

that pressure causes a much larger decrease in  $B'$  for methanol solutions than for aqueous solutions. This can be understood on the basis of the Debye-Onsager theory of electrolytic conduction. Onsager calculated  $B$  in the relation

$$A = A_0 - Bx^{\frac{1}{2}}$$

where the  $A$ 's are molar conductances and  $x$  is the concentration in mole l.<sup>-1</sup>. For a 1:1-electrolyte his theory gives<sup>5</sup>

$$B = \frac{8.15 \times 10^5 A_0}{(DT)^{\frac{3}{2}}} + \frac{81.9}{(DT)^{\frac{1}{2}} \eta},$$

where  $D$  is the dielectric constant of the solvent,  $\eta$  is its viscosity in poises, and  $T$  is the temperature (°K). Changing to molal units,

$$B' = \frac{8.15 \times 10^5 A_0' \rho^{\frac{1}{2}}}{(DT)^{\frac{3}{2}}} + \frac{81.9 \rho^{\frac{3}{2}}}{(DT)^{\frac{1}{2}} \eta},$$

where  $\rho$  is the specific gravity of the solution. The quantities  $\rho$ ,  $\eta$ ,  $D$  and  $A_0'$  are all pressure dependent. Bridgman<sup>4, 6, 7</sup> has measured  $\rho$  and  $\eta$  for methanol and water at high pressures, and Kyropoulos<sup>8</sup> has measured  $D$ . Some values of  $A_0'$  are given in table 6. From these data it is possible to calculate  $B'$ : the results are shown in the last column of table 6.

Clearly the Onsager values of  $B'$  change with pressure in much the same way as the experimental values. For methanol the numerical agreement is not good, but it is known that, even at atmospheric pressure, the Onsager formula applies only approximately to methanol solutions.<sup>9</sup> The decrease of  $B'$  in methanol at high pressures is caused principally by the large increase in viscosity of the solvent, which reduces the electrophoretic effect.

#### IONIZATION CONSTANTS

At 45° C the ionization constant  $K$  of piperidine in methanol increases from  $2.8 \times 10^{-6}$  mole kg<sup>-1</sup> at 1 atm to  $3.1 \times 10^{-3}$  mole kg<sup>-1</sup> at 12,000 atm. The value of  $K$  for piperidine in water at atmospheric pressure and 45° C is  $1.2 \times 10^{-3}$  mole kg<sup>-1</sup>.<sup>10</sup> From this it might be said that methanol at 12,000 atm is a better "ionizing" solvent than water at 1 atm. But it should be emphasized that the change of ionization with pressure arises only partly from the changed properties of the solvent; at least half of the pressure effect is due to the compression of the ions (the factor ( $a$ ) below). This was not appreciated by Kritschewsky,<sup>11</sup> who attributed the whole of the pressure effect to the change in dielectric constant of the medium, and was thereby forced to adopt unrealistic values for ionic radii.

In fig. 1 we compare the effects of high pressures on the ionization of ammonia in water and of piperidine in methanol. The quantity  $\Delta \bar{G}_p^\circ - \Delta \bar{G}_1^\circ$  is the difference between the standard free energy of ionization at the pressure  $p$  atm and the corresponding value at 1 atm. It is defined by

$$\Delta \bar{G}_p^\circ - \Delta \bar{G}_1^\circ = -RT \ln (K_p/K_1).$$

Some density measurements in this laboratory<sup>3</sup> have shown that  $\partial \Delta \bar{G}^\circ / \partial p$  for the ionization of piperidine in water at 1 atm is less negative than it is for the ionization of ammonia in the same solvent. We can safely conclude from this that the plot of  $\Delta \bar{G}_p^\circ - \Delta \bar{G}_1^\circ$  against pressure for the piperidine + water system would lie above the curve for the ammonia + water system. The difference between the two experimental curves in fig. 1 must therefore be ascribed to the change of solvent.

In previous papers<sup>1, 2</sup> we have suggested that the increase in ionization of a weak electrolyte at high pressures is caused by the lowering of the free energy of solvation of its ions. This can be estimated by calculating the Born solvation

energy<sup>12</sup> of a pair of ions of about the same size as those of the weak electrolyte, and allowing for (a) the change in the mean radius of the ions with pressure, and (b) the change in the dielectric constant of the solvent with pressure. We have given<sup>2</sup> the results of this calculation for the ions  $\text{Cs}^+ + \text{F}^-$  in water. We have now made similar calculations for the same pair of ions in methanol. The factor

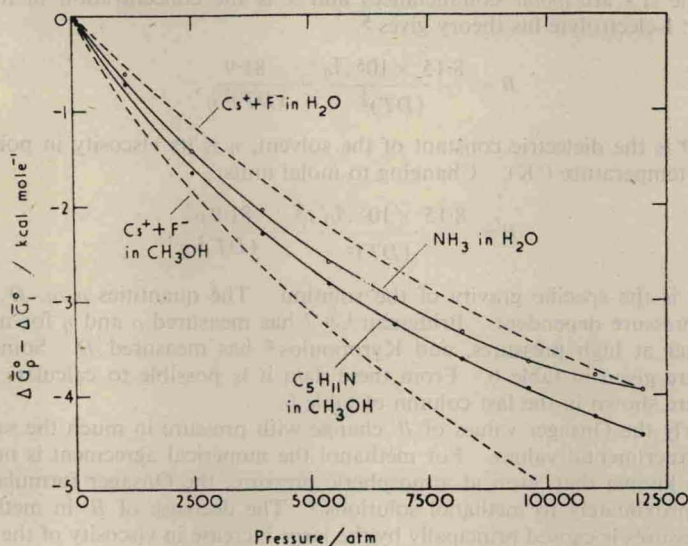


FIG. 1.—Full curves: the ionization free energies of weak bases; dotted curves: the theoretical solvation energies of the ions  $\text{Cs}^+ + \text{F}^-$ . All the data are for 45°C.

(a) is, of course, unaltered by the change of solvent but the factor (b) is more important for methanol than for water because of the larger percentage increase in the dielectric constant of methanol at high pressures.<sup>8</sup> Fig. 1 shows that the change from water to methanol shifts the predicted solvation energies in the same direction as it does the experimental free energies of ionization.

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<sup>1</sup> Buchanan and Hamann, *Trans. Faraday Soc.*, 1953, **49**, 1425.

<sup>2</sup> Hamann and Strauss, *Trans. Faraday Soc.*, 1955, **51**, 1684.

<sup>3</sup> Hamann and Lim, *Austral. J. Chem.*, 1954, **7**, 329.

<sup>4</sup> Bridgman, *Proc. Amer. Acad. Arts Sci.*, 1925, **61**, 57.

<sup>5</sup> MacInnes, *Principles of Electrochemistry* (Reinhold Pub. Corp., New York, 1939), p. 327.

<sup>6</sup> Bridgman, *Proc. Amer. Acad. Arts Sci.*, 1913, **49**, 1.

<sup>7</sup> Bridgman, *Proc. Amer. Acad. Arts Sci.*, 1912, **48**, 307.

<sup>8</sup> Kyropoulos, *Z. Physik*, 1926, **40**, 507.

<sup>9</sup> Unmack, Murray-Rust and Hartley, *Proc. Roy. Soc. A*, 1930, **127**, 228.

<sup>10</sup> Hantzsch and Sebaldt, *Z. physik. Chem.*, 1899, **30**, 258.

<sup>11</sup> Kritschewsky, *Acta physicochim.*, 1938, **8**, 181.

<sup>12</sup> Born, *Z. Physik*, 1920, **1**, 45.