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

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

| electrolyte : | sodium bromide | sodium methoxide | piperidinium bromide | piperidine |
|---|---|---|---|---|
| conc/mole $kg^{-1}$ : | 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 $kg^{-1}$ : | 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. | | Λ′ | |
|---|---|---|---|---|
| sodium bromide | conc/mole $kg^{-1}$ : | 0·00075 | 0·00137 | 0·00269 |
| | 1 | 74·3 | 71·5 | 69·6 |
| | 3000 | 45·4 | 44·8 | 44·2 |
| sodium methoxide | conc/mole $kg^{-1}$ : | 0·00609 | 0·0140 | 0·0312 |
| | 1 | 70·5 | 64·1 | 58·7 |
| | 3000 | 45·9 | 44·4 | 43·7 |
| piperidinium bromide | conc/mole $kg^{-1}$ : | 0·000532 | 0·00216 | 0·00415 |
| | 1 | 84·9 | 78·4 | 75·2 |
| | 3000 | 48·6 | 47·5 | 46·1 |
| piperidine | conc/mole $kg^{-1}$ : | 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

$$C_5H_{11}N + CH_3OH \rightleftharpoons C_5H_{11}NH^+ + CH_3O^-,$$

and the basic ionization constant $K$ is defined as

$$K = (a_{C_5H_{11}NH^+})(a_{CH_3O^-})/a_{C_5H_{11}N}\ ,$$

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

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

| pressure/atm. | $10^6$ $K$/mole kg$^{-1}$ | pressure/atm. | $10^6$ $K$/mole kg$^{-1}$ |
|---|---|---|---|
| 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. | $10^6$ $K$/mole kg$^{-1}$ | pressure/atm. | $10^6$ $K$/mole kg$^{-1}$ |
|---|---|---|---|
| 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 |
| | $KOCOCH_3$ † | 1 | 113 | 80 | 85 |
| | | 3000 | 117 | 87 | 75 |
| (ii) methanol as solvent: | NaBr ‡ | 1 | 79 | 190 | 171 |
| | | 3000 | 46 | 44 | 83 |
| | $C_5H_{11}NHBr$ ‡ | 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 [4] 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