equation (12); the dashed curves are based on the truncated equation of Lown *et al.*[10] using their estimated values of ΔV_0 and $\Delta\kappa_0$, and the dotted curve for water is given by Owen and Brinkley's equation (5), using the value of $\Delta\kappa_0$ measured by Kearns.[4]

Table 2. Relative molal ionization constants at high pressures

Experimental values of K_P/K_0 are in ordinary type. Calculated values of K_P/K_0 were derived from equation (12) and are in *italics*

K_P/K_0 values at pressures P (kbar)											
1	2	3	4	5	6	7	8	9	10	11	12
Acetic Acid in Water at 25°C; ΔV_0 $-11\cdot7$ cm^3 mol^{-1}											
1·546[A]	2·201	3·047									
1·541	*2·219*	*3·033*									
Self-ionization of Water at 25°C; ΔV_0 $-21\cdot4$ cm^3 mol^{-1}											
2·19[B]	4·18	7·25	12·0	18·6	27·6	38·9	51·3				
2·17	*4·20*	*7·38*	*12·0*	*18·5*	*27·0*	*37·8*	*51·1*				
Ammonium Hydroxide in Water at 45°C; ΔV_0 $-29\cdot0$ cm^3 mol^{-1}											
	6·02[C]		26·2		75·2		174		320		494
	6·38		*24·8*		*69·6*		*157*		*304*		*522*

[A] Mean values from the results of Hamann and Strauss,[12] Ellis and Anderson[13] and Lown *et al.*[10]
[B] From the measurements of Linov and Kryukov.[6]
[C] From the measurements of Hamann and Strauss.[12] The values listed here differ slightly from those originally published. A correction has been applied for changes in the cell constant of the conductance cell caused by the high pressure phase transitions[14–16] of Teflon.

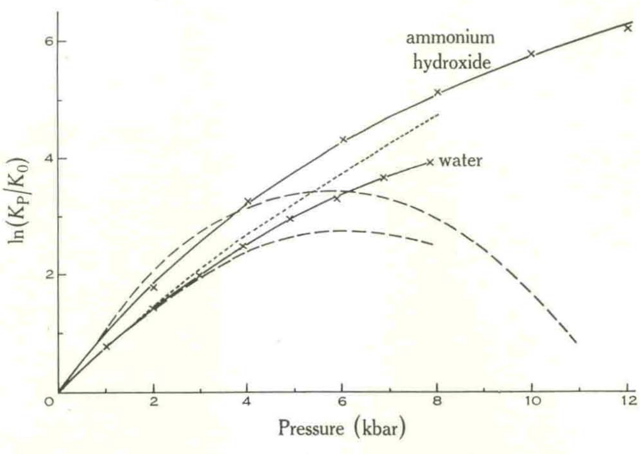

Fig. 2. A logarithmic plot of the ionization constant of ammonium hydroxide in water at high pressures, at 45°C, and of water at 25°C. The solid curves are given by equation (12), the dashed curves by the equation of Lown *et al.*[17] and the dotted curve by Owen and Brinkley's equation (5).

El'yanov's analysis (see Tables 2 and 3 of ref.[9]) shows that the function Φ is effectively independent of the temperature for ionization reactions in water—at least between 18 and 75°C. It follows that it should be possible to apply equation (12) over a range of temperatures using a constant value of $b = 9{\cdot}2\times10^{-5}$ bar^{-1}. Table 3 and Fig. 3 show that it gives a good description of the ionization of acetic acid in water over the very wide range of temperatures from 25 to 225°C, at pressures between 0 and 3 kbar.[17] At 225°C, water has a dielectric constant of only 30 to 40 in that range of pressures,[18] so that it is quite a different medium from ordinary water at 25°C. Nevertheless, the formula still applies, with the same value of b.

Table 3. Relative molal ionization constants of acetic acid in water at high pressures
Experimental values of K_P/K_0 are in ordinary type and calculated values are in *italics*

Temp. (°C)	ΔV_0 (cm^3 mol^{-1})	K_P/K_0 values at pressures P (kbar) 0·4	1·0	1·4	2·0	2·4	3·0
25	$-11{\cdot}3_5$	1·19[A]	1·52	1·76	2·16	2·47	2·98
		1·19[B]	*1·52*	*1·77*	*2·17*	*2·46*	*2·93*
225	$-36{\cdot}4_5$	1·41[A]	2·29	3·00	4·34	5·43	7·76
		1·40[B]	*2·24*	*2·98*	*4·43*	*5·64*	*7·92*

[A] Experimental values of Lown, D. A., Thirsk, H. R., and Lord Wynne-Jones, *Trans. Faraday Soc.*, 1970, **66**, 51.
[B] Values calculated from formula (12), with $b = 9{\cdot}2\times10^{-5}$ bar^{-1}.

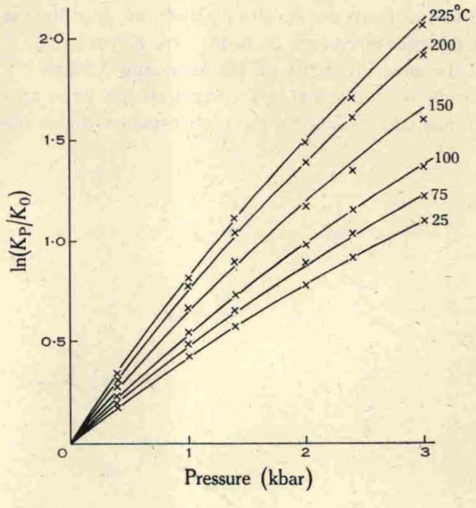

Fig. 3. A logarithmic plot of the ionization constant of acetic acid in water at high pressures and high temperatures. The curves are given by equation (12).

The Pressure Dependence of ΔV

Substitution of (12) into (1) and (3) gives the following relationships

$$\Delta V_P = \Delta V_0/(1+bP)^2 = W\Delta V_0 \tag{13}$$

$$\Delta\kappa_P = 2b\Delta V_0/(1+bP)^3 = X\Delta V_0 \tag{14}$$

which describe the pressure dependences of ΔV and $\Delta\kappa$. When $P = 0$, (14) reduces to $\Delta\kappa_0 = 2b\Delta V_0 = (1{\cdot}84\times10^{-4}$ bar$^{-1}) \times \Delta V_0$, which is fairly close to the proportionality observed by Lown *et al.* (see the discussion of equation (7)).

[17] Lown, D. A., Thirsk, H. R., and Lord Wynne-Jones, *Trans. Faraday Soc.*, 1970, **66**, 51.
[18] Tödheide, K., in 'Water—A Comprehensive Treatise' (Ed. F. Franks) Vol. 1, p. 492 (Plenum Press: New York 1972).