
KBr									
$D(0) \times 10^4$	3.747	−0.9306	−1.028	−0.5682	−2.021	−2.844	−0.0347	−2.888	−3.684
$D(1) \times 10^4$	1.543	1.446	1.224	1.028	0.8814	0.7534	0.5494	0.3867	0.3339
$D(2) \times 10^8$	−6.411	−5.933	−4.990	−4.184	−3.566	−3.142	−2.445	−1.744	−2.204
$D(3) \times 10^{12}$	8.515	7.531	6.055	4.977	3.884	3.559	2.770	1.419	3.117
KI									
$D(0) \times 10^4$	0.5503	−1.186	−1.122	−1.137	−1.286	−4.549	−1.758	−7.638	−3.225
$D(1) \times 10^4$	1.341	1.240	1.023	0.8372	0.7016	0.5811	0.3850	0.2461	0.1388
$D(2) \times 10^8$	−6.269	−5.788	−4.731	−3.915	−3.416	−2.992	−2.230	−1.912	−1.513
$D(3) \times 10^{12}$	8.581	7.700	5.759	4.540	3.943	3.569	2.465	2.463	2.060
KNO_3									
$D(0) \times 10^4$	0.3480	−1.275	−0.4411	−1.160	−1.593	−0.3279	−0.1232	−2.900	−1.369
$D(1) \times 10^4$	1.233	1.139	0.9449	0.7688	0.6411	0.5348	0.3664	0.2183	0.1286
$D(2) \times 10^8$	−5.747	−5.306	−4.424	−3.608	−3.163	−2.735	−2.254	−1.545	−1.544
$D(3) \times 10^{12}$	7.771	6.959	5.454	4.172	3.772	3.096	2.911	1.379	2.492

Table IV. Adequacy of Equation 2 in Representing $(\kappa_p/\kappa_1)^\circ$

	Temperature, 25°C			
	CsCl		KI	
Pressure, atm	Measured	Calcd	Measured	Calcd
200	1.0127	1.0123	1.0092	1.0100
800	1.0398	1.0396	1.0299	1.0291
1500	1.0506	1.0509	1.0315	1.0319
2000	1.0490	1.0492	1.0247	1.0249

constant. Our constancy of better than 0.01°C and absolute certainty of 0.05°C are sufficient to ensure an accuracy of 0.1% in the conductance ratios. To ensure thermal equilibration after each incremental change of pressure, readings were always taken as a function of time; the final resistance reading was not recorded unless constancy had been apparent for about 30 min.

Even when intrinsic point-by-point accuracy and reproducibility are good, and scatter is kept to a minimum by observing the mentioned precautions, errors may exist in the process of extrapolation to infinite dilution. Without the aid of the theoretical limiting slopes, the tendency is to draw the best

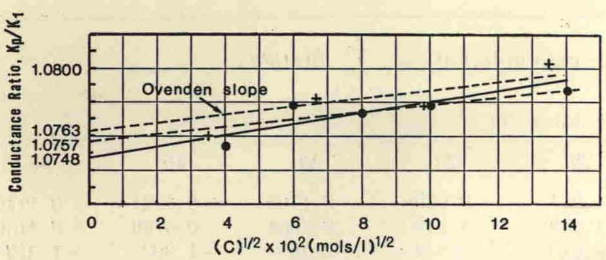

Figure 1. Extrapolation of conductance ratios to infinite dilution for KCl at 25°C

+ Ovenden, 2010 atm (27) ● Present work, 1925 atm
—— Theoretical limiting slope - - - Hand-drawn slopes

straight line through the data points. This generally leads to slopes too low and an extrapolant too high because the deviations from the limiting slope are negative at the higher concentrations (*9*). With this in mind, the extrapolation through the concentration-dependent data can be carried out more confidently (Figure 1).

Figure 1 shows that a single experimental point appropriately placed can yield an accurate infinite dilution value when used in conjunction with the theoretical limiting slope. This practice assumes that measurements can be made with enough confidence to rely upon a single data point at each temperature for a given salt system. In this regard, we carried out many hundreds of individual measurements prior to our point-slope program. The uncertainty in the single point is no greater than that introduced in extrapolating from a typically scattered set; thus, the procedure is justified by the saving of time.

Previous workers have variously treated the concentration dependence of κ_p/κ_1. Körber found that for KCl solutions κ_p/κ_1 decreased monotonically in the range 10^{-4}–$3N$—i.e., the concentration dependence was in the wrong direction (*26*). Ellis (*7*) reported that in the range 10^{-3}–$10^{-1}N$ for KCl and HCl the effect of concentration was negligible. One practice is to disregard the relatively small concentration dependence and to take results at one concentration, say 10 mM (*22*). This procedure introduces a systematic pressure- and temperature-dependent error at infinite dilution (0.35% at 25°C and 2000 atm for NaCl) (*9*).

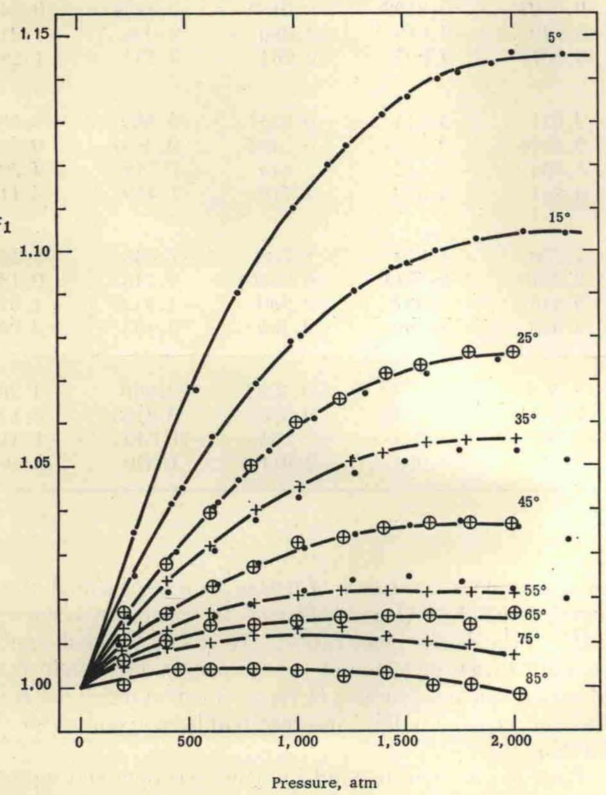

Figure 2. Conductance of KCl solutions at infinite dilution as function of pressure

⊕,+ Ovenden (27) ● Present work

The most careful work to date is that of Ovenden (*27*). Figure 2 compares our infinite dilution data with those of Ovenden for KCl. Agreement is excellent—typically 0.1% and never worse than 0.2%—contrasted with previous disagreements in the literature, even at high concentrations as discussed by Ellis (*7*), Hamann (*10*), and Horne et al. (*22*).

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