[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

The Heat Capacity and Entropy of Calcium Oxalate from 19 to 300° Absolute. The Entropy and Free Energy of Oxalate Ion

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The determination of the entropy of oxalate ion is an important step in the program for the evaluation of ionic entropies,[1] since we wish to use its value in obtaining the entropies of a number of positive ions, especially those of the rare earth group. Moreover, it is of interest theoretically, as there are but few simple divalent negative ions.

The heat capacity of $CaC_2O_4 \cdot H_2O$ was measured directly from 19.31 to 300°K. using the experimental method described by Latimer and Greensfelder.[1c] The heat of solution and free energy of solution were calculated from solubility data. The entropy of calcium ion was calculated from existing data.

Material.—The calcium oxalate used was prepared by precipitation

TABLE I

HEAT CAPACITY OF $CaC_2O_4 \cdot H_2O$

Molecular weight, 146.09

T, °K.	C_p/mole in cal./deg.	T, °K.	C_p/mole in cal./deg.	T, °K.	C_p/mole in cal./deg.
19.31	0.602	81.72	12.218	210.69	28.436
23.16	1.048	87.06	13.178	219.51	29.331
26.12	1.628	91.54	13.948	224.66	29.619
27.21	1.813	97.28	14.922	228.12	29.953
28.99	2.153	101.36	15.626	232.52	30.086
30.10	2.334	105.74	16.314	236.58	31.063
33.72	3.006	111.25	17.150	241.26	30.732
37.76	3.819	117.98	18.043	247.18	32.138
40.55	4.191	123.74	19.087	249.39	31.593
44.95	5.045	128.81	19.834	256.82	32.182
49.22	5.886	133.99	20.182	257.39	32.561
52.41	6.495	138.95	20.800	264.60	33.424
52.96	6.616	144.15	21.363	267.20	33.524
55.64	7.123	149.34	22.194	272.12	33.780
59.87	7.938	154.90	22.858	275.43	34.108
63.31	8.658	160.69	23.500	281.39	34.722
65.75	9.163	165.55	24.190	283.10	36.329
68.81	9.723	173.23	24.860	291.41	36.082
72.13	10.471	180.71	25.703	299.23	36.537
76.53	11.300	194.87	27.226	299.78	36.418

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[1] For the general theory and previous determinations see (a) Latimer and Buffington, THIS JOURNAL, **48**, 2297 (1926); (b) Latimer, *ibid.*, **48**, 2868 (1926); (c) Latimer and Greensfelder, *ibid.*, **50**, 2202 (1928); (d) Latimer, *J. Phys. Chem.*, **31**, 1267 (1927); (e) Latimer and Kasper, THIS JOURNAL, **51**, 2293 (1929); (f) Greensfelder and Latimer, *ibid.*, **50**, 3286 (1928); (g) Latimer and Ahlberg, *ibid.*, **52**, 549 (1930); (h) Latimer and Ahlberg, *Z. physik. Chem.*, Abt. A, **148**, 464 (1930); (i) Latimer and Ahlberg, THIS JOURNAL, **54**, 1900 (1932).

from calcium chloride solution with ammonium oxalate. The chloride solution was kept at about 70° and the precipitation took place over a period of three days. The reaction mixture was stirred constantly. The precipitated material was washed by decantation until the washings gave no test for chloride with silver nitrate. This washed material was dried at 105° and the dried product showed 100.007% $CaC_2O_4 \cdot H_2O$ on the basis of oxide formed on ignition. Specific heat measurements were made on a sample weighing 73.50 g.

Measurements.—The molal heat capacity values fall on a smooth curve up to 200°K. and deviate only slightly above that temperature. The experimental data are given in Table I and are shown graphically in Fig. 1. The temperature intervals employed in various regions were as follows: 19 to 30°K., about 3° per run; 30 to 200°K., about 5° per run; above 200°K., from 5 to 8° per run.

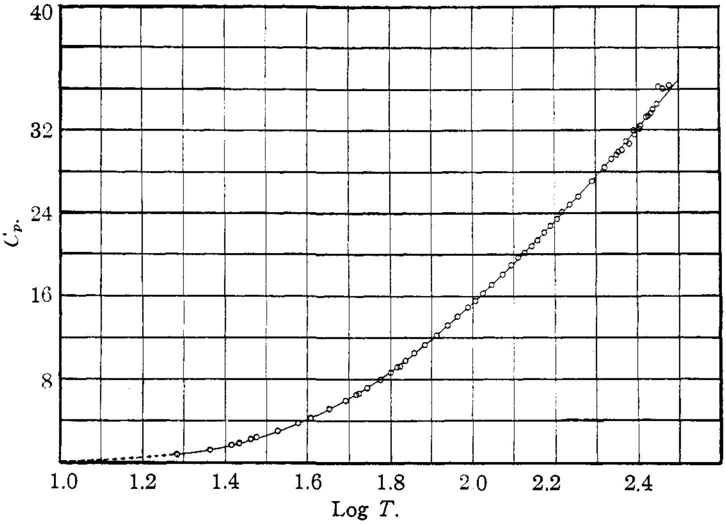

Fig. 1.—Molal heat capacity of calcium oxalate.

Entropy of Calcium Oxalate.—The entropy of calcium oxalate was obtained by a graphical integration of the expression $S = \int_0^T C_p \, d \ln T$ using the curve shown in Fig. 1. The curve below 19.31°K. was extrapolated by means of the Debye T^3 rule. A summary of the entropy calculations is given in Table II.

TABLE II

ENTROPY OF CALCIUM OXALATE

0–19.31°K.	Extrapolation	0.08 E. U.
19.31–298.1°K.	Graphical	37.20 E. U.
Entropy of calcium oxalate at 298.1°K.		37.28 E. U.

Heat of Solution.—The heat of solution of calcium oxalate was calculated from the solubility–temperature coefficient data of Kohlrausch[2] by means of the relation $\Delta H = -R\frac{\mathrm{d}\ln K}{\mathrm{d}(1/T)}$. The solubility product, K, was evaluated from the molal solubility and the activity coefficient, γ, calculated from the Debye–Hückel expression $-\log\gamma = cz^2\sqrt{\mu}$. The factor c has the values 0.505 at 25° and varies as $(TD)^{-3/2}$, where T is the absolute temperature and D the corresponding dielectric constant. Fosbinder[3] finds this expression for log γ to hold for calcium sulfate up to a molality of 0.01. The solubility of calcium oxalate at 25° is 4.85×10^{-5} mole per liter,[2] and the hydrolysis is negligible at this concentration. This calculation leads to a value of 5087 calories for ΔH. The data are shown graphically in Fig. 2a. Holleman[4] and Aumeras[5] give the same values for the solubility at 18 and 20°, respectively, as does Kohlrausch.

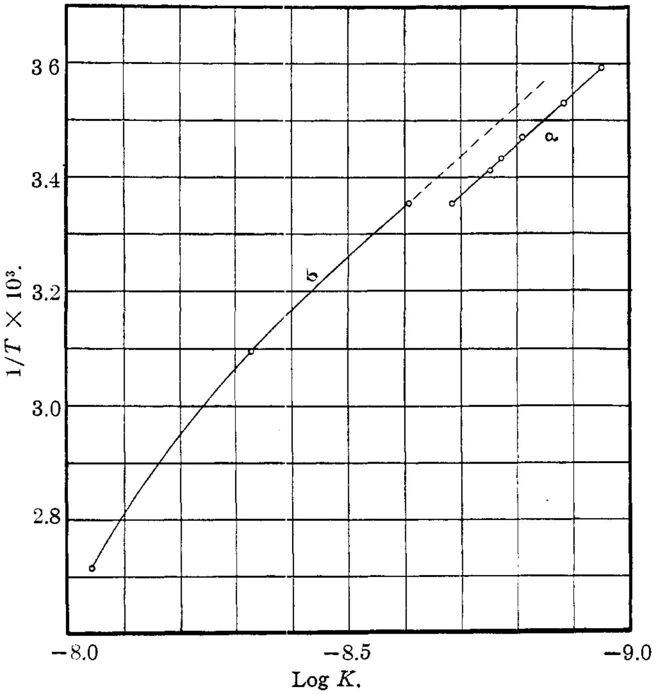

Fig. 2.—Solubility of calcium oxalate.

Assuming the three values given by Richards, McCaffrey and Bisbee[6] to constitute a smooth curve, as shown in Figure 2b, the slope of this

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(2) Kohlrausch, *Z. physik. Chem.*, **64**, 168 (1908).

(3) Fosbinder, THIS JOURNAL, **51**, 1345 (1929).

(4) Holleman, *Z. physik. Chem.*, **12**, 129 (1893).

(5) Aumeras, *J. chim. phys.*, **24**, 43 (1927).

(6) Richards, McCaffrey and Bisbee, *Z. anorg. Chem.*, **28**, 71 (1901).

curve at 25° is the same as that of the curve obtained from Kohlrausch's data, thus giving the same value for the heat of solution.

Free Energy of Solution.—The free energy of solution was calculated from the above data, using the expression $\Delta F^\circ = -RT \ln K$. The values obtained were 11,740 calories (Richards and co-workers) and 11,843 calories (Kohlrausch). The mean of these gives 11,791 calories as the value of ΔF°.

Coupled with the heat of solution above this gives for the entropy of solution of calcium oxalate:

$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta F^\circ}{T} = \frac{5087 - 11{,}791}{298.1} = -22.5$$

Entropy of Oxalate Ion.—Using this value for the entropy of solution, the entropy of the solid as given above and the entropy of water 16.9, as calculated by Giauque,[7] we have for the sum of the entropies of calcium and oxalate ions, 37.28 − 22.5 − 16.9 = −2.12.

In order to determine the entropy of the oxalate ion in respect to $H^+ = 0$, the data summarized in Table III were used to evaluate the entropy of the calcium ion.

TABLE III

THE ENTROPY OF IONIZATION OF WATER AND THE ENTROPY OF CALCIUM HYDROXIDE IN AQUEOUS SOLUTION

	Entropy of substance 298.1°K.	ΔH cal.	ΔF cal.	ΔS E. U.	Sum of ionic entropies, E. U.
H_2O	16.9[7]	13,329[8]	19,122[9]	−19.43	− 2.53
$Ca(OH)_2$	18.24[10]	−3,385[9]	6,960[9]	−34.7	−16.5

From these values the entropies referred to $S^\circ_{H^+} = 0$ are: OH^-, −2.53 and Ca^{++}, −11.4. Using the sum of the entropies of calcium and oxalate ions as given above, we have for the oxalate ion $S^\circ_{298.1} = 11.4 - 2.1 = 9.3$ E. U.

Free Energy of Oxalate Ion.—Roth and Eyemann[11] give −28,110 calories for the heat of neutralization of oxalic acid. Using this with the "Critical Tables" value for the heat of formation of the aqueous acid and Rossini's[8] heat of ionization of water and correcting to 298.1°K. we have

$$H_2 + 2C(g) + 2O_2 = 2H^+ + C_2O_4^= \quad \Delta H = -195{,}000 \text{ calories}$$

Using the entropies H_2, 31.2;[12] C (graphite), 1.3;[13] O_2, 49.0;[14] H^+, 0 and $C_2O_4^=$, 9.3, we calculate $\Delta S = 9.3 - 31.2 - 2.6 - 98.0 = -123$.

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(7) Giauque, to be published in *Phys. Rev.*

(8) Rossini, *Bur. Standards J. Research*, **6**, 847 (1931). The values for ΔH, ΔF and ΔS for water refer, of course, to the reaction, $H_2O(l) = H^+ + OH^-$, and for $Ca(OH)_2$ to $Ca(OH)_2(s) = Ca^{++} + 2OH^-$.

(9) "International Critical Tables." The ΔH of solution for $Ca(OH)_2$ has been corrected to 298.1, using Rossini's value for $\bar{C}_p$ of OH^- and a calculated value of 14 cal./deg. for Ca^{++}. See Rossini, *Bur. Standards J. Research*, **7**, 47 (1931).

(10) Nernst and Schwers, *Sitzb. Akad. Wiss., Berlin*, 366 (1914); Koref, *Ann. Physik*, [4] **36**, 61 (1911); Ewald, *ibid.*, [4] **44**, 1213 (1914). Heat capacity data were obtained from these sources and the entropy calculated by the method used for calcium oxalate above.

(11) Roth and Eyemann, *Z. physik. Chem.*, **143**, 321 (1929).

(12) Giauque, THIS JOURNAL, **52**, 4816 (1930).

(13) Lewis, Gibson and Latimer, *ibid* **44**, 1008 (1922).

(14) Giauque and Johnston, *ibid.*, **51**, 2300 (1929).

With the heat of reaction as given above, this gives $\Delta F^\circ = -195{,}000 + (298.1 \times 123) = -158{,}000$ calories for the free energy of formation of oxalate ion.

Summary

The specific heat of $CaC_2O_4 \cdot H_2O$ has been measured from 19 to 300°K. and the entropy of the salt determined by graphical integration. Coupling this value with the entropy of solution and the entropy of calcium ion as herein calculated, the entropy of oxalate ion has been determined. A value for the free energy of oxalate ion has been calculated.

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Solubility of Nitrogen in Liquid Ammonia at 25° from 25 to 1000 Atmospheres

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Very few measurements have been made on the solubility of gases in liquid ammonia. The most extensive were made by Larson and Black[1] on the solubility of a 3 : 1 hydrogen–nitrogen mixture over a temperature range from −25 to +22° and up to 150 atmospheres. A rough incidental measurement of the solubility of hydrogen in liquid ammonia at −70° was made by Schlubach and Ballauf.[2] Aside from the practical importance, the knowledge of solubilities is of importance for any theory of solutions.

Apparatus and Procedure

Figure 1 shows the apparatus. Synthetic ammonia was fractionated and the middle portion was condensed into steel cylinder A of about 1400 cc. capacity. Nitrogen at a pressure somewhat in excess of the final equilibrium pressure was introduced and the steel cylinder after being disconnected, was shaken by means of the eccentric D. The shaking motion was stopped after a few hours and the pressure was adjusted to the final value through C which was connected both to the piston gage and the compression system. The apparatus was then shaken at this pressure and if necessary the procedure was repeated, until equilibrium was established as indicated by no further pressure change. Several independent sets of runs were taken at each pressure. No trend was observed in the results, showing that equilibrium must have been reached.

The receiving apparatus was evacuated up to the mercury seal maintained in the capillary between G and the buret system H. E was immersed in liquid air. Valve B was then opened slightly, permitting a mixture of ammonia and nitrogen to enter the receiving apparatus. The ammonia was condensed in E and the nitrogen expanded into the Toepler pump. When the sample was considered to be sufficiently large, valve B was closed and the Toepler pump G was operated in order to transfer the nitrogen into

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[1] Larson and Black, *Ind. Eng. Chem.*, **17**, 715 (1925).

[2] Schlubach and Ballauf, *Ber.*, **54**, 2825 (1921).