

Preprinted from the Journal of the Chemical Society,
October, 1961, (917), pages 4678—4680.

917. The First Acid Dissociation Constant of Hydrogen Sulphide at High Pressures.

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PREVIOUS papers¹⁻³ 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 (cycles/sec.)	P (atm.)			Frequency (cycles/sec.)	P (atm.)		
	1	1000	2000		1	1000	2000
500	2.07	2.86	3.80	2000	2.16	3.01	4.06
1000	2.10	2.95	3.99	5000	2.18	3.05	4.12

TABLE 2.

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

(Value of Λ^1 in parentheses.)

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

Method. Previous values¹ 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_a , was obtained from the equation

$$K_a = m^{-1} \gamma_{\pm}^2 (1000L'/\Lambda^{\rho_r})^2,$$

i.e.,

$$L' = 10^{-3} \Lambda^{\rho_r} K_a^{\frac{1}{2}} m^{\frac{1}{2}} / \gamma_{\pm}.$$

The symbols are as defined in the previous papers.

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 $\gamma_{\pm}$ 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.

TABLE 3.

Values of $\Lambda^1 \rho_r$ used in calculation of K_a .

P (atm.)	1	500	1000	1500	2000
$\Lambda^1 \rho_r$	417	439	454	467	480

TABLE 4.

First acid dissociation constant, K_a , for hydrogen sulphide at 25°.

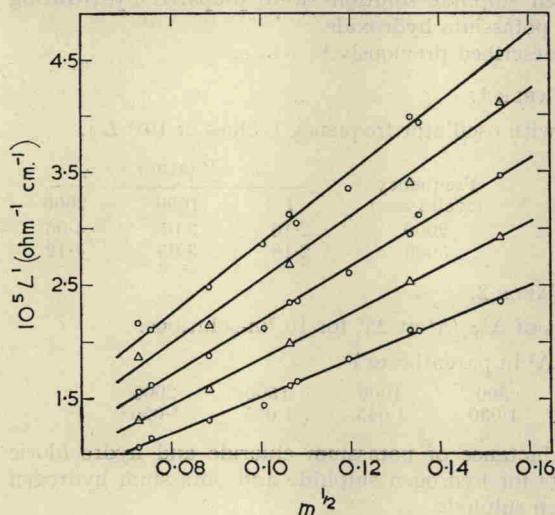
P (atm.)	1	500	1000	1500	2000
$10^7 K_a$	1.54	2.10	2.76	3.56	4.25

 $\Delta V^1 = -15.0$ c.c. mole⁻¹.

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^{-2} m. Table 3 contains the values of $\Lambda^1 \rho_r$ used for calculating K_a .

The Figure presents the specific conductance of hydrogen sulphide solutions as a function of $m^{1/2}$ 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 $\text{ohm}^{-1} \text{cm}^{-1}$) for hydrogen sulphide as a function of $m^{1/2}$.

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 dioxide¹ ($\Delta V^1 = -26.5$), 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 -7 to -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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[Received, May 8th, 1961.]

¹ Ellis, J., 1959, 3689.

² Clark and Ellis, J., 1960, 247.

³ Ellis and Anderson, J., 1961, 1765.

⁴ Hamann, "Physico-chemical Effects of Pressure," Butterworths, London, 1957.