The Heat Capacity and Entropy of Silver Sulfate from 14 to 300°K. The Entropy of Sulfate Ion

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The heat capacity of Ag_2SO_4 has been measured from 14 to 300°K and the entropy of the salt determined by graphical integration. By coupling this value with the entropy of solution and the entropy of silver ion, the entropy of sulfate ion in aqueous solution has been evaluated.

THE determination of the entropy of silver sulfate is the first[1] of a series of investigations which, along with existing requisite data, should serve to establish the entropy of aqueous sulfate ion with a good degree of precision.

The heat capacity of Ag_2SO_4 was measured from 14 to 300°K by employing the experimental method of Latimer and Greensfelder.[1] Thomsen's[2] heat of solution was used and the free energy of solution was calculated from solubility data. The entropy of Ag^+ has been recalculated by the authors from the most recent data available. Twelve independent computations with a maximum deviation from the mean of 0.3 e.u. give $S^0{}_{298.1}$ of $Ag^+ = 18.3$ e.u.

MATERIAL

Silver sulfate of C.P. quality was recrystallized twice from concentrated H_2SO_4. The salt was washed and then ignited to 400°C to insure the absence of occluded H_2SO_4. A portion of the sample fused to a clear pale yellow liquid. The sample showed an Ag content (by precipitation of AgCl) of 69.11 percent, whereas theoretical is 69.19 percent. It is undoubtedly purer than the analysis indicates. Specific heat measurements were made on a sample weighing 257.444 g. (0.82562 mols).

MEASUREMENTS

The molal heat capacity values fall on a smooth curve which has several points of double inflection. These points of inflection undoubtedly represent an actual property of the salt since the results are reproducible to ±0.05 percent. More-over, $CaC_2O_4 \cdot H_2O$[1] which was measured in the same calorimeter and with the same $R - T$ scale did not exhibit such a phenomenon. The experimental results are presented in Table I and shown graphically as a function of log T in Fig. 1. The temperature intervals employed in various regions were as follows: below 30°K, about 3° per run; 30 to 200°K, about 5° per run; above 200°K, from 5 to 8° per run.

ENTROPY OF SILVER SULFATE

The entropy of Ag_2SO_4 was obtained by graphical integration of the expression $S = \int_0^{298.1} C_p \, d \ln T$

TABLE I.

T°K	Molal C_p	T°K	Molal C_p	T°K	Molal C_p
14.60	2.12	78.74	17.43	160.89	24.49
16.18	2.22	82.89	17.96	166.26	24.81
18.61	3.44	87.18	18.45	171.72	25.18
21.76	4.64	91.44	18.92	177.95	25.77
25.32	5.73	95.96	19.38	184.45	26.01
28.46	6.61	100.89	19.92	191.52	26.41
32.31	7.76	105.77	20.33	198.96	26.84
36.77	9.15	110.29	20.80	206.62	27.34
40.90	10.42	114.97	21.06	213.81	27.57
44.78	11.49	119.80	21.52	220.94	27.88
49.11	12.52	124.38	21.87	229.02	28.23
53.62	13.28	128.87	22.19	236.88	28.52
57.41	13.94	133.34	22.43	245.44	28.81
61.46	14.69	138.00	22.84	255.06	29.35
65.87	15.17	142.79	23.18	265.41	29.89
70.03	16.20	147.34	23.61	275.77	30.43
73.84	16.83	151.74	23.80	285.24	30.80
75.50	16.98	156.15	24.17	296.20	31.36

[1] Measurements on Hg_2SO_4, $CaSO_4 \cdot 2H_2O$ and $BaSO_4$ are yet unpublished. For complete reference to the general theory and previous work, see the authors, J. Am. Chem. Soc. **55**, 971 (1933).

[2] Thomsen, *Thermochemistry*, p. 52. Longmans Green and Co., 1908. Translated by K. A. Burke.
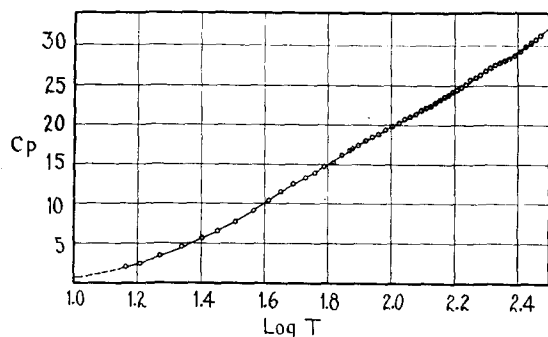
FIG. 1. The heat capacity of Ag_2SO_3.

from the curve shown in Fig. 1. The curve was extrapolated below 14°K by means of the Debye T^3 rule, $\theta = 88.01$. A summary of the entropy calculations is given in Table II.

TABLE II.

| 0–14°K | Extrapolation | 0.624 e.u. |
| 14–298.1°K | Graphical | 47.134 e.u. |

Entropy at 298.1°K of $Ag_2SO_3 = 47.76 \pm 0.05$ percent.

HEAT OF SOLUTION

Thomsen[2] gives ΔH of solution at 18°C as 4480 cal. This value was corrected to infinite dilution by means of a value[3] based on the similarity of Ag_2SO_4 and K_2SO_4 solutions. This

was then corrected to 25°C by employing the partial molal heat capacities of Randall and Rossini.[4] We have then: $Ag_2SO_4(s) = Ag_2SO_4(aq)$; $\Delta H^0_{298.1} = 4207$ cal.

FREE ENERGY OF SOLUTION

Chloupek and Danes[5] find that a saturated solution of Ag_2SO_4 at 25°C is 0.026888 m. This agrees well with the solubility of Harkins and others.[6] We have used 0.533[7, 8] for the corresponding activity coefficient. The free energy of solution is given by $\Delta F^0_{298.1} = -1363.8$ log $[4 \times (0.533 \times 0.02689)^3] = 6722$ cal.

ENTROPY OF SULFATE ION

Substituting in the equation $\Delta S^0 = (\Delta H^0 - \Delta F^0)/T$, we have for the reaction, $Ag_2SO_4(s) = 2Ag^+ + SO_4^{--}$ (hypothetical one molal solution); $\Delta S^0_{298.1} = -8.4$, which yields in turn, by application of the third law: $-8.4 = 2 \times 18.3 + S^0_{SO_4^{--}} - 47.8$; $S^0_{298.1}$ of $SO_4^{--} = 2.8$ e.u.

In spite of the uncertainty in correcting Thomsen's[2] heat of solution to the standard state at 25°C, we regard 2.8 as being reliable to 1.0 e.u.

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[3] Lange and Streeck, Zeits. f. physik. Chemie A157, 1 (1931).

[4] Randall and Rossini, J. Am. Chem. Soc. 51, 323 (1929).

[5] Chloupek and Danes, Collection of Czeckoslovak Chemical Communications 4, 124 (1932).

[6] Harkins, J. Am. Chem. Soc. 33, 1813 (1911); other references in this paper. Hill and Simmons, J. Am. Chem. Soc. 31, 821 (1909); Zeits. f. physik. Chemie 67, 594 (1909). Rothmund, Zeits. f. physik. Chemie 69, 523 (1910). Drucker, Zeits. f. anorg. Chemie 28, 362 (1901).

[7] Lewis and Randall, *Thermodynamics and Free Energy of Chemical Substances*, McGraw-Hill, New York, 1923.

[8] Hass and Jellinek, Zeits. f. physik. Chemie A162, 167 (1932). 0.533 compares favorably with values obtained for similar salts by these workers.