

where  $\kappa$  is the specific conductance in  $\text{ohm}^{-1} \text{cm}$ , corrected for the contribution of the solvent, and  $c$  is the concentration of electrolyte in  $\text{mole kg}^{-1}$ .

TABLE 1.—MOLAL CONDUCTANCES IN METHANOL AT 25° C

electrolyte :	sodium bromide	sodium methoxide	piperidinium bromide	piperidine
conc/mole $\text{kg}^{-1}$ :	0.00137	0.000756	0.00106	0.0348
press./atm				
1	71.5	74.5	82.3	1.12
1000	59.0	61.5	66.7	1.66
2000	51.5	53.8	56.3	2.32
3000	44.8	47.8	48.9	3.05

TABLE 2.—MOLAL CONDUCTANCES IN METHANOL AT 45° C

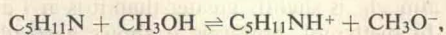
electrolyte :	sodium bromide	sodium methoxide	piperidinium bromide	piperidine
conc/mole $\text{kg}^{-1}$ :	0.00930	0.0140	0.0110	0.3967
press./atm				
1	80.5	80.8	86.0	0.344
1100	67.9	70.2	75.3	0.520
2500	56.4	58.3	62.7	0.84
4000	46.7	51.4	52.5	1.25
5400	42.6	46.3	44.3	1.73
6800	38.0	43.8	39.0	2.34
8200	31.7	37.9	30.5	2.68
9600	26.5	32.7	25.8	3.18
11000	23.1	28.0	22.5	3.56
12000	19.9	24.0	20.0	3.79

TABLE 3.—CHANGE OF MOLAL CONDUCTANCE WITH CONCENTRATION  
IN METHANOL AT 45° C

electrolyte	pressure/atm.	$\Lambda'$			
sodium bromide		conc/mole $\text{kg}^{-1}$ :	0.00075	0.00137	0.00269
	1		74.3	71.5	69.6
	3000		45.4	44.8	44.2
sodium methoxide		conc/mole $\text{kg}^{-1}$ :	0.00609	0.0140	0.0312
	1		70.5	64.1	58.7
	3000		45.9	44.4	43.7
piperidinium bromide		conc/mole $\text{kg}^{-1}$ :	0.000532	0.00216	0.00415
	1		84.9	78.4	75.2
	3000		48.6	47.5	46.1
piperidine		conc/mole $\text{kg}^{-1}$ :	0.0348	0.1283	0.4548
	1		1.118	0.620	0.328
	3000		3.05	1.78	0.858

## IONIZATION CONSTANTS

The ionization of piperidine in methanol is represented by the formula



and the basic ionization constant  $K$  is defined as

$$K = (a_{\text{C}_5\text{H}_{11}\text{NH}^+})(a_{\text{CH}_3\text{O}^-})/a_{\text{C}_5\text{H}_{11}\text{N}},$$

the  $a$ 's being molal activities. Tables 4 and 5 list values of  $K$  calculated from our experimental results by the method described previously.<sup>1</sup>

TABLE 4.—IONIZATION CONSTANT OF PIPERIDINE IN METHANOL AT 25° C

pressure/atm.	10 <sup>6</sup> K/mole kg <sup>-1</sup>	pressure/atm.	10 <sup>6</sup> K/mole kg <sup>-1</sup>
1	6.1	1000	21.9
100	7.2	2000	56
250	8.6	3000	126
500	14.6		

TABLE 5.—IONIZATION CONSTANT OF PIPERIDINE IN METHANOL AT 45° C

pressure/atm.	10 <sup>6</sup> K/mole kg <sup>-1</sup>	pressure/atm.	10 <sup>6</sup> K/mole kg <sup>-1</sup>
1	2.8	6800	480
1100	8.6	8200	860
2500	38	9600	1400
4000	103	11000	2300
5400	240	12000	3100

## DISCUSSION

## CONDUCTANCES

There are two marked differences between the high pressure behaviour of  $\Lambda'$  for strong salts in methanol and in water. In methanol,  $\Lambda'$  for a particular concentration is reduced much more by pressure than it is in water. Also, the concentration dependence of  $\Lambda'$  which is almost unaffected by pressure in water, is greatly reduced at high pressures in methanol. These changes can be judged from the effect of pressure upon the quantities  $\Lambda_0'$  and  $B'$  in the Kohlrausch relation,

$$\Lambda' = \Lambda_0' - B'c^{\frac{1}{2}},$$

where  $c$  is the molal concentration of the salt and  $\Lambda_0'$  is its molal conductance at infinite dilution. Table 6 lists some values of  $\Lambda_0'$  and  $B'$  for the two solvents.

TABLE 6.—THE QUANTITIES  $\Lambda_0'$  AND  $B'$  AT 25° C

	electrolyte	pressure/atm.	$\Lambda_0'$	$B'$ expt.	$B'$ calc.
(i) water as solvent:	KCl*	1	149	90	94
		3000	158	75	85
	KOCOCH <sub>3</sub> †	1	113	80	85
		3000	117	87	75
(ii) methanol as solvent:	NaBr ‡	1	79	190	171
		3000	46	44	83
	C <sub>5</sub> H <sub>11</sub> NHBr ‡	1	89	225	179
		3000	50	60	85

\* ref. (1).

† measurements made as part of some earlier work (ref. (2)).

‡ this work.

In water at 3000 atm,  $\Lambda_0'$  is slightly greater than it is at 1 atm; at higher pressures it decreases. In methanol, however, it shows a steady and much larger decrease over the whole range to 12,000 atm. This difference in behaviour is probably due to the greater relative increase in the viscosity<sup>4</sup> of methanol at high pressures.

The experimental values of  $B'$  in table 6 are subject to fairly large uncertainties, possibly as much as  $\pm 20$  units at 3000 atm. Nevertheless they show clearly