

parameter  $\hat{a}$ , and an arbitrary but reasonable value  $(5 \text{ \AA})^{12}$  was assumed for this in the parameter fit. The molar association constant,  $K_\gamma$ , 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  $K_\gamma$  after lengthy iteration.

Equation (2) was evaluated at each experimental concentration and the values of  $K_\gamma$  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  $\Lambda^0$ , accurate to  $\pm 2$  in the last figure.

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

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

<sup>a</sup> 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.<sup>3</sup> The conductances measured by Detoit and Duperthuis<sup>13</sup> and the  $\Lambda^0$  values obtained from them by Walden<sup>14</sup> are higher than those found by extrapolating our values. Doubts about their reliability were already expressed by Walden.<sup>15</sup>

<sup>12</sup> Janz, G. J., and Tait, M. J., *Can. J. Chem.*, 1967, **45**, 1101.

<sup>13</sup> Detoit, P., and Duperthuis, H., *J. Chim. phys.*, 1908, **6**, 726.

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

<sup>15</sup> Walden, P., *Z. phys. Chem.*, 1911, **78**, 257.

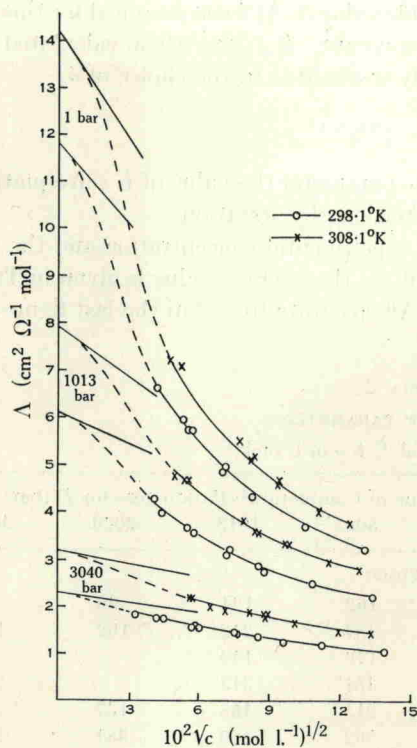


Fig. 1.—Conductance of NaI in Bu<sup>1</sup>OH as a function of concentration at 1, 1013, and 3040 bar. The solid curves are calculated from equation (1).

TABLE 3

THERMODYNAMIC QUANTITIES FOR ION ASSOCIATION  
 $\Delta G$  and  $\Delta H$  in  $\text{kJ mol}^{-1}$ ;  $\Delta S$  in  $\text{J mol}^{-1} \text{K}^{-1}$ ;  $\Delta V$  in  $\text{cm}^3 \text{mol}^{-1}$

Quantity <sup>a</sup>	Thermodynamic Quantities at $303.1^\circ\text{K}$ for $P$ (bar)				
	1	506	1013	2026	3040
mmpI in Acetone					
$\Delta G$	-22.8	-22.1	-21.2	-20.8	-20.5
$\Delta H$	+19	+16	+24	+32	+27
$\Delta S$	+140	+130	+150	+170	+150
$\Delta V$		+16	+16	+4	+3
mmpI in Bu <sup>1</sup> OH					
$\Delta G$	-27.2	-26.6	-26.1	-25.7	-26.0
$\Delta V$		+17	+8	+4	0
NaI in Bu <sup>1</sup> OH					
$\Delta G$	-23.0	-22.3	-21.6	-20.6	-20.0
$\Delta H$	+4.2	+5.0	+6.3	+7.1	+7.9
$\Delta S$	88	+92	+92	+92	+92
$\Delta V$		+17	+13	+10	+6

<sup>a</sup> Errors:  $\Delta G \pm 0.3 \text{ kJ mol}^{-1}$ ;  $\Delta H \pm 0.6 \text{ kJ mol}^{-1}$ ;  $\Delta S \pm 3.5\%$ ;  $\Delta V \pm 1 \text{ cm}^3 \text{mol}^{-1}$ .