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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 -H₂O 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

$$SO_2(g) \longrightarrow SO_2(aq) \xrightarrow{K_1} H_2SO_3 \xrightarrow{K_2} H^+ + HSO_3^-$$

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 m μ 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}

The effects of pressure on ionization in the systems ammonia-water⁸ and carbon dioxide-water⁹ 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 $K_{\rm a}$ values. The necessary activity corrections were made at each ionic strength and pressure.

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.

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

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
КНSO ₃ , 0.01—0.15м	(120)	1.031	1.052	1.062	1.065
KH ₂ PO ₄ , 0.002-0.1M	(99.2)	1.033	1.053	1.068	1.074
КОАс, 0.001—0.05м	(106)	1.026	1.042	1.045	1.048

TABLE 2. Apparent acid dissociation constant K_a (×100) for "sulphurous acid" (H₂O + SO₂) at 25°.

P (atm.)	1	500	1000	1500	2000
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	$2 \cdot 1$	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

 $\begin{array}{l} \Delta V^1 = -19.7 \mbox{ c.c. mole^{-1}; } \Delta V^{2000} = -15.2 \mbox{ c.c. mole^{-1}.} \\ \mbox{Average } \Delta K = -2.3 \times 10^{-3} \mbox{ atm.}^{-1} \mbox{ c.c. mole}^{-1}. \end{array}$

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

P (atm.)	1	500	1000	1500	2000
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

 $\Delta V^{1} = -15.5 \text{ c.c. mole}^{-1}; \quad \Delta V^{2000} = -10.7 \text{ c.c. mole}^{-1}.$ Average $\Delta K = -2.4 \times 10^{-3} \text{ atm.}^{-1} \text{ c.c. mole}^{-1}.$

TABLE 4. Effect of pressure on the ionization of acetic acid. Comparison of two sets of values of the acid dissociation constant K_a (×10⁵) at high pressures and 25°.

Author	Ka1	Ka ⁵⁰⁰	Ka ¹⁰⁰⁰	Ka ²⁰⁰⁰	ΔV^1	ΔV^{2000}	$10^{3}\Delta K$
This work	1.77	2.24	2.75	3.88	-12.1	-7.4	-2.4
Hamann ⁸	1.71	1	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 $-16\cdot 2$ c.c. mole⁻¹, obtained by density measurements,¹¹ for the first ionization constant of phosphoric acid is in reasonable agreement with our value ($-15\cdot 5$ 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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917. The First Acid Dissociation Constant of Hydrogen Sulphide at High Pressures.

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PREVIOUS papers ¹⁻³ showed the large effect of pressure on the ionisation of weak acids of the hydrated gas type such as "carbonic acid" and "sulphurous acid," compared with simple weak acids such as acetic and phosphoric acid. The work on carbon dioxide was part of a programme on the chemistry of mineral deposition under high pressures and high temperatures. Results are now given from conductance measurements at 25° of the effect of pressure on the ionisation of hydrogen sulphide, also a dissolved gas weak acid and important in natural mineral-forming processes.

Experimental.—*Materials and apparatus.* Hydrogen sulphide was prepared by the reaction of "AnalaR" sodium sulphide with dilute sulphuric acid. Pure nitrogen was passed for an hour through the distilled water (specific conductance 1.4×10^{-6} ohm⁻¹ cm.⁻¹) used for making the sulphide solutions. Potassium hydrogen sulphide solutions were prepared by titrating hydrogen sulphide solutions to pH 9.3 with potassium hydroxide.

The apparatus used was similar to that described previously.¹

TABLE 1.

Hydrogen sulphide: variation in L' with oscillator frequency (values of 10^{-5} L').

Frequency		P (atm.	.)	Frequency	P (atm.)		
(cycles/sec.)	1	1000	2000	(cycles/sec.)	1	1000	2000
500	2.07	2.86	3.80	2000	2.16	3.01	4.06
1000	$2 \cdot 10$	2.95	3.99	5000	2.18	3.05	4.12

TABLE 2.

Potassium hydrogen sulphide: values of $\Lambda^{P} \rho_{r} / \Lambda^{1}$ at 25° for 10⁻³m-solutions.

(Value of Λ^1 in parentheses.)

P (atm.)	 1	500	1000	1500	2000
$\Lambda^{\rm P} \rho_{\rm r} / \Lambda^1$	 (139)	1.030	1.045	1.055	1.065

Method. Previous values ¹ for the conductance of potassium chloride and hydrochloric acid were combined with the present results for hydrogen sulphide and potassium hydrogen sulphide to provide values of K_a for hydrogen sulphide.

Corrections for the conductance of the distilled water were made as before.¹

At the concentrations of hydrogen sulphide used (0.01-0.001m), ionization is less than 1%. Within this degree of accuracy the concentrations of un-ionized hydrogen sulphide can be equated to the total sulphide in solution. The first molal dissociation constant, $K_{\rm a}$, was obtained from the equation

$$egin{aligned} K_{
m a} &= m^{-1} \gamma_{\pm}{}^2 \ (1000 L' / \Lambda' arphi_{
m p})^2, \ L' &= 10^{-3} \Lambda' arphi_{
m r} K_{
m a}{}^{rac{1}{2}} \ m^{rac{1}{2}} / \gamma_{\pm}. \end{aligned}$$

i.e.,

At the low ion concentrations ($\sim 10^{-5}$ m) the value for the sum of the molar conductances Λ' of the H⁺ and HS⁻ ions can be taken as constant at each pressure, and the value of γ_{\pm}^* equated to unity.

By plotting L' against $m^{\frac{1}{2}}$, a line of slope $10^{-3}\Lambda' \rho_r K_a^{\frac{1}{2}}$ was obtained for each pressure, and hence the value of K_a obtained.

Bright platinum electrodes were used in the conductance cell as it was considered this would minimize their interaction with the sulphide solutions. To check any polarisation effects, results were obtained for several different oscillator frequencies. Table 1 gives typical values of L' (ohm⁻¹ cm.⁻¹) for a solution of hydrogen sulphide.

Values o	of $\Lambda^1 \rho_r u$	sed in calcul	ation of H	Ka.	
$P (atm.) \dots $ $\Lambda' \rho_r \dots$	1 417	500 439	$\begin{array}{r}1000\\454\end{array}$	$\begin{array}{r}1500\\467\end{array}$	$\begin{array}{r} 2000\\ 480 \end{array}$
	1994 1193	TABLE 4.			
First acid dissociatio	on const	ant, $K_{\rm a}$, for	hydrogen	sulphide a	t 25°.
P (atm.) 10 ⁷ K _a	$1 \\ 1.54$	$500 \\ 2.10$	$ \begin{array}{r} 1000 \\ 2.76 \end{array} $	1500 3·56	$2000 \\ 4.25$
	$\Delta V^1 = -$	-15.0 c.c. mo	le ⁻¹ .		

TABLE 3.

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The ratios of high- and low-pressure L' values are constant above 1000 cycles and this frequency was used throughout, for convenience. Similar small frequency effects were observed with bright gold electrodes.

Results.—Table 2 gives for potassium hydrogen sulphide the values of $\Lambda^{p} \rho_{r} / \Lambda^{1}$, which within experimental error were constant at concentrations below 10⁻²m. Table 3 contains the values of $\Lambda' \rho_r$ used for calculating K_a .

The Figure presents the specific conductance of hydrogen sulphide solutions as a function of $m^{\frac{1}{2}}$ at the different pressures. Table 4 contains the values of K_{a} derived from the results shown in the Figure, and the change in partial molar volume on ionization at one atmosphere (ΔV^{1}).



Specific conductance $(L' in ohm^{-1} cm.^{-1})$ for hydrogen sulphide as a function of $m^{\frac{1}{2}}$.

Curves relate, reading downwards, to 2000, 1500, 1000, 500, and 1 atm.

Discussion .- The effect of pressure on the first dissociation constant of hydrogen sulphide is less than that for the dissolved gases carbon dioxide $(\Delta V^1 = -26.5)$, sulphur dioxide³ ($\Delta V^1 = -19.7$), and ammonia⁴ ($\Delta V^1 = -28.9$). ΔV^1 for hydrogen sulphide is similar to that for other simple weak acids, for which the values range from about -7to -16 c.c. mole⁻¹ (e.g., salicylic,² formic,⁴ benzoic,² acetic,³ and phosphoric acid: ³ -7.2, -8.8, -10.6, -12.1, and -15.5 c.c. mole⁻¹, respectively). It is therefore confirmed that large negative ΔV^1 values arise only where hydration equilibria are involved in the ionization processes, for example, with carbon dioxide, sulphur dioxide, and ammonia.

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