

Table 1 lists values of the functions  $W$  and  $X$  defined by (13) and (14). Table 4 compares 'experimental' values<sup>19,20</sup> of  $\Delta V_p$  (estimated graphically from the slopes of plots of  $RT \ln K_p$  against  $P$ ) for the ionization of 4-methoxybenzoic acid and ammonium hydroxide in water, with values calculated from equation (13). The maximum discrepancy is about 10% and is of the same order as the experimental errors.

**Table 4. Molar volume changes (in  $\text{cm}^3 \text{mol}^{-1}$ ) for ionization reactions at high pressures**  
Experimental values of  $\Delta V_p$  are in ordinary type, calculated values in *italics*

$\Delta V_p$ at various pressures $P$ (kbar)									
0	0.5	1.0	1.5	2.0	2.5	3.0	5.0	7.5	10.0
4-Methoxybenzoic Acid in Water at 25°C									
-11.32 <sup>A</sup>	-10.25	-9.35	-9.12	-8.22	-7.89	-7.66			
(-11.32) <sup>B</sup>	-10.35	-9.50	-8.74	-8.07	-7.48	-6.95			
Ammonium Hydroxide in Water at 45°C									
-28.5 <sup>C</sup>					-19.0		-14.0	-10.0	-7.0
(-28.5) <sup>B</sup>					-18.7		-13.3	-9.9	-7.7

<sup>A</sup> Values from the work of Fischer, A., Mann, B. R., and Vaughan, J., *J. Chem. Soc.*, 1961, 1093.

<sup>B</sup> Values from equation (13).

<sup>C</sup> Values from Hamann, S. D., 'Physico-Chemical Effects of Pressure' p. 152 (Butterworths: London 1957).

### The Electrostatic Theory of Ionization Reactions Under Pressure

It has been shown<sup>20</sup> that a semi-quantitative explanation of the influence of pressure on ionization equilibria in solution lies in its general effect in raising the dielectric constants of solvents, and so lowering the standard free energies of dissolved ions with respect to those of un-ionized molecules. Expressed in another way, the principal contributions to  $\Delta V$  come from interactions between the ions and solvent (electrostriction).

The simplest theory of these interactions is given by Born's<sup>21</sup> model of an ion as a conducting sphere of radius  $r$  immersed in a continuum of dielectric constant  $\epsilon$ . The work needed to increase the charge of such an ion from zero to  $ze$  is  $z^2e^2/2r\epsilon$  and the corresponding change in molar free energy in an ionization reaction is therefore

$$\Delta G_{e1} = Ne^2\theta/2\epsilon \quad (15)$$

where  $N$  is Avogadro's constant and  $\theta$  denotes the sum

$$\theta = \sum_{\text{products}} z^2/r - \sum_{\text{reactants}} z^2/r \quad (16)$$

Formula (15) gives just the electrostatic part of the total Gibbs free energy change for reaction,  $\Delta G$ , but for simplicity we shall assume that it is the only part which is significantly affected by pressure.<sup>20</sup>

We shall also make the assumption that  $\theta$  is independent of pressure, which is equivalent to supposing that the ions are effectively incompressible. That assumption

<sup>19</sup> Fischer, A., Mann, B. R., and Vaughan, J., *J. Chem. Soc.*, 1961, 1093.

<sup>20</sup> Hamann, S. D., 'Physico-Chemical Effects of Pressure' p. 152 (Butterworths: London 1957).

<sup>21</sup> Born, M., *Z. Phys.*, 1920, 1, 45.

is not always necessary, and some treatments have allowed for the compressibilities of the ions in specific cases.<sup>20,22</sup> We make it here for the sake of generality.

With the above assumptions, the change of  $\Delta G$  with pressure is

$$\Delta G_P - \Delta G_0 = \frac{1}{2} Ne^2 \theta (1/\epsilon_P - 1/\epsilon_0) \quad (17)$$

or, in a differential form

$$\partial \Delta G / \partial P = \Delta V = -(Ne^2 \theta / 2\epsilon) (\partial \ln \epsilon / \partial P) \quad (18)$$

In particular

$$\Delta V_0 = -(Ne^2 \theta / 2\epsilon_0) (\partial \ln \epsilon / \partial P)_0 \quad (19)$$

and substitution of this value in (17) gives

$$\Delta G_P - \Delta G_0 = -\Delta V_0 \epsilon_0 (\partial P / \partial \ln \epsilon)_0 (1/\epsilon_P - 1/\epsilon_0) \quad (20)$$

We have established empirically that the free energy change  $\Delta G_P - \Delta G_0$  for ionization reactions is given, from (12), by

$$\Delta G_P - \Delta G_0 = \Delta V_0 P / (1 + bP) \quad (21)$$

so that, if (20) is also to apply, it is necessary that the pressure dependence of the dielectric constant be described by the relationship

$$\frac{1}{\epsilon_P} - \frac{1}{\epsilon_0} = -\frac{P}{1 + bP} \frac{1}{\epsilon_0} \left( \frac{\partial \ln \epsilon}{\partial P} \right)_0 \quad (22)$$

Inserting the experimental values of  $\epsilon_0$  and  $(\partial \ln \epsilon / \partial P)_0$  for water at 25°C<sup>23</sup> and the value  $b = 9.2 \times 10^{-5} \text{ bar}^{-1}$ , we obtain

$$\epsilon_P = (1 + 9.2 \times 10^{-5} P) / (1.2757 \times 10^{-2} + 5.725 \times 10^{-7} P) \quad (23)$$

where  $P$  is in bars. Table 5 shows that values of  $\epsilon_P$  calculated from this formula agree excellently with the experimental values of Lees<sup>24</sup> at pressures up to 10 kbar.

Table 5. The dielectric constant of water at 25°C  
P in kbar

P	$\epsilon_{\text{calc.}}^A$	$\epsilon_{\text{expt.}}^B$	P	$\epsilon_{\text{calc.}}$	$\epsilon_{\text{expt.}}$	P	$\epsilon_{\text{calc.}}$	$\epsilon_{\text{expt.}}$
0	(78.39)	78.39	4	90.91	90.57	8	100.13	100.22
1	81.92	81.87	5	93.47	93.13	9	102.07	102.41
2	85.17	85.00	6	95.85	95.58	10	103.88	104.55
3	88.16	87.88	7	98.06	97.94			

<sup>A</sup> Calculated from equation (23).

<sup>B</sup> From the measurements of Lees.<sup>14</sup> A correction has been applied for an error of about 1% in the pressure scale, which Lees based on Bridgman's value of the freezing pressure of mercury at 0°C.

Dr M. Nakahara, of the Department of Chemistry, Kyoto University, Kyoto, Japan (personal communication), has examined our relationships (12) and (21) in a converse manner, observing that an empirical relationship which Dunn and

<sup>22</sup> Whalley, E., *J. Chem. Phys.*, 1963, **38**, 1400.

<sup>23</sup> Owen, B. B., Miller, R. C., Milner, C. E., and Cogan, H. L., *J. Phys. Chem.*, 1961, **65**, 2065.

<sup>24</sup> Lees, W. L., Dissertation, Harvard University, 1949.