The Heat Capacities and Entropies of Calcium and Barium Sulfates from 15 to 300°K. The Entropy and Free Energy of Sulfate Ion

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The Heat Capacities and Entropies of Calcium and Barium Sulfates from 15 to 300°K. The Entropy and Free Energy of Sulfate Ion

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The heat capacities of $BaSO_4$ and small precipitated crystals of $CaSO_4 \cdot 2H_2O$ have been measured from 15 to 300°K. The heat capacity of large naturally occurring gypsum crystals was measured from 60 to 274°K. The C_p against log T plots of the molal heat capacities of the two samples of $CaSO_4 \cdot 2H_2O$ differing in crystal surface by a factor of roughly 10^6 show slight deviations from each other. We believe these variations to be outside the limits of experimental error. However, they do not produce a change in entropy at 298.1°K. $S°_{298.1}$ of $CaSO_4 \cdot 2H_2O$ and $BaSO_4$ were determined to be 46.36 and 31.51 E.U. respectively with an accuracy of 0.05 percent. The final value of $S°_{298.1}$ of SO_4^{--} from this series of measurements is 3.5 E.U. The free energy of formation of SO_4^{--} has been calculated as $-175,300$ cal.

THE determination of the entropies of calcium and barium sulfates enables a further check to be made on the entropy of sulfate ion in solution.[1]

Calcium Sulfate Dihydrate

This salt was chosen in this series for two reasons: (1) the thermal data for the reaction

$$CaSO_4 \cdot 2H_2O = Ca^{++} + SO_4^{--} + 2H_2O$$
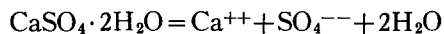
appear to be unusually good and (2) they afford a convenient medium for investigating the effect of crystal size on the entropy of solids, since large natural crystals of gypsum of high purity are easily available along with the usual precipitated material.

The heat capacity of precipitated $CaSO_4 \cdot 2H_2O$ was measured from 14 to 300°K by the experimental method of Latimer and Greensfelder.[1] Heat capacity measurements on the natural crystals were obtained from 60 to 274°K. The agreement between the two sets of results at lower temperatures precluded the necessity of extending measurements on the larger material to 14°K.

Material

Baker and Adamson's C.P. $CaSO_4 \cdot 2H_2O$ was intimately stirred with water and then filtered by suction. After drying, a sample of material was heated to 520°C in a muffle furnace and showed a water content of 20.85 percent as compared with the theoretical value of 20.93 percent. The sample contained no carbonate or barium and showed only a trace of sodium. The crystals were approximately 1μ in length. Specific heat measurements were made on a sample weighing 67.783 grams (0.3937 moles).

The natural gypsum was obtained from a large clear single crystal (500 g) which had a water content of 20.88 percent. The size of the pieces used was limited only by the size of the calorimeter. About three-fourths of the material were pieces longer than 1 cm and no fine powder was added. Measurements were made on a sample weighing 95.630 g (0.5554 moles).

Measurements

From 62 up to 103°K the C_p of the larger crystals lies not more than 0.1 C_p units below that of the smaller crystals. At 103°K the two curves cross and up to 144°K the curve for the large material falls about the same amount above that for the small material. The areas between the curves in these two regions, being very nearly equal and of opposite sign, cancel each other and therefore do not affect the entropy
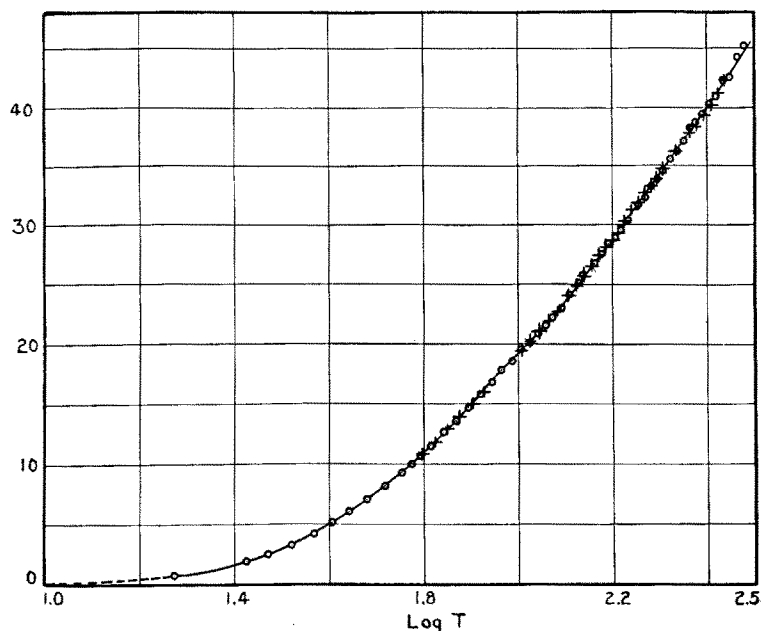
[1] For complete references to the general theory and previous work in this field, see the authors, (a) J. Am. Chem. Soc. **55**, 971 (1933); (b) J. Chem. Phys. **1**, 424 (1933).

FIG. 1. Molal heat capacity of $CaSO_4 \cdot 2H_2O$. Circles, small crystals, plusses, large crystals.

of the solid at 144°K. Beginning at 144°K the C_p of the large crystals again rises above that of the small ones, the deviation between the two curves reaching a maximum of 0.3 C_p units at 174°K. At 206°K the curves again cross, the C_p of the large crystals falling below that of the small. The maximum deviation between them is again 0.3 C_p units and is reached at about 240°K. Above this temperature the two curves again approach coincidence. The areas between the curves in these last two regions cancel each other so that the entropies of the two forms agree within 0.01 E.U. This is well within the limit of error of the method. Thus, while the heat capacity curves show definite differences (on a larger scale plot than Fig. 1) for the two crystal magnitudes, the entropy of the solid material at 298.1°K is not affected. The temperature intervals employed were as follows: below 30°K about 3° per run; 30 to 200°K about 5° per run and above 200°K, about 8° per run. (See Table I.)

Entropy of CaSO₄·2H₂O

The entropy of $CaSO_4 \cdot 2H_2O$ was obtained by graphical integration of the expression

$$S°_{298.1} = \int_0^{298.1} C_p \, d \ln T$$

with a large scale curve similar to that shown in Fig. 1. The curve was extrapolated to 0°K by

TABLE I. $CaSO_4 \cdot 2H_2O$.

| T	Molal C_p	T	Molal C_p	T	Molal C_p	T	Molal C_p
				Small Crystals			
18.70	0.68	69.29	12.61	128.39	24.09	203.45	34.63
26.71	1.90	73.72	13.62	134.97	25.13	210.22	35.65
29.64	2.48	78.41	14.71	140.21	25.80	217.27	36.32
33.18	3.20	83.24	15.79	145.36	26.68	224.91	37.20
37.11	4.21	88.04	16.83	150.72	27.51	231.90	38.33
40.36	5.15	92.37	17.81	155.86	28.41	238.23	38.79
43.77	5.99	96.80	18.58	160.80	28.92	245.64	39.54
47.84	6.98	101.26	19.47	165.73	29.61	254.02	40.36
51.98	8.19	105.59	20.15	170.86	30.36	263.29	41.01
56.56	9.33	109.84	20.85	179.79	31.68	272.18	42.30
59.47	10.03	114.04	21.52	185.78	32.34	282.11	42.63
62.00	10.73	118.22	22.25	191.39	33.25	292.67	44.29
65.34	11.54	123.62	22.95	197.61	33.93	302.10	45.17
				Large Crystals			
62.40	10.79	115.89	21.95	158.83	28.84	203.57	34.83
66.74	11.85	120.88	22.75	162.93	29.50	216.12	36.35
70.84	12.91	127.59	23.97	168.21	30.30	231.29	37.93
75.20	13.92	133.12	24.85	173.77	31.28	239.57	38.38
80.05	14.99	138.32	25.70	179.48	31.89	247.81	39.37
84.70	16.02	143.42	26.48	185.26	32.71	256.44	40.23
101.38	19.42	148.83	27.35	190.98	33.28	265.23	41.34
105.96	20.34	153.84	28.15	196.78	34.05	274.13	42.25
110.77	21.18						

means of the Debye T^3 rule, $\theta = 167.2$. A summary of the entropy calculation is given in Table II.

TABLE II.

0–19.95°K	Extrapolation	0.263 E.U.
19.95–298.1°K	Graphical	46.097 E.U.

Entropy at 298.1 of $CaSO_4 \cdot 2H_2O = 46.36$ E.U. ± 0.05 percent

Heat of solution

Lange and Monheim[2] give 273 ± 20 calories per mole as the heat of solution of $CaSO_4 \cdot 2H_2O$ at infinite dilution and 298.1°K. This value has been used in the present calculation. We have then:

$$CaSO_4 \cdot 2H_2O(s) = CaSO_4 \cdot 2H_2O(aq) \quad \Delta H = 273 \text{ cal.}$$
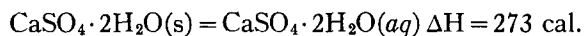
Free energy of solution

Lange and Monheim[2] give the solubility of $CaSO_4 \cdot 2H_2O$ as 0.0156 mole per 1000 grams of water, which agrees well with that given by Fosbinder.[3]

The activity coefficient of $CaSO_4 \cdot 2H_2O$ in a saturated solution is given by Fosbinder[3] as 0.312. The free energy of solution is

$$\Delta F^\circ_{298.1} = -1363.8 \log [(0.0156)(0.312)]^2$$
$$= 6308 \text{ calories.}$$

Entropy of sulfate ion

Substituting the above values in the equation, $\Delta S^\circ = (\Delta H^\circ - \Delta F^\circ)/T$, we obtain for the reaction $CaSO_4 \cdot 2H_2O(s) = Ca^{++} + SO_4^{--} + 2H_2O$ (hypothetical one molal solution) $\Delta S^\circ_{298.1} = -20.2$ E.U. Using the values $S^\circ_{298.1}$ of $Ca^{++} = -11.4$,[1] $S^\circ_{298.1}$ of $H_2O = 16.9$[4] and applying the third law, we obtain:

$$-20.2 = S^\circ_{298.1}SO_4^{--} - 11.4 + 33.8 - 46.4;$$
$$S^\circ_{298.1}SO_4^{--} = 3.8 \text{ E.U.}$$

BARIUM SULFATE

The heat capacity of $BaSO_4$ was measured from 15 to 300°K by the same experimental method as before.[1] Muller's[5] data on the heat of

solution and Neuman's[6] data on the solubility and activity coefficient of barium sulfate were used to calculate the entropy change involved in the transfer of one mole of barium sulfate from the solid state to an hypothetical one molal solution. The entropy of Ba^{++} was recalculated from the data of Latimer and Ahlberg[1] on barium and thallous nitrates. A survey of the existing data on the thallous halides gives 28.6 E.U. as the most consistent value for the standard entropy of Tl^+. This is the same value as that employed by Latimer and Ahlberg. Using 28.6 E.U. gives as the standard entropy of NO_3^- a value of 36.9 E.U. This figure yields 0.8 E.U. for the entropy of Ba^{++} in its standard state.

Material

Barium sulfate of C.P. quality was recrystallized twice from concentrated sulfuric acid. The salt was washed repeatedly with hot distilled water to remove excess acid. After the washing it was found necessary to ignite the salt to constant weight in order to remove the last traces of acid. Specific heat measurements were carried out on a sample weighing 83.043 g (0.78290 mol.) All weights were reduced to vacuum standard.

Measurements

The molal heat capacity values fall on a smooth curve which exhibits several points of double inflection. At the higher temperatures the points deviate somewhat. This is because of large radiation corrections necessary at these temperatures, and to the possible presence of water vapor in the apparatus. The experimental results are presented in Table III and graphically as a

TABLE III. $BaSO_4$.

T	Molal C_p	T	Molal C_p	T	Molal C_p	T	Molal C_p
15.72	0.75	65.96	9.91	124.84	15.68	201.87	20.12
18.62	0.93	69.61	10.39	130.19	16.03	210.18	20.65
21.49	1.40	73.63	10.94	135.48	16.37	218.44	20.98
24.42	1.86	77.79	11.47	140.83	16.71	228.03	21.57
26.83	2.36	81.73	11.84	146.18	17.00	237.28	21.82
30.56	3.19	85.52	12.34	151.76	17.41	246.86	21.92
34.94	4.04	89.65	12.85	158.06	17.77	256.21	22.60
39.83	5.13	94.22	13.31	164.59	18.17	267.62	23.47
44.75	6.13	104.17	14.11	171.16	18.51	277.68	23.71
49.69	7.10	109.29	14.52	178.13	18.89	288.69	24.30
54.95	8.04	114.25	14.92	185.78	19.36	298.23	24.14
60.49	8.99	119.44	15.27	193.94	19.81		

[2] Lange and Monheim, Zeits. f. physik. Chemie **A150**, 349 (1930).

[3] Fosbinder, J. Am. Chem. Soc. **51**, 1345 (1929).

[4] Giauque and Ashley, Phys. Rev. **43**, 1 (1933).

[5] Muller, Bull. Soc. Chim. **23**, 13 (1918).

[6] Neuman, J. Am. Chem. Soc. **55**, 879 (1933).
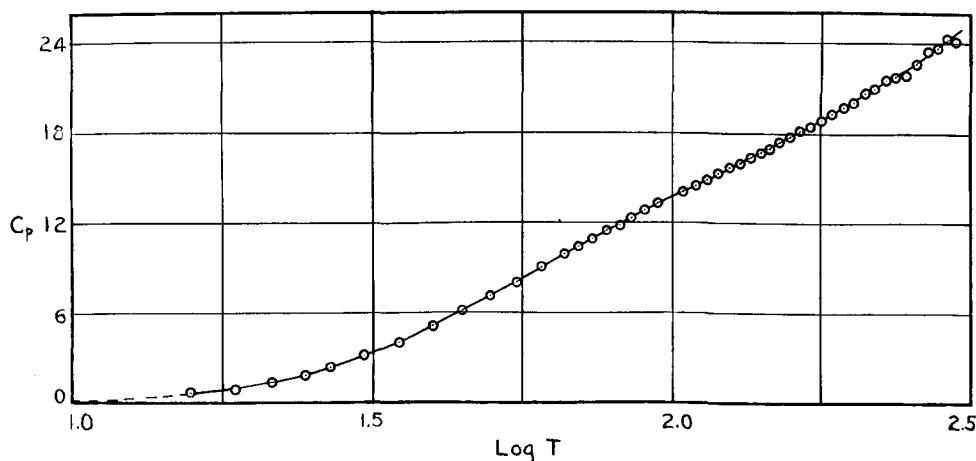
FIG. 2. Molal heat capacity of $BaSO_4$.

function of $\log T$ in Fig. 2. The heating intervals employed in various temperature regions were the same as with calcium sulfate.

Entropy of barium sulfate

The entropy of $BaSO_4$ was obtained by graphical integration of the expression

$$S_{298.1} = \int_0^{298.1} C_p d \ln T$$

from the curve shown in Fig. 2. The curve was extrapolated below 15°K by means of the Debye T^3 rule, $\theta = 148.4$. A summary of the entropy calculation is given in Table IV.

TABLE IV.

0–20°K Integration of T^3 expression	0.379 E.U.
20–298.1°K Graphical	31.134 E.U.

Entropy at 298.1°K of $BaSO_4 = 31.51 \pm 0.05$ percent

Heat and free energy of solution

Muller[5] gives $\Delta H^\circ_{298.1}$ of solution as 5455 cal. Neuman's[6] data yield $\Delta F^\circ_{298.1}$ of solution equal to 13,718 from the equation $\Delta F^\circ_{298.1} = -1363.8 \log (\gamma m)^2$, where $\gamma = 0.977$ and $m = 0.957 \times 10^{-5}$ $m/1$.

Entropy of solution

Substituting the above values in the equation $\Delta S^\circ = (\Delta H^\circ - \Delta F^\circ)/T$, we have for the reaction $BaSO_4(s) = Ba^{++} + SO_4^{--}$ (hypothetical one molal

solution); $\Delta S^\circ_{298.1} = -27.7$ E.U. Application of the third law yields

$$-27.7 = 0.8 + S^\circ_{SO_4^{--}} - 31.5; \quad S^\circ_{SO_4^{--}} = 3.0 \text{ E.U.}$$

Summary of values for the entropy of sulfate ion

From the three separate determinations, i.e., from silver sulfate, calcium sulfate and barium sulfate, we find the entropy of sulfate ion to be 2.8, 3.8 and 3.0 E.U., respectively. The agreement is good considering the difficulties of obtaining accurate values for the entropies of solution. The solution entropy appears to be much more reliable for the calcium sulfate and we believe the entropy, 3.8 E.U. obtained from the measurements on this salt to be accurate to 0.5 E.U. Giving some weight to the other values, however, we have chosen 3.5 as the best value for the entropy of sulfate ion ($S^\circ_{H^+} = 0$) in hypothetical 1 molal solution.

The free energy of sulfate ion

The heat of formation of sulfuric acid is rather accurately known. Roth, Graw and Meischner[7] give for the reaction

$$S_{rh} + H_2(g) + 2O_2(g) = H_2SO_4(1)$$
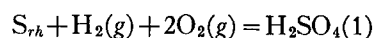
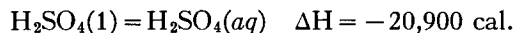$$\Delta H^\circ_{298.1} = -194,150 \pm 100 \text{ cal.}$$

Correcting this to 298.1°K we have
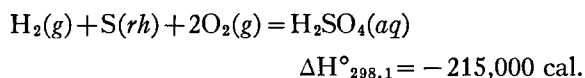
$$\Delta H^\circ_{298.1} = -194,120 \pm 100 \text{ cal.}$$

Extrapolation of the heat of dilution data of

[7] Roth, Graw and Meischner, Zeits. f. anorg. Chemie 193, 161 (1930).

Graw and Roth[8] and Brönsted[9] to infinite dilution gives

$$H_2SO_4(1) = H_2SO_4(aq) \quad \Delta H = -20,900 \text{ cal.}$$

Combining these, we have

$$H_2(g) + S(rh) + 2O_2(g) = H_2SO_4(aq)$$
$$\Delta H°_{298.1} = -215,000 \text{ cal.}$$

Then using the entropies $S°_{298.1}$ of $H_2 = 31.23$, $S°_{298.1}$ of $S = 7.6$, $S°_{298.1}$ of $O_2 = 49.03$, $S°_{298.1}$ of $SO_4^{--} = 3.8$, $\Delta S°_{298.1}$ for the above reaction is -133 E.U.

Substituting these values in the equation $\Delta F° = \Delta H° - T\Delta S°$, we calculate for the free energy of formation of aqueous sulfuric acid, $\Delta F°_{298.1} = -175,300$ cal. This value is just outside the limits of error (± 1000 cal.) set by Lewis and Randall[10] on Bichowsky's value of 176,500 calories.

The authors extend their thanks to Sally R. Hicks for her assistance with the calculations.

[8] Graw and Roth, Zeits. f. anorg. Chemie 188, 184 (1930).

[9] Brönsted, Zeits. f. physik. Chemie 68, 693 (1910).

[10] Lewis and Randall, *Thermodynamics and the Free Energy of Chemical Substances*, McGraw Hill Book Company, New York, 1923.