

At low ionic strengths the following approximate relation holds, Λ (molal) = Λd , where d is the density of the solution. This equation is valid at all concentrations used in the present experiments within the possible experimental error.

In this work the product Λd is used instead of the term molal conductance, as the former emphasises that the increase in conductance with pressure is due to both a volume factor and one involving the mobility of the ions.

The results are reported as the ratios Λ^P_{pr}/Λ^1 where Λ^P and Λ^1 are the molar conductances

TABLE 1.

P (atm.)	500	1000	1500	2000	2500	3000
ρ_r	1.021	1.039	1.058	1.073	1.088	1.103

TABLE 2. *Hydrochloric acid: values of Λ^P_{pr}/Λ^1 (M = molar concentrations at $P = 1$).*

(Owen and Sweeton's values ¹¹ of Λ^1 in parentheses.)

M	P (atm.)	M	P (atm.)
	1 500 1000 2000 3000		1 500 1000 2000 3000
25°	0.1 (391.3) 1.050 1.088 1.152 1.193	45°	0.1 (502.2) 1.034 1.068 1.120 1.158
	0.01 (412.0) 1.051 1.089 1.152 1.191		0.01 (530.5) 1.034 1.066 1.118 1.156
	0.01 (421.4) 1.050 1.087 1.151 1.191		0.001 (544.2) 1.033 1.067 1.117 1.154
	0.0001 (424.7) 1.05 1.10 1.16 1.21		
35°	0.1 (447.3) 1.040 1.074 1.127 1.164	55°	0.1 (554.0) 1.032 1.062 1.112 1.148
	0.01 (472.3) 1.041 1.075 1.128 1.162		0.01 (586.5) 1.032 1.063 1.113 1.149
	0.001 (483.3) 1.041 1.070 1.126 1.165		0.001 (602.3) 1.033 1.065 1.115 1.150
	0.0001 (487.0) 1.04 1.09 1.14 1.18		
		65°	0.1 (603.0) 1.031 1.060 1.105 1.142
			0.01 (640.5) 1.030 1.060 1.106 1.140
			0.001 (657.5) 1.029 1.062 1.108 1.142

Values of Λ_0^P/Λ_0^1 for hydrochloric acid solutions.

Temp.	P (atm.)	1	500	1000	2000	3000
25°		(426.2)	1.028	1.048	1.074	1.080
35		(489.2)	1.020	1.034	1.051	1.056
45		(550.3)	1.013	1.027	1.042	1.048
55		(609.5)	1.012	1.025	1.039	1.043
65		(666.8)	1.009	1.022	1.032	1.035

TABLE 3. *Potassium chloride: values of Λ^P_{pr}/Λ^1 .*

(Λ^1 values in parentheses up to 45° from Gunning and Gordon,¹² and at 55° and 65° from the present work.)

M	P (atm.)	1	500	1000	2000	3000
25°	0.1	(129.0)	1.031	1.052	1.069	1.061
	0.01	(141.3)	1.031	1.052	1.068	1.058
	0.001	(147.0)	1.032	1.054	1.069	1.064
	0.0001	(149.3)	1.03	1.06	1.08	1.07
35°	0.1	(154.7)	1.023	1.044	1.052	1.044
	0.01	(169.9)	1.024	1.040	1.049	1.042
	0.001	(176.9)	1.025	1.04(5)	1.05(5)	1.05(0)
	0.1	(180.3)	1.020	1.038	1.044	1.030
45°	0.01	(199.7)	1.021	1.035	1.040	1.026
	0.001	(208.1)	1.02(0)	1.03(5)	1.04(1)	1.03(0)
	0.1	(208.3)	1.015	1.026	1.035	1.023
	0.01	(230.1)	1.017	1.028	1.033	1.021
55°	0.001	(241.0)	1.02	1.03(1)	1.04(0)	1.03(0)
	0.1	(235.5)	1.014	1.026	1.026	1.011
	0.01	(262.3)	1.015	1.025	1.027	1.012
	0.001	(278.2)	1.01(5)	1.02(3)	1.02(6)	1.01(7)

Values of Λ_0^P/Λ_0^1 for KCl solutions.

(Λ_0^1 values to 45° from Gunning and Gordon¹² in parentheses.)

Temp.	P (atm.)	1	50	1000	2000	3000
25°		(149.9)	1.011	1.014	0.996	0.964
35		(180.5)	1.004	1.004	0.979	0.947
45		(212.5)	1.000	0.997	0.971	0.931
55		(246.0)	0.996	0.989	0.965	0.927
65		(281.3)	0.994	0.987	0.957	0.917

of the electrolytes at a pressure P and at 1 atm., respectively. ρ_r is the corresponding density ratio ρ^P/ρ^1 for water at the temperature. Values of ρ_r taken from Dorsey¹⁰ and given in Table 1 represent the solution densities within $\pm 0.2\%$ in the temperature range 25–65°.

Electrolyte solutions ranging from 0.1 to 0.0001M were examined up to 3000 atm. at temper-

TABLE 4. Potassium hydrogen carbonate: values of $\Lambda^P\rho_r/\Lambda^1$.

(Λ^1 values in parentheses based on Shedlovsky and MacInnes's results¹² up to 40°, and the present work.)

M		P (atm.)					M		P (atm.)				
	1	500	1000	2000	3000		1	500	1000	2000	3000		
25°	0.1	(97.7)	1.025	1.041	1.050	1.034	45°	0.1	(138)	1.014	1.020	1.021	1.004
	0.01	(110.1)	1.026	1.042	1.048	1.031		0.01	(155.0)	1.013	1.022	1.023	1.002
	0.001	(115.3)	1.024	1.041	1.049	1.033		0.001	(163.5)	1.115	1.024	1.025	1.005
	0.0001	(117.3)	1.03	1.05	1.06	1.04							
35°	0.1	(118)	1.019	1.031	1.034	1.019	55°	0.1	(158)	1.012	1.016	1.014	0.994
	0.01	(131.8)	1.018	1.030	1.033	1.017		0.01	(178.5)	1.010	1.015	1.012	0.992
	0.001	(139.2)	1.020	1.032	1.032	1.016		0.001	(189.0)	1.014	1.014	1.015	0.996
							65°	0.1	(181)	1.008	1.013	1.002	0.986
								0.01	(202.8)	1.007	1.010	1.004	0.984
								0.001	(189.0)	1.009	1.012	1.004	0.987

Values of Λ_0^P/Λ_0^1 for KHCO_3 solutions.

Temp.	P (atm.)	1	500	1000	2000	3000
25°		(118.0)	1.005	1.002	0.978	0.937
35		(141.5)	0.999	0.992	0.963	0.922
45		(179.3)	0.993	0.985	0.954	0.909
55		(192.8)	0.989	0.977	0.944	0.901
65		(219)	0.987	0.974	0.936	0.894

TABLE 5. The effect of pressure on the conductance of the distilled water used in the experiments: Typical values of specific conductivity $\times 10^6$ ($\text{ohm}^{-1} \text{cm}^{-1}$).

Temp.	P (atm.)	1	1000	2000	3000
25°		1.5	2.1	2.7	3.0
45		3.2	5.0	5.9	6.5
65		5.1	7.4	9.3	11.5

atures between 25° and 65°. The results for 10^{-4}M -solutions were of little significance above 35° because of the high solvent correction to the conductances.

Tables 2 to 4 give, in order, the change in conductivity with pressure for solutions of hydrochloric acid, potassium chloride, and potassium hydrogen carbonate. Table 5 gives the change in conductivity for water in equilibrium with the cell assembly.

The values of $\Lambda^P\rho_r/\Lambda^1$ did not change significantly with concentration in the range 0.1–0.0001M. At the end of each of the Tables 2–4 values for the ratio Λ^P/Λ_0^1 are given for the electrolytes. To obtain these values it was assumed that the effects of pressure on conductance remained constant down to infinitely small electrolyte concentrations.

Wherever possible, accurate values of Λ^1 from other measurements^{11–13} are included with the conductance ratios in the Tables. The units of the Λ values reported are $\text{cm}^2 \text{ohm}^{-1} \text{mole}^{-1}$.

Table 6 gives the results for the changes with pressure of the apparent dissociation constant K_a of carbonic acid. The product $\Lambda\rho_r$ (and hence $\alpha = \Lambda\rho_r/\Lambda^1\rho_r$) was obtained from the specific conductivities L' by the relation $\Lambda\rho_r = 1000L'/m\rho^1$, where ρ^1 is the density of the acid solution ($\sim$ water) at 1 atm. pressure.

The volume change on ionisation at infinite dilution was calculated from the slope of $\log(K_a^P/K_a^1)$ versus pressure graphs at 1 atm. (ΔV^1) and at 3000 atm. (ΔV^{3000}).

$$(\delta \ln K_a)/(\delta P)_{T,m} = -\Delta V/RT \quad (-\delta \Delta V/\delta P)_{T,m} = \Delta K \approx (\Delta V^{3000} - \Delta V^1)/3000$$

From the latter relation the average value for the change in compressibility (ΔK) on ionisation in the pressure range 1–3000 atm. was obtained at each temperature.