342. *The Effect of Pressure on the First Acid Dissociation Constants of " Sulphurous " and Phosphoric Acids.*

By A. J. Ellis and D. W. Anderson.

By means of conductance measurements at 25°, the changes with pressure of the first dissociation constants for " sulphurous " and phosphoric acids were determined up to 2000 atmospheres. The effect of pressure on the ionisation of the sulphur dioxide–water system is much less than for two other hydrated-gas systems, ammonia and carbon dioxide, but the effect is greater than for simple weak acids.

The evidence available shows that in aqueous solutions of sulphur dioxide the un-ionized sulphur species consist mainly of uncombined sulphur dioxide molecules, with sulphurous acid (H_2SO_3) molecules, if present, in very minor amounts. The studies include Raman,[1,2] infrared,[3,4] and ultraviolet absorption [5] techniques.

The results from infrared spectra are the most convincing. Sulphur dioxide solutions in water show only the infrared absorption bands typical of SO_2 molecules in the liquid and the gaseous state. Even at −190° there is no evidence from infrared measurements for a SO_2–H_2O combination.[3]

This contrasts with the earlier results given by Maass *et al.*,[6,7] who attempted to calculate from vapour-pressure and conductance measurements the proportions of combined and uncombined sulphur dioxide in the system

$$SO_2(g) \rightleftharpoons SO_2(aq) \overset{K_1}{\rightleftharpoons} H_2SO_3 \xleftarrow{K_2} H^+ + HSO_3^-$$

Their calculations have little quantitative significance owing to the neglect of activity corrections at high ionic strengths, and to incomplete information on the ionic conductance of the bisulphite ion.

More recently, De Maine [5] showed that the total un-ionized sulphur dioxide in aqueous solution has an extinction coefficient at 278 mμ very similar to that for sulphur dioxide dissolved in organic solvents and in the gas phase. From his spectrophotometric measurements he suggested that the system may be more complex than the simple three-step equilibrium outlined above, but his work is subject to the same criticisms as that of Maass *et al.*[6,7]

[1] Rao, *Proc. Indian Acad. Sci.*, 1944, *A*, **20**, 292.
[2] Simon and Waldmann, *Z. anorg. Chem.*, 1956, **283**, 359.
[3] Falk and Giguere, *Canad. J. Chem.*, 1958, **36**, 1121.
[4] Jones and McLaren, *J. Chem. Phys.*, 1958, **28**, 995.
[5] De Maine, *J. Chem. Phys.*, 1957, **26**, 1036, 1049.
[6] Boyd-Campbell and Maass, *Canad. J. Res.*, 1930, **2**, 42.
[7] Morgan and Maass, *Canad. J. Res.*, 1931, **5**, 162.

The effects of pressure on ionization in the systems ammonia–water[8] and carbon dioxide–water[9] have been reported. We now compare the effects of pressure on the apparent first ionization constant for these two systems and for the sulphur dioxide–water system. Results are also presented for the first acid dissociation constant for phosphoric acid as a simple inorganic acid with a dissociation constant similar to the apparent dissociation constant of sulphurous acid. The effect of pressure on the ionization of acetic acid was redetermined as a check on the reproducibility of the high-pressure conductance method between workers.

EXPERIMENTAL

Materials and Apparatus.—Reagents used were of " AnalaR " quality and were not purified further. Sulphur dioxide solutions were prepared in bulk from B.D.H. liquid sulphur dioxide, and portions run quickly into the conductance cell. Potassium hydrogen sulphite solutions were made by adjusting sulphur dioxide solutions to pH 4·5 with potassium hydroxide solution. A pH meter was used.

The apparatus used was essentially the same as in the previous papers of this series.[9,10]

Method.—The methods of calculation and symbols are as given in a previous paper.[10] Published values of the conductances in water at high pressures for hydrochloric acid and potassium chloride[9] were used in conjunction with those given below for the acids and their potassium salts in order to derive K_a values. The necessary activity corrections were made at each ionic strength and pressure.

TABLE 1. *Values of $\Lambda^P\rho_r/\Lambda^1$ for potassium salts at 25° over a concentration range. (Values of Λ^1 for* 0·01M-*solutions in parentheses.)*

P (atm.)	1	500	1000	1500	2000
$KHSO_3$, 0·01—0·15M	(120)	1·031	1·052	1·062	1·065
KH_2PO_4, 0·002—0·1M	(99·2)	1·033	1·053	1·068	1·074
KOAc, 0·001—0·05M	(106)	1·026	1·042	1·045	1·048

TABLE 2. *Apparent acid dissociation constant K_a (× 100) for " sulphurous acid " ($H_2O + SO_2$) at 25°.*

P (atm.)	1	500	1000	1500	2000
100 × Concn (M)					
1·17	1·39	2·0	3·1	4·6	6·4
1·80	1·44	2·1	3·0	4·7	6·2
2·32	1·40	2·1	3·1	4·6	6·5
6·35	1·40	2·1	3·2	4·7	6·2
9·7	1·33	2·0	3·0	4·4	6·2
23·4	1·39	2·0	3·0	4·5	6·4

$\Delta V^1 = -19{\cdot}7$ c.c. mole^{-1}; $\Delta V^{2000} = -15{\cdot}2$ c.c. mole^{-1}.
Average $\Delta K = -2{\cdot}3 \times 10^{-3}$ atm.$^{-1}$ c.c. mole^{-1}.

TABLE 3. *First acid dissociation constant K_a (× 100) for phosphoric acid at high pressures and 25°.*

P (atm.)	1	500	1000	1500	2000
Concn. (M)					
0·00576	0·71	0·98	1·33	1·69	2·10
0·01	0·67	0·90	1·20	1·55	2·01
0·1	0·88	1·21	1·64	2·12	2·55

$\Delta V^1 = -15{\cdot}5$ c.c. mole^{-1}; $\Delta V^{2000} = -10{\cdot}7$ c.c. mole^{-1}.
Average $\Delta K = -2{\cdot}4 \times 10^{-3}$ atm.$^{-1}$ c.c. mole^{-1}.

Results.—Table 1 gives the conductance ratio results for the three potassium salts: Table 2 summarizes the results for sulphur dioxide ionization under pressure at 25°, and Table 3 gives similar information for phosphoric acid at 25°. Results from the present work and from other authors are compared for acetic acid in Table 4. V is the partial molar volume, and ΔK is the change in compressibility on ionisation.

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[8] Hamann, " Physico-chemical Effects of Pressure." Butterworths, London, 1957.

[9] Ellis, *J.*, 1959, 3689.

[10] Clark and Ellis, *J.*, 1960, **247**.

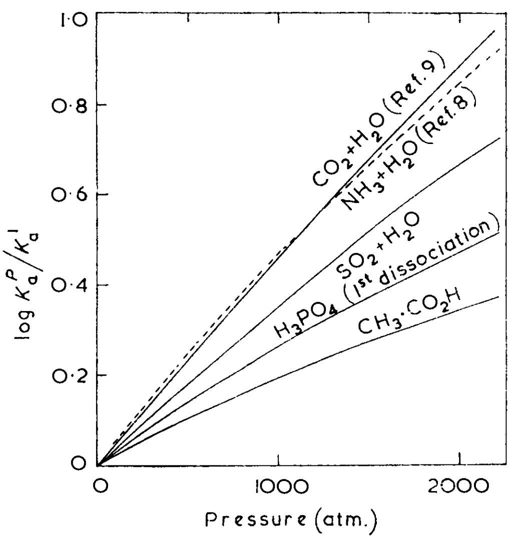
The differences between the ratios obtained for each salt at constant pressure and at various concentrations were within the limits of experimental error.

TABLE 4. *Effect of pressure on the ionization of acetic acid. Comparison of two sets of values of the acid dissociation constant* K_a ($\times 10^5$) *at high pressures and* 25°.

Author	K_a^1	K_a^{500}	K_a^{1000}	K_a^{2000}	ΔV^1	ΔV^{2000}	Average $10^3\Delta K$
This work	1·77	2·24	2·75	3·88	−12·1	−7·4	−2·4
Hamann[8]	1·71	—	2·70	3·91	−12·2	−7·3	−2·5

DISCUSSION

The Figure, which summarizes the results for the three acids as a graph of log (K_a^P/K_a^1) against pressure (superscripts refer to pressures), also includes published results for the ionization of ammonia[8] and carbon dioxide[9] at 25°. There is good agreement between the present results for acetic acid and those of Hamann.[8] A value of ΔV^1 equal to −16·2 c.c. mole^{-1}, obtained by density measurements,[11] for the first ionization constant of phosphoric acid is in reasonable agreement with our value (−15·5 c.c./mole).



The change with pressure of the ionization of sulphur dioxide solutions is less than for ammonia and carbon dioxide. It is, however, greater than the effects for the simple weak acids, acetic and phosphoric, as would be expected if sulphur dioxide is only slightly hydrated in solution.

As there is little reason for the partial molar volume of the bisulphite ion to be unusually high, the lower pressure effect for sulphur dioxide solutions relative to the other two hydrated gas systems must be due to a low partial molar volume for sulphur dioxide in solution. This is possibly owing to sulphur dioxide, with its high dipole moment and large radius, interacting with and tending to collapse the open structure of liquid water. Carbon dioxide by comparison is a smaller molecule with zero dipole moment. Ammonia, although having a high dipole moment, is of a similar size to the water molecules and probably has a smaller effect than sulphur dioxide on the water structure.

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[11] Smith, Diss., 1943, Yale University.