

parameter \hat{a} , and an arbitrary but reasonable value (5 \AA)¹² was assumed for this in the parameter fit. The molar association constant, K_γ , was then calculated from equation (2) and was found to be relatively insensitive to the choice of \hat{a} .

$$K_\gamma = (1-\gamma)/\gamma^2 c f^2 \quad (2)$$

If \hat{a} was treated as an additional adjustable parameter the value of K_A in equation (1) was found to approach the value of K_γ after lengthy iteration.

Equation (2) was evaluated at each experimental concentration and the values of K_γ were found to have a spread of $\pm 10\%$; the average value is given in Table 2. The other rows in Table 2 give values of Λ^0 , accurate to ± 2 in the last figure.

TABLE 2
CONDUCTANCE PARAMETERS
 Λ^0 in $\text{cm}^2 \Omega^{-1} \text{mol}^{-1}$, K_γ in l. mol^{-1}

Salt	T (°K)	Para- meter	Value of Conductance Parameters for P (bar)				
			1	506	1013	2026	3040
Acetone							
mmpI	293·1	Λ^0	198	162	124	90	68
		K_γ	596	487	242	162	133
	303·1	Λ^0	209	170	140		74
		K_γ	638	451	313		210
	313·1	Λ^0	262	215	168	127	93
		K_γ	1010	782	469	384	277
NaI	298·1	Λ^0	184 ^a				
		K_A	170 ^a				
Bu ¹ OH							
mmpI	303·1	Λ^0	16·2	11·1	8·20	4·84	3·20
		K_γ	4795	3212	2670	2203	2402
NaI	298·1	Λ^0	11·8	8·50	6·20	3·62	2·30
		K_γ	858	599	440	281	219
	308·1	Λ^0	14·3	10·5	7·90	4·87	3·20
		K_γ	914	647	483	313	245

^a Ref. 12.

Some measured conductances are plotted against \sqrt{c} in Figure 1. The solid curves are drawn through values calculated from equation (1) and the straight lines give the Onsager tangents. The dashed interpolations follow the pattern of a type III phoreogram.³ The conductances measured by Detoit and Dupertuis¹³ and the Λ^0 values obtained from them by Walden¹⁴ are higher than those found by extrapolating our values. Doubts about their reliability were already expressed by Walden.¹⁵

¹² Janz, G. J., and Tait, M. J., *Can. J. Chem.*, 1967, **45**, 1101.

¹³ Detoit, P., and Dupertuis, H., *J. Chim. phys.*, 1908, **6**, 726.

¹⁴ Walden, P., in "Landolt-Börnsteins Tabellen", 5th Edn, Suppl. Vol. 1, p. 632. (Springer: Berlin 1961.)

¹⁵ Walden, P., *Z. phys. Chem.*, 1911, **78**, 257.

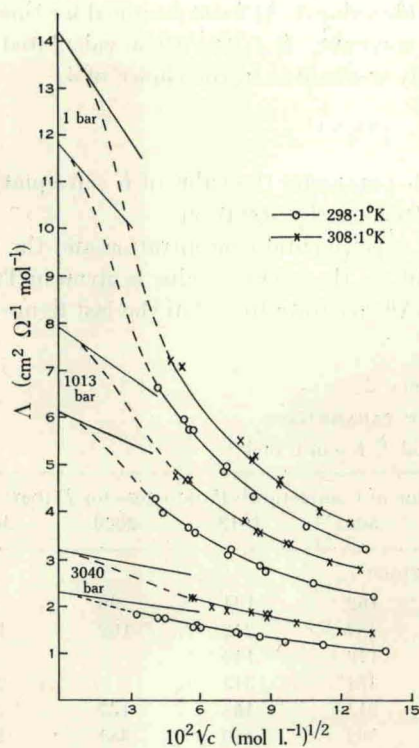


Fig. 1.—Conductance of NaI in Bu¹OH as a function of concentration at 1, 1013, and 3040 bar. The solid curves are calculated from equation (1).

TABLE 3

THERMODYNAMIC QUANTITIES FOR ION ASSOCIATION
 ΔG and ΔH in kJ mol⁻¹; ΔS in J mol⁻¹ K⁻¹; ΔV in cm³ mol⁻¹

Quantity ^a	Thermodynamic Quantities at 303.1°K for <i>P</i> (bar)				
	1	506	1013	2026	3040
mmpI in Acetone					
ΔG	-22.8	-22.1	-21.2	-20.8	-20.5
ΔH	+19	+16	+24	+32	+27
ΔS	+140	+130	+150	+170	+150
ΔV		+16	+16	+4	+3
mmpI in Bu ¹ OH					
ΔG	-27.2	-26.6	-26.1	-25.7	-26.0
ΔV		+17	+8	+4	0
NaI in Bu ¹ OH					
ΔG	-23.0	-22.3	-21.6	-20.6	-20.0
ΔH	+4.2	+5.0	+6.3	+7.1	+7.9
ΔS	88	+92	+92	+92	+92
ΔV		+17	+13	+10	+6

^a Errors: $\Delta G \pm 0.3$ kJ mol⁻¹; $\Delta H \pm 0.6$ kJ mol⁻¹; $\Delta S \pm 3.5\%$; $\Delta V \pm 1$ cm³ mol⁻¹.