

25. Spectrophotometric Determination of the Acid Dissociation Constants of Hydrogen Sulphide.

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The first acid dissociation constant of hydrogen sulphide has been found by spectrophotometry to be 9.5×10^{-8} at 25° , and the second to be 1.0×10^{-14} at 20° . The method was based on the fact that HS^- ions absorb strongly at 2300 \AA , whereas for H_2S molecules and S^{2-} ions the absorption is much less. The logarithm of the molar extinction coefficient at 2300 \AA for HS^- ions is 3.90 ± 0.01 .

VALUES in the literature for both the first (K_1) and the second (K_2) acid dissociation constant of hydrogen sulphide are not in good agreement. As the HS^- ion absorbs strongly in the ultraviolet region at 2300 \AA ^{1,2} Robinson and Biggs's method³ for determining the dissociation constants of weak acids and bases can be applied.

The first thermodynamic dissociation constant is given by $K_1 = a_{\text{H}}\gamma_{\text{HS}}\alpha/(1 - \alpha)$, where a_{H} is the hydrogen-ion activity, α is the fraction of sulphide present as HS^- (at pH's where the S^{2-} ion concentration can be neglected), and γ_{HS} is the activity coefficient of this ion. The activity coefficient of the H_2S molecules is assumed to be unity at the concentrations used. The degree of dissociation, α , was obtained from measurements of the molal extinction coefficient of hydrogen sulphide in buffered solutions (pH 6.5—7.2), in acid solutions (pH 1.0—3.0), and in solutions at pH 10.5.

Buffers of known hydrogen-ion activity^{4,5} were used at various ionic strengths. At each, γ_{HS} was calculated by the equation suggested by Davies,⁶ $-\log \gamma = [0.5 \mu^{1/2}/(1 + \mu^{1/2})] - 0.1\mu$, and a value of K_1 obtained. The values of K_1 showed little significant variation with ionic strengths between 0.01 and 0.4.

The second dissociation constant can be expressed by the equation $K_2 = a_{\text{H}}\gamma_{\text{S}^{2-}}\alpha'/(1 - \alpha')\gamma_{\text{HS}} = K_w\gamma_{\text{S}^{2-}}\alpha'/(1 - \alpha')m_{\text{OH}}\gamma_{\text{OH}}\gamma_{\text{HS}}$, where K_w is the thermodynamic dissociation constant of water, $\gamma_{\text{S}^{2-}}$ and γ_{OH} the activity coefficients of the S^{2-} ions and the

¹ Noda, Kuby, and Lardy, *J. Amer. Chem. Soc.*, 1953, **75**, 913.

² Orgel, *Quart. Reviews*, 1954, **8**, 428.

³ Robinson and Biggs, *Trans. Faraday Soc.*, 1955, **51**, 901.

⁴ Bates and Acree, *J. Res. Nat. Bur. Stand.*, 1943, **30**, 129.

⁵ *Idem, ibid.*, 1945, **34**, 373.

⁶ Davies, *J.*, 1938, 2093.

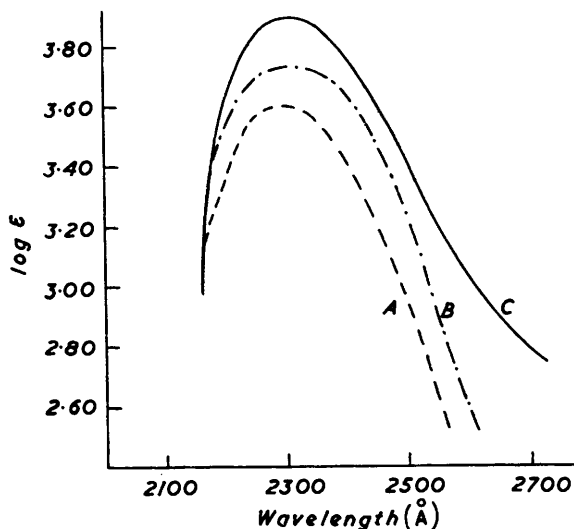
OH^- ions respectively, and m_{OH} the molality of hydroxide. α' is the fraction of sulphide present as S^{2-} in alkaline solutions where the H_2S concentration can be neglected.

As K_2 is of the order of 10^{-14} , measurements must be made in strongly alkaline solutions for the fraction of S^{2-} ions to be appreciable. Solutions of lithium, sodium, and potassium hydroxides were used at concentrations ranging from 0.25 to 2.5 molal, and values of K_2' obtained by assuming the activity-coefficient ratio $\gamma_{\text{S}^{2-}}/(\gamma_{\text{OH}^-}\gamma_{\text{HS}^-})$ to be unity. It is not possible to calculate the true value for this ratio, but from the trend of K_2' with hydroxide concentration a useful approximation for the thermodynamic dissociation constant K_2 can be obtained.

EXPERIMENTAL

Methods and Materials.—Absorption spectra were measured with a Beckman model DU spectrophotometer in a room maintained at constant temperature. Matched fused silica cells with a 1 cm. light-path were used.

In the experiments for determining K_2 , standardised carbonate-free lithium hydroxide, sodium hydroxide, and potassium hydroxide solutions were used to control the alkalinity.



Hydrogen sulphide was prepared by treating "AnalaR" sodium sulphide with dilute sulphuric acid. Precautions against oxidation of the solutions by the atmosphere were unnecessary at neutral pH's, but the alkaline solutions were prepared in oxygen-free water, and transferred in a nitrogen atmosphere. Oxidation of hydrogen sulphide by the air occurs much more rapidly in alkaline solutions.

Concentrations were estimated by adding a known weight of sulphide solution to acidified iodine, and back-titrating the excess of iodine with standard thiosulphate.

The absorption of the HS^- ion at 2300 Å in borate buffers obeys Beer's law, and from the slope of the absorption *versus* concentration graph the logarithm of the molar extinction coefficient ($\log \epsilon$) is 3.90 ± 0.01 . This average represents twenty results on sulphide solutions ranging from 10^{-6} to 3×10^{-4} M. For comparison, the values reported by Orgel² and by Noda, Kuby, and Lardy¹ are 3.68 and 3.88 respectively.

In the Figure $\log \epsilon$ is plotted against wavelength for hydrogen sulphide in M- (A) and 0.5M- (B) sodium hydroxide solutions, and in a borate buffer (C) of pH 11.15. At high alkalinities no peak or inflection in the curves appears which would correspond to the absorption of the S^{2-} ion. For molecular hydrogen sulphide in a 0.01N-hydrochloric acid solution $\log \epsilon$ is 1.49 at 2300 Å.

In these tables, D is the observed optical density of the solutions at 2300 Å. α is obtained from D and the known absorption of the HS^- ions and hydrogen sulphide molecules. The pH of the buffers ($-\log m_{\text{H}^+}\gamma_{\text{H}^+}$ from Bates and Acree's data^{4,5}) is altered slightly by the addition of

hydrogen sulphide. Column 6 shows the pH of the solutions corrected for this effect by Robinson and Biggs's method.³

TABLE 1. *Results for K_1 by use of phosphate buffers⁴ at $25^\circ \pm 1^\circ$ containing $(\text{KH}_2\text{PO}_4) : (\text{Na}_2\text{HPO}_4) : (\text{NaCl}) = 1 : 1.529 : 1$ molar.*

$\mu^{\frac{1}{2}}$	D	Total H_2S (10^4m)	α	Buffer pH	Corrected pH	$-\log \gamma_{\text{HS}}$	$\text{p}K_1$
0.412	0.876	2.03	0.542	6.966	6.962	0.129	7.02
0.281	0.867	1.88	0.579	7.064	7.057	0.101	7.02
0.228	0.614	1.30	0.595	7.110	7.105	0.088	7.03
0.139	1.045	2.14	0.613	7.202	7.171	0.059	7.03
0.113	1.12	2.29	0.613	7.229	7.180	0.049	7.03

TABLE 2. *Results for K_1 by use of phosphate buffers⁴ at $25^\circ \pm 1^\circ$ containing $(\text{KH}_2\text{PO}_4) : (\text{Na}_2\text{HPO}_4) : (\text{NaCl}) = 1 : 0.6376 : 1$ molar.*

$\mu^{\frac{1}{2}}$	D	Total H_2S (10^4m)	α	Buffer pH	Corrected pH	$-\log \gamma_{\text{HS}}$	$\text{p}K_1$
0.449	0.565	2.18	0.323	6.564	6.562	0.135	7.02
0.336	0.719	2.55	0.351	6.640	6.637	0.114	7.02
0.192	0.872	2.79	0.391	6.766	6.753	0.077	7.02
0.127	0.680	2.06	0.413	6.835	6.814	0.055	7.02
0.105	1.15	3.52	0.408	6.860	6.809	0.046	7.02

TABLE 3. *Results for K_1 by use of phosphate buffers⁵ at $25^\circ \pm 1^\circ$ containing equimolar KH_2PO_4 and Na_2HPO_4 , and no sodium chloride.*

$\mu^{\frac{1}{2}}$	D	Total H_2S (10^4m)	α	Buffer pH	Corrected pH	$-\log \gamma_{\text{HS}}$	$\text{p}K_1$
0.633	1.06	3.34	0.395	6.671	6.669	0.154	7.01
0.447	0.890	2.57	0.433	6.772	6.770	0.135	7.02
0.316	0.790	2.10	0.471	6.860	6.856	0.110	7.02
0.200	0.410	1.01	0.506	6.959	6.955	0.079	7.02
0.141	0.910	2.19	0.520	7.018	6.999	0.060	7.02

From the three series of results the average value for $\text{p}K_1$ is 7.02.

TABLE 4. *The second acid dissociation constant of hydrogen sulphide at 20° .*

NaOH Solutions				LiOH Solutions			
Alkali concn. (m) ...	2.46	1.00	0.50	0.25	Alkali concn. (m)	1.00	1.00
$\text{p}K_2'$	14.00	13.96	13.97	13.96	$\text{p}K_2'$	13.89	13.89
$\gamma_{\pm} (\text{NaOH})$	0.709	0.678	0.690	0.716	$\gamma_{\pm} (\text{LiOH})$	0.554	0.554
KOH Solutions							
Alkali concn. (m) ...	5.00	2.00	1.00	0.50	0.25		
$\text{p}K_2'$	14.8	14.01	13.83	13.81	13.91		
$\gamma_{\pm} (\text{KOH})$	1.72	0.888	0.756	0.732	0.749		

Table 4 gives the values obtained for $K_2' = K_w \alpha' / (1 - \alpha') m_{\text{OH}}$ in different alkali solutions. Each value of $\text{p}K_2'$ is derived from a series of approximately six experiments in the particular alkali solution. In each series the HS^- concentrations found from the optical absorption of the solutions at 2300 \AA were plotted against the total sulphide concentrations found by iodine titration. The fraction $\alpha' / (1 - \alpha')$, and hence the average $\text{p}K_2$, was obtained from the slope of this graph. The total sulphide concentrations used in these experiments were in the range 5×10^{-6} to $7 \times 10^{-4}\text{m}$.

The variations in the mean activity coefficients, γ_{\pm} , of the pure alkali hydroxide solutions, as reported by Robinson and Stokes,⁷ are given for comparison in Table 4. The values of $\text{p}K_2$ from sodium and potassium hydroxide solutions show a trend with concentration similar to the values of γ_{\pm} for the particular alkali solution. Extrapolation of graphs of $\text{p}K_2$ versus alkali concentration from 0.25m to zero ionic strength, where $\gamma_{\text{S}}/\gamma_{\text{HS}}\gamma_{\text{OH}} = 1$, gives a value of $\text{p}K_2$ of 14.00.

⁷ Robinson and Stokes, "Electrolyte Solutions," Butterworths Scientific Publications, London, 1955.

TABLE 5. *Acid dissociation constants of hydrogen sulphide.*

Source	Method	$10^7 K_1$	$10^{14} K_2$	Temp.
This work	Spectrophotometric	0.95	—	25°
Kubli ^a	—	—	1.0	20
Epprecht ^b	Potentiometric	0.873	36.3	„
Yui ^c	„	3.31	—	18
Yui ^c	„	1.24	—	25
Knox ^d	Hydrolysis	—	0.12	18
Kuster and Heberlein ^e	„	—	6.0	„
Auerbach ^f	Conductance	0.91	—	„
Walker and Cormack ^g	„	0.57	—	„
Konopik and Leberl ^h	Colorimetric pH	—	7.9	20

^a Kubli, *Helv. Chim. Acta*, 1946, **29**, 1962. ^b Epprecht, *ibid.*, 1938, **21**, 205. ^c Yui, *Sci. Rep. Tohoku Univ.*, 1951, **35**, 53. ^d Knox, *Z. Elektrochem.*, 1906, **12**, 477. ^e Kuster and Heberlein, *Z. anorg. Chem.*, 1905, **43**, 53. ^f Auerbach, *Z. physikal. Chem.*, 1904, **49**, 220. ^g Walker and Cormack, *J.*, 1900, **77**, 5. ^h Konopik and Leberl, *Monatsh.*, 1949, **80**, 781.

Table 5 gives for comparison some of the values reported previously for K_1 and K_2 . The discrepancies in values of K_2 possibly arise from the instability of alkaline sulphide solutions in air. Although it is unlikely that the present value presented for K_2 is more accurate than $\pm 20\%$, this is a distinct improvement over the uncertainties which existed previously.

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