

**COMMONWEALTH OF AUSTRALIA**  
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This paper reports the first measurements of the effect of pressure on the ionization of a weak electrolyte in a non-aqueous solvent. The electrical conductance of methanolic solutions of piperidine, piperidine hydrochloride, sodium piperide and sodium methoxide have been measured at 3000 atm at 25°C, and at 12,000 atm at 45°C. The results show that the basic ionization constant of piperidine is unaffected at 45°C, increases from  $3.6 \times 10^{-4}$  mole/litre at 1 atm to  $3.100 \times 10^{-4}$  mole/litre at 12,000 atm. This is a greater pressure effect than has been found in aqueous solutions of weak bases. It has been suggested that the observed increase in the basic ionization constant is due to enhanced solvation of the ions at high pressures.

**IONIZATION OF PIPERIDINE IN METHANOL TO 12,000 ATM**

In earlier papers<sup>1,2</sup> we showed that pressure causes a large increase in the ionization of weak acids and bases in water, and that the increase arises from the enhanced solvation of the ions at high pressures. We have now extended our measurements to solutions of a weak base in methanol, to see how the pressure effect depends upon the nature of the ionizing solvent. The base was piperidine. It would have been preferable to use one of the methylamines whose ionization constants had previously been measured in water at high pressures,<sup>3</sup> but unfortunately they were too little ionized in methanol to give significant ionization constants by the conductance method.

**EXPERIMENTAL**

**Materials.**—The experimental procedure was the same as in the earlier work.<sup>1</sup> The conductance measurements at 3000 atm at 25°C were made in a glass cell described previously,<sup>1</sup> those at 12,000 atm at 45°C were made in a Teflon cell,<sup>2</sup> even care was taken to keep moisture from the solutions and the conductance cells.

**Piperidine.**—Analytical grade piperidine was distilled with fresh quinoline, then distilled from magnesium activated to red heat. It was finally distilled several times from calcium chloride. The product had a specific conductance of  $1.4 \times 10^{-10}$  ohm<sup>-1</sup> cm<sup>-1</sup> at 25°C. The sodium piperide, sodium methoxide, piperidine hydrochloride and piperidine hydrochloride were prepared as in earlier work.

**RESULTS**

The sources and magnitudes of uncertainties were the same as in the earlier measurements.<sup>1</sup>

**CONDUCTANCE**

The conductance of each electrolyte was measured over a range of concentrations and pressures; some typical results are given in Tables 1 and 2. Tables 1 and 2 illustrate how the conductance changes with pressure at particular concentrations. Table 3 shows how the change with concentration at particular pressures. The quantities listed are molar conductances  $\Lambda$ , calculated from the relation

$$\Lambda = \frac{\kappa}{c}$$

# IONIZATION OF PIPERIDINE IN METHANOL TO 12,000 ATM

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This paper reports the first measurements of the effect of pressure on the ionization of a weak electrolyte in a non-aqueous solvent. The electrical conductances of methanolic solutions of piperidine, piperidinium bromide, sodium bromide and sodium methoxide have been measured to 3000 atm at 25° C, and to 12,000 atm at 45° C.

The results show that the basic ionization constant of piperidine in methanol at 45° C increases from  $2.8 \times 10^{-6}$  mole kg<sup>-1</sup> at 1 atm, to  $3100 \times 10^{-6}$  mole kg<sup>-1</sup> at 12,000 atm. This is a greater pressure effect than has been found in aqueous solutions of weak bases; it can be ascribed to the proportionally greater increase in the dielectric constant of methanol at high pressures.

In earlier papers<sup>1,2</sup> we showed that pressure causes a large increase in the ionization of weak acids and bases in water, and that the increase arises from the enhanced solvation of the free ions at high pressures.

We have now extended our measurements to solutions of a weak base in methanol, to see how the pressure effect depends upon the nature of the ionizing solvent. The base was piperidine. It would have been preferable to use one of the methylamines whose ionization constants had previously been measured in water to high pressures,<sup>1,2</sup> but unfortunately they are too little ionized in methanol to give significant ionization constants by the conductance method.

## EXPERIMENTAL

**METHOD.**—The experimental procedure was the same as in the earlier work.<sup>1,2</sup> The conductance measurements to 3000 atm at 25° C were made in a glass cell described previously;<sup>1</sup> those to 12,000 atm at 45° C were made in a Teflon cell.<sup>2</sup> Great care was taken to keep moisture from the reagents and the conductance cells.

**MATERIALS.**—Analytical grade methanol was refluxed with fresh quicklime, then distilled from magnesium activated by iodine. It was finally distilled several times from anhydrous copper sulphate. The product had a specific conductance of  $1.1 \times 10^{-6}$  ohm<sup>-1</sup> cm at 45° C. The sodium bromide, sodium methoxide, piperidine and piperidinium bromide were specimens which had been used in earlier work.<sup>3</sup>

## RESULTS

### ACCURACY

The sources and magnitudes of inaccuracies were the same as in the earlier measurements.<sup>2</sup>

### CONDUCTANCES

The conductance of each electrolyte was measured for a range of concentrations and pressures: some typical results are given in tables 1 to 3. Tables 1 and 2 illustrate how the conductances change with pressure for particular concentrations. Table 3 shows how they change with concentration for particular pressures. The quantities listed are *molar* conductances  $A'$ , calculated from the relation

$$A' = 1000 \kappa/c,$$