834. *Thermodynamics of Ion Association. Part V.* Dissociation of the Bisulphate Ion.*

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The thermodynamic dissociation constant of the bisulphate ion, as redetermined by a precision e.m.f. method between 0° and 45°, is compared with those by other workers, and the derived heat of dissociation, $\Delta H = -5{\cdot}6 \pm 0{\cdot}2$ kcal./mole, is in good agreement with the calorimetric value.

The extension of our thermodynamic study[1] of the formation of ion pairs between univalent ions of opposite sign to similarly charged ions of higher valency type, such as sulphates of bivalent cations, requires a reliable value for the second dissociation constant of sulphuric acid. The cell employed was similar to that used by Davies, Jones, and Monk[2]

$$H_2,Pt \mid HCl, H_2SO_4 \mid AgCl\text{–}Ag$$

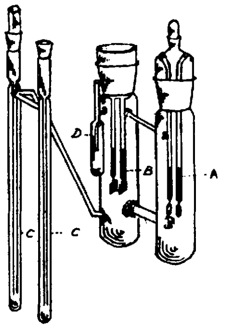
who obtained e.m.f.s to within ±100 μv. Using a more refined apparatus and different cell design, we were able to make measurements at lower ionic strengths, and e.m.f.s were determined to within ±15 μv from 0° to 45°.

Experimental

Solutions were made up by weight with conductivity water prepared by mixed-bed deionisation.[3]

Constant-boiling hydrochloric acid was prepared by distillation of the "AnalaR" acid diluted to a specific gravity of 1·14, recommended modifications being introduced.[4,5,6] Concentrations were determined by estimating the chloride gravimetrically as silver chloride;[7] these agreed to within ±0·01% and were within ±0·01% of the theoretical concentration. Sulphuric acid solutions were made by dilution of three different samples of "AnalaR" acid; duplicate sulphate determinations as barium sulphate[7] agreed to ±0·02%.

The e.m.f. cell.



The e.m.f. cell (Figure) was of the conventional H pattern, similar to that used by Noyes and Ellis.[8] Two hydrogen pre-saturators, *C*, were made integral with the hydrogen-electrode compartment, as recommended by Harned and Morrison,[9] and the modifications of Ashby, Crook, and Datta[10] were also incorporated. The electrodes were supported in the compartments with standard ground-glass cones and each cell contained a pair of silver–silver chloride, *A*, and hydrogen electrodes, *B*, enabling four estimates of e.m.f. to be made. A guard tube, *D*, was fitted to the hydrogen electrode compartment and any liquid collecting in it was immediately removed.

Hydrogen electrodes consisted of stout platinum foil (0·4 × 2·5 cm.) welded to platinum wire (0·05 cm. diam.). A very thin coat of platinum black was deposited on them by electrolysis at about 0·2 A/cm.^{2} for 2 min. in 2·5% of chloroplatinic acid in N-hydrochloric acid, the current being reversed every 15 sec. The platinum black was removed with aqua regia after every alternate run and a fresh deposit

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* Part IV, *J.*, 1958, 3706.

[1] Nair and Nancollas, *J.*, 1957, 318.

[2] Davies, Jones, and Monk, *Trans. Faraday Soc.*, 1951, **48**, 921.

[3] Davies and Nancollas, *Chem. and Ind.*, 1950, **7**, 129.

[4] Foulk and Hollingworth, *J. Amer. Chem. Soc.*, 1923, **45**, 1223.

[5] Titus and Smith, *ibid.*, 1941, **63**, 3266.

[6] Shaw, *Ind. Eng. Chem.*, 1926, **18**, 1065.

[7] Vogel, "A Text Book of Quantitative Analysis," Longmans, London, 1947.

[8] Noyes and Ellis, *J. Amer. Chem. Soc.*, 1917, **39**, 2532.

[9] Harned and Morrison, *Amer. J. Science*, 1937, **33**, 161.

[10] Ashby, Crook, and Datta, *Biochem. J.*, 1954, **56**, 190.

made. Electrodes were stored in conductivity water saturated with hydrogen. Spectroscopically pure silver oxide (Johnson Matthey & Co.) was used in the preparation of silver–silver chloride electrodes which were of the thermal electrolytic type incorporating at least 150—200 mg. of silver as recommended by Bates.[12] They were warmed in water at 50° for 2 hr. after chloridising [10] and stored in darkness in dilute, oxygen-free potassium chloride solution. Good platinum–Pyrex seals were ensured with all electrodes by casting a little Araldite resin in the bottom of the electrode tubes.

Cylinder hydrogen was freed from oxygen by passing through a " deoxo " purifier (Baker Platinum Division, Engelhard Industries Ltd., London) and saturated with water vapour in a series of bubblers. Solutions were bubbled with hydrogen for at least 1 hr. before use. Electrodes were washed three times with solution in a washing apparatus in which provision was made for hydrogen bubbling; they were then quickly transferred to the cell which was swept out with hydrogen. Filling was carried out in an all-glass apparatus by means of hydrogen pressure; the cells were placed in a thermostat, and a steady slow stream of hydrogen was maintained in the hydrogen electrode compartment. The thermostat could be maintained at any temperature between 0° and 45° to within ±0·005°. Temperatures were measured with platinum resistance thermometers, constructed as suggested by Barber,[13] and calibrated at the triple point of water and at several other temperatures below 100° against a resistance thermometer kindly lent by Dr. S. P. Datta which had an N.P.L. standardisation. Barber and Herington's [14] procedure was followed in constructing triple-point cells and in water purification. Thermometers were connected in series with a standard 25 ohm resistance maintained at 25° and a current of 1 mA was passed, the potential drop being measured with a vernier potentiometer. In order that e.m.f. measurements could be made at " round " temperatures a series of Beckmann thermometers to be used in the thermostat were calibrated with the resistance thermometers and were frequently checked.

E.m.f.s were measured with a precision vernier potentiometer (Type P.10., Croydon Precision Instrument Co.) in the range with direct reading to 10 μv. Further subdivision could be made from the deflection of the sensitive moving coil galvanometer (Type 41127, Cambridge Instrument Co.) used as a null detector with lamp and scale at 1 metre. Two Weston standard cells (Cambridge Instrument Co.) were kept permanently at 25° in an oil thermostat; their e.m.f. never differed by more than 20 μv.

Four cells could be accommodated in the thermostat and they required 3—4 hr. to come to equilibrium initially. Thereafter the e.m.f. remained constant to within 10 μv for more than ½ hr. and different combinations of electrodes agreed to within 20 μv. At subsequent temperatures the cells reached equilibrium within 1 hr. Observed e.m.f.s were corrected for pressure after adjusting barometer readings for latitude and temperature.

RESULTS AND DISCUSSION

The standard potential of the silver–silver chloride electrode may vary [15] by as much as 200 μv, probably owing to small differences in the structure of the solid phases. Since the mean activity coefficient, $\gamma_{\pm}$, of 0·01 molal hydrochloric acid is uncertain only to about 0·0005, which corresponds to 30 μv, each electrode was standardised in this solution and the recommended $\gamma_{\pm}$ values [15] employed to calculate E°: $\gamma_{\pm} = 0{\cdot}908$ at 0° and 0·904 at 25°. At other temperatures, $\gamma_{\pm}$ values were obtained from [16]

$$\log \gamma_{\pm} = Am^{\frac{1}{2}}/(1 + m^{\frac{1}{2}}) + 0{\cdot}234m$$

which, with use of the appropriate values of the Debye–Hückel constant A, gives the same $\gamma_{\pm}$ values at 0° and 25° when $m = 0{\cdot}01$m. The E° values of different sets of electrodes never differed from Harned and Ehlers's values [17] by more than 230 μv. Purlee and

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[11] Harned, *J. Amer. Chem. Soc.*, 1929, **51**, 416.

[12] Bates, " Electrometric pH Determinations," Wiley, New York, 1954, p. 200.

[13] Barber, *J. Sci. Instr.*, 1950, **27**, 47.

[14] Barber and Herington, *J. Appl. Phys.*, 1954, **5**, 41.

[15] Bates, Guggenheim, Harned, Ives, Janz, Monk, Robinson, Stokes, and Wynne-Jones, *J. Chem. Phys.*, 1956, **25**, 361.

[16] Guggenheim and Prue, *Trans. Faraday Soc.*, 1954, **50**, 231.

[17] Harned and Ehlers, *J. Amer. Chem. Soc.*, 1932, **54**, 1350; 1933, **55**, 2179.

Grunwald[18] observed similar differences with silver–silver chloride electrodes formed either by chloridising silver mirrors or thermoelectrolytically.

The e.m.f. of the cell

$$H_2,Pt \mid HCl(m_1),\ H_2SO_4(m_2) \mid AgCl\text{–}Ag$$

may be written

$$E = E^\circ - k \log a_{H^+}a_{Cl^-}$$

or

$$-\log m_{H^+} = (E - E^\circ)/k + \log m_1 + 2 \log \gamma_\pm$$

where $k = 2{\cdot}3026\boldsymbol{RT/F}$ and has the values given by Robinson and Stokes,[19] and m_1 and m_2 represent molal concentrations. The ionic strength

$$I = 2m_{H^+} - (m_1 + m_2)$$

$$m_{HSO_4^-} = m_1 + 2m_2 - m_{H^+}$$

and

$$m_{SO_4^{2-}} = m_2 - m_{HSO_4^-}$$

Activity coefficients were obtained from[20]

$$-\log \gamma_z = Az^2 [I^{\frac{1}{2}}/(1 + I^{\frac{1}{2}}) - 0{\cdot}2I]$$

A being the Debye–Hückel constant, (kg./mole)$^{\frac{1}{2}}$, at the appropriate temperature.[21]

The thermodynamic dissociation constant $k_2 = m_{H^+}m_{SO_4^{2-}}\gamma_2/m_{HSO_4^-}$ was obtained by successive approximations of I and the results are given in Table 1.

The k_2 values are compared with those of Davies, Jones, and Monk[2] in Table 2. The differences between them may be accounted for almost completely by the use of the same A values in the calculations. The value at 25° of Davies, Jones, and Monk is based on $A = 0{\cdot}50$. Substitution of the Debye–Hückel value, 0·5085, brings k_2 into agreement with the present work. Recalculated values from Davies, Jones, and Monk's data are shown in Table 2.

At 25° there are many k_2 data, many of which have been reviewed elsewhere.[19] Hamer,[22] studying the cell $H_2,Pt \mid Na_2SO_4,\ NaHSO_4,\ NaCl \mid AgCl\text{–}Ag$, obtained a value of 0·0120; the data have been recalculated[2] with allowance for the formation of $NaSO_4^-$ ions to give $k_2 = 0{\cdot}0102$. Hamer[23] has re-examined the e.m.f. data using different values of ion-size parameter, a_i, and extrapolating to infinite dilution and has suggested that the k_2 values from the acid–acid cell[2] converge to a single value whereas his original data do not. This extrapolation procedure is open to objection, however, since it produces impossible β values in the activity-coefficient expression:

$$-\log \gamma_z = Az^2I^{\frac{1}{2}}/(1 + Ba_iI^{\frac{1}{2}}) + \beta I$$

The spectrophotometric value[24] ($k_2 = 0{\cdot}0104 \pm 0{\cdot}0003$) is usually regarded[19] as the most reliable. It is based, however, on a method which neglects the formation of $NaSO_4^-$ in sodium sulphate solutions and, moreover, a negative value for the ion size ($a_i = -5{\cdot}8$ Å) was apparently used.[23] Kerker[25] has recalculated conductance and transference-number data by the method of Sherrill and Noyes,[1] who obtained originally $k_2 = 0{\cdot}0118$,[26] and

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[18] Purlee and Grunwald, *J. Phys. Chem.*, 1955, **59**, 1112.

[19] Robinson and Stokes, " Electrolyte Solutions," Butterworths, London, 1955.

[20] Davies, *J.*, 1938, 2093.

[21] Manor, Bates, Hamer, and Acree, *J. Amer. Chem. Soc.*, 1943, **65**, 1765.

[22] Hamer, *J. Amer. Chem. Soc.*, 1934, **56**, 860.

[23] Hamer, Symposium on Structure of Electrolyte Solutions, Electrochem. Soc., Washington, May 1953; personal communication.

[24] Young, Klotz, and Singleterry, based on dissertations of the last two; University of Chicago, 1940, quoted in ref. 19.

[25] Kerker, *J. Amer. Chem. Soc.*, 1957, **79**, 3664.

[26] Sherrill and Noyes, *ibid.*, 1926, **48**, 1861.

TABLE 1. *E.m.f. measurements.*

No.	10^3m_1	10^3m_2	No.	10^3m_1	10^3m_2	No.	10^3m_1	10^3m_2	No.	10^3m_1	10^3m_2
1	1·2711	1·3498	6	5·0645	3·6773	11	6·7748	5·4093	16	2·8003	3·1488
2	1·8441	1·8564	7	5·1554	5·5379	12	5·3530	7·1315	17	2·3264	2·2471
3	2·1606	2·2481	8	6·7047	3·8888	13	8·1637	8·4059	18	3·2284	2·6627
4	2·3804	2·0919	9	2·0278	2·0131	14	5·7665	10·1000	19	2·7147	2·7006
5	3·5560	2·9684	10	4·6073	5·4429	15	2·1500	1·7383	20	3·8725	4·1791

No.	$E - E°$	10^3I	$10^3m_{H^+}$	$10^3m_{HSO_4^-}$	10^2k_2
		Temp. 0°			
1	0·29131	5·058	3·8394	0·1312	2·66
2	0·27541	6·941	5·3206	0·2362	2·60
3	0·26791	8·255	6·3320	0·3248	2·60
4	0·26583	8·060	6·2660	0·2981	2·62
5	0·24864	11·429	8·9764	0·5164	2·79
		Temp. 5°			
6	0·23929	14·331	11·537	0·8825	2·28
7	0·23366	18·813	14·753	1·4781	2·38
8	0·22920	16·311	13·452	1·0300	2·27
		Temp. 15°			
6	0·24843	13·842	11·292	1·1273	1·59
7	0·24280	17·909	14·301	1·9301	1·58
8	0·23795	15·788	13·191	1·2914	1·61
		Temp. 25°			
1	0·31904	4·769	3·6961	0·2754	1·07
2	0·30179	6·503	5·1005	0·4553	1·11
3	0·29371	7·677	6·0431	0·6137	1·11
4	0·29146	8·724	5·9632	0·6009	1·03
5	0·27280	10·510	8·5163	0·9765	1·13
7	0·25193	17·144	13·9187	2·3125	1·14
9	0·29737	7·049	5·5441	0·5099	1·14
10	0·25593	16·498	13·273	2·2204	1·14
11	$0{\cdot}24276_4$	18·300	15·244	2·3493	1·15
12	$0{\cdot}24726_6$	20·285	16·386	3·2300	1·12
		Temp. 25° (*contd.*)			
13	$0{\cdot}23092_4$	25·040	20·826	4·1498	1·15
14	0·23979	26·02	20·954	5·0454	1·12
15	0·29734	6·485	5·1866	0·4400	1·09
16	0·28032	10·131	8·0410	1·0570	1·05
17	0·29126	7·788	6·1804	0·6415	1·07
18	0·22760	9·543	7·7160	0·8378	1·12
		Temp. 35°			
2	0·31245	6·298	4·9995	0·5573	0·824
3	0·30418	7·396	5·9026	0·7543	0·806
9	0·30787	6·833	5·4371	0·6170	0·859
17	0·30164	7·504	6·0393	0·7833	0·777
18	0·28749	9·208	7·5994	1·0044	0·827
20	0·27490	12·830	10·441	1·7897	0·868
		Temp. 45°			
1	0·34145	4·517	3·5690	0·4017	0·622
2	0·32323	6·076	4·8881	0·6683	0·614
3	0·31468	7·140	5·7742	0·8826	0·615
9	0·31864	6·530	5·2854	0·7678	0·598
17	0·31210	7·221	5·8975	0·9251	0·580
18	0·29752	8·834	7·3625	1·1914	0·603
19	0·30382	8·444	6·9296	1·1863	0·592
20	0·28465	12·203	10·127	2·1033	0·622

TABLE 2. *Values of k_2.*

	0°	5°	15°	25°	35°	45°
Davies, Jones, and Monk [2]	—	1·73	1·43	1·03	0·78	—
Recalculated	—	1·90	1·56	1·09	0·80	—
Present work	2·62	2·31	1·59	1·10	0·82	0·60

has derived a value of 0·0102. There is still some doubt, however, about the value to be used for the conductance of the sulphate ion in such calculations. Kentama [27] has reported a value of 0·0114 from solubility measurements with silver sulphate.

The heat of dissociation of the bisulphate ion has been obtained by the method of least squares from the good linear plot of log k_2 against T^{-1}. The heat and entropy values agree well with the calorimetric values of Pitzer [28] as shown in Table 3.

TABLE 3. *Thermodynamic properties.*

	ΔH (kcal./mole)	ΔG (kcal./mole)	ΔS (cal. deg.$^{-1}$ mole^{-1})
Pitzer [28]	$-5{\cdot}2 \pm 0{\cdot}5$	2·62	$-26{\cdot}3$
Present work	$-5{\cdot}6 \pm 0{\cdot}2$	2·67	$-27{\cdot}7$

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[27] Kentama, *Suomen Kem.*, 1957, **1**, 30.

[28] Pitzer, *J. Amer. Chem. Soc.*, 1937, **59**, 2365.