

classical second ionization constant of oxalic acid can also be computed. These values agree with ours within ± 0.03 pK unit throughout the range of Harned and Fallon's measurements ($\mu = 0.03$ to 0.17).

From a large-scale graph of the foregoing pK_2' values against the square root of ionic strength, it can be seen that the effect of sodium and ammonium chlorides is the same, but that the graph for potassium chloride lies above the other, the divergence beginning at about $\sqrt{\mu} = 0.4$.

Solubility of Calcium Oxalate in Formate Buffers

Buffers of formic acid and ammonium formate were prepared. Each buffer was 0.36 M with ammonium formate, and therefore had an ionic strength of 0.36. The concentration of formic acid in the buffers was varied. The solubility of calcium oxalate monohydrate at 25° was determined in each of these buffers as described in the previous paper. The pH of each filtrate was also determined with the Beckman pH meter. The results are presented in Table II.

The values in the last column were calculated by equation (4) with $S' = 4.97 \times 10^{-8}$ and $K_2' = 1.97 \times 10^{-4}$. Good agreement is obtained between the observed and theoretical solubilities up to 0.5 M formic acid. Greater concentrations of formic acid not only increase the hydrogen-ion

TABLE II
SOLUBILITY OF CALCIUM OXALATE IN FORMATE BUFFERS

Molarity of HCOOH	pH	Solubility of CaC_2O_4 , molarity $\times 10^4$	
		Observed	Calculated
0.0000	5.96	2.23	(2.23)
.0246	4.75	2.26	2.32
.0437	4.53	2.47	2.39
.0778	4.25	2.66	2.53
.138	4.02	2.86	2.73
.246	3.75	3.18	3.09
.437	3.50	3.48	3.60
.778	3.23	4.03	4.47
1.38	2.93	4.84	5.88
2.46	2.60	5.89	8.30

activity but also alter the solvent properties of the medium. Since equation (4) does not take the latter effect into account, it is not accurate in high concentrations of formic acid.

Summary

The semiclassical second ionization constant of oxalic acid has been determined at ionic strengths from 0 to 1 in the presence of sodium, potassium, and ammonium chlorides. The solubility of calcium oxalate monohydrate in formate buffers of constant ionic strength has been studied. Good agreement between observed and theoretical solubilities has been found.

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The Specific Heats at Low Temperatures of Anhydrous Sulfates of Iron, Magnesium, Manganese, and Potassium.¹

BY G. E. MOORE² AND K. K. KELLEY³

The Pacific Experiment Station of the Bureau of Mines for the past year has been engaged primarily in determining thermodynamic values of substances important in the metallurgy of strategic materials, particularly manganese and chromium. It is desirable to have these data not only for compounds of these metals themselves but also for the compounds of the metals associated with them in the ores and from which they must be separated. This paper deals with low-temperature specific heat measurements of anhydrous sulfates of iron, magnesium, manganese and potassium.

Materials.—Reagent quality ferrous sulfate heptahydrate was heated slowly for several days to 125°, while evacuating with an oil-pump. It was then transferred to a high-vacuum line (mercury diffusion pump) and the heating continued. It was found necessary to heat to 235° to remove the last of the water, and some decomposition was unavoidable at this temperature. Analysis gave 37.30% Fe and 63.1% SO_4 compared with the theoretical figures 36.77 and 63.23%. Ferric iron corresponding to 1.6% Fe_2O_3 also was determined. Upon the basis of the iron analyses, which are the more significant, the purity of the sample is 98.4%. Higher purity would be desirable, but tests conducted at various stages in the dehydration process indicated that it is not possible to dry completely without decomposition. A 124.02-g. sample of this material was used in the measurements.

Reagent quality magnesium sulfate heptahydrate was dehydrated by heating in air in large nickel crucibles, the final temperature (400°) being maintained for two hours.

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This procedure is essentially that recommended by Archibald.⁴ Analysis gave 33.60% MgO; theoretical 33.49%. No calcium was found by the procedure given by Hillebrand and Lundell⁵ for detecting small amounts of calcium in the presence of large amounts of magnesium. A small amount of magnesium oxide as such was found in the sample and directly determined by titration as 0.10 to 0.15%. The specific-heat measurements were made on a 142.95-g. sample.

Manganous sulfate tetrahydrate, reagent quality, was dehydrated by heating in air up to 400°, and this temperature was maintained overnight. After crushing and screening the heating was repeated, 400° being held for several hours.⁶ The manganese content of the product was determined by precipitation as sulfide, washing and converting to anhydrous sulfate. This resulted in 36.33% (theoretical 36.38%). Sulfate analyses gave 63.77% (theoretical 63.62%). A 152.03-g. sample was used in the measurements.

Reagent quality anhydrous potassium sulfate was heated to 140° and used without further purification. Analysis for sulfate showed the material to be at least 99.7% pure. The sample used in the measurements contained 169.05 g.

Specific Heats.—The methods and apparatus used in the present work are the same as previously employed.⁷ The results of the specific heat measurements, expressed in defined calories (1 calorie = 4.1833 int. joules), are given in Table I and shown graphically in Fig. 1. The formula masses employed and given in Table I are in accord with the 1941 International Atomic Weights.

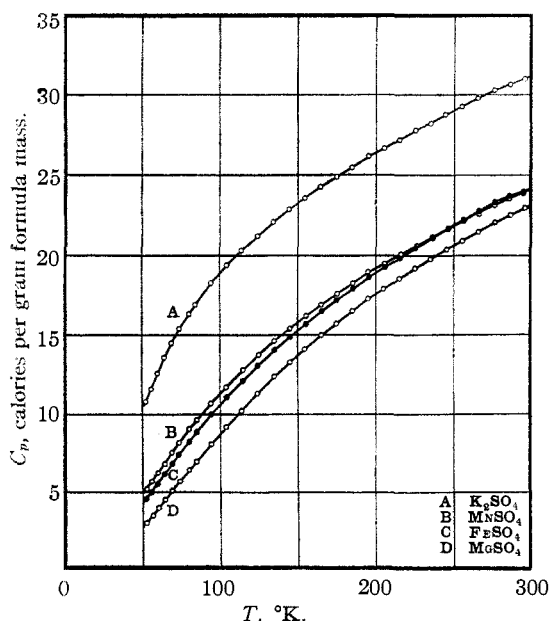


Fig. 1.—Specific heats of anhydrous sulfates.

(4) Archibald, "Preparation of Pure Inorganic Substances," John Wiley and Sons, New York, N. Y., 1932, p. 92.

(5) Hillebrand and Lundell, "Applied Inorganic Analysis," John Wiley and Sons, New York, N. Y., 1929, p. 488.

(6) The authors are indebted to Dr. G. W. Marks, Bureau of Mines, for dehydrating this material.

(7) Kelley, *THIS JOURNAL*, **63**, 1137 (1941).

TABLE I
SPECIFIC HEAT OF FeSO_4 (151.91 g.)

T , °K.	C_p cal./deg. mole	T , °K.	C_p cal./deg. mole	T , °K.	C_p cal./deg. mole
53.0	4.528	115.1	12.09	216.0	19.80
56.4	4.963	124.7	13.02	225.8	20.42
60.2	5.503	135.5	14.01	236.6	21.06
64.8	6.194	145.5	14.84	246.3	21.63
69.5	6.863	155.4	15.64	256.1	22.19
73.7	7.419	165.7	16.47	266.2	22.73
80.5	8.277	175.5	17.16	276.2	23.30
85.1	8.827	185.9	17.89	285.9	23.68
94.8	9.971	196.0	18.60	294.9	23.94
104.5	11.01	206.2	19.22		

Specific Heat of MgSO_4 (120.38 g.)

53.3	2.988	114.1	10.19	215.3	18.50
57.2	3.449	124.6	11.28	225.4	19.16
61.0	3.923	135.3	12.32	235.5	19.73
65.1	4.483	145.3	13.23	245.8	20.36
69.8	5.079	154.9	14.06	255.6	20.89
74.4	5.674	165.3	14.93	265.8	21.45
80.7	6.438	175.0	15.67	276.2	22.03
85.3	6.991	185.4	16.47	286.1	22.50
94.7	8.086	195.2	17.22	295.4	22.91
104.4	9.161	205.5	17.87		

Specific Heat of MnSO_4 (150.99 g.)

53.1	5.173	115.2	12.75	216.3	20.02
56.6	5.664	125.2	13.71	226.1	20.59
60.6	6.250	135.1	14.58	236.1	21.11
65.0	6.919	145.1	15.35	246.5	21.67
69.5	7.571	155.6	16.16	256.3	22.14
74.0	8.182	165.4	16.87	266.2	22.55
80.5	9.007	175.8	17.55	276.1	23.13
85.4	9.604	185.6	18.21	285.8	23.52
94.4	10.63	196.3	18.90	294.7	23.83
104.2	11.68	206.0	19.43		

Specific Heat of K_2SO_4 (174.25 g.)

52.7	10.73	114.0	20.26	215.1	27.13
56.1	11.52	124.2	21.15	225.5	27.74
60.3	12.51	134.2	22.03	235.2	28.17
64.8	13.54	144.6	22.82	244.8	28.71
69.2	14.45	154.7	23.51	255.1	29.23
74.2	15.36	164.6	24.21	265.2	29.72
80.2	16.29	175.0	24.83	276.0	30.26
84.2	16.87	184.8	25.42	286.1	30.60
94.5	18.22	195.4	26.11	295.4	30.99
104.7	19.34	205.3	26.61		

Figure 1 shows that all four substances exhibited normal behavior throughout the temperature range studied. Consequently, no discussion of the character of the specific heat curves appears necessary, and there are no previous data with which to compare. It should be mentioned that a small correction, ranging from 0.05 to 0.10%, depending on the temperature, has been applied to the magnesium sulfate results to compensate for the small quantity of oxide detected in the analysis.

No corrections for impurities were applied in the other instances.

It is desirable to record here that the heat capacity curve of the empty calorimeter was re-determined completely at the conclusion of the measurements reported in this paper. In the interim between these calibration measurements and the preceding set some 20 substances had been studied, a few minor repairs had been made, and a new White potentiometer had been installed. The new calibrations agree so well with the old that no error, in the specific heats of the substances studied in the interim, greater than 0.05% may be attributed to the combined sources of lack of constancy in the heat capacity of the empty calorimeter and difference in measuring instruments.

Entropies.—The entropies at 298.16°K. were obtained in the usual manner; the measured portions between 50.12° and 298.16°K. were computed graphically from C_p vs. $\log T$ curves, and the portions below 50.12°K. were extrapolated. For the latter purpose, the specific heat curves were fitted with the function sums listed below, and the temperature range represented is given in parentheses.

$$\text{FeSO}_4: D\left(\frac{176}{T}\right) + 2E\left(\frac{329}{T}\right) + 2E\left(\frac{801}{T}\right),$$

(51 to 200°K.)

$$\text{MgSO}_4: D\left(\frac{242}{T}\right) + 2E\left(\frac{378}{T}\right) + 2E\left(\frac{866}{T}\right) + E\left(\frac{1683}{T}\right),$$

(51 to 298°K.)

$$\text{MnSO}_4: D\left(\frac{163}{T}\right) + 2E\left(\frac{304}{T}\right) + 2E\left(\frac{813}{T}\right),$$

(51 to 220°K.)

$$\text{K}_2\text{SO}_4: D\left(\frac{132}{T}\right) + 3E\left(\frac{198}{T}\right) + 2E\left(\frac{738}{T}\right),$$

(51 to 225°K.)

The results are shown in Table II. Some correction of the ferrous and manganous sulfate values may be necessary to compensate for unextracted magnetic entropy when the pertinent data become available. The assigned errors apply

TABLE II
ENTROPIES AT 298.16°K. CAL./DEG. MOLE

	FeSO ₄	MgSO ₄	MnSO ₄	K ₂ SO ₄
50.12°K. (extrap.)	2.10	1.10	2.72	4.82
50.12–298.16°K. (graph.)	23.60	20.78	24.07	37.21
$S_{298.16}$	25.7 ± 0.3	21.9 ± 0.2	26.8 ± 0.3	42.0 ± 0.6

only to the measurements and normal extrapolations made and do not allow for this contingency.

Previous entropy values have been reported for magnesium and potassium sulfates only⁸; 20 ± 2 and 44.8, respectively, have been estimated from decomposition data. The present values, of course, are preferable.

Related Thermal Data.—Free-energy-of-formation values from the elements, calculated from the third law of thermodynamics, are shown in column 4 of Table III. These values are based upon the present entropy results, the entropies of the elements,⁸ and heat-of-formation data adopted by Bichowsky and Rossini,⁹ except in the instance of manganous sulfate, for which the recent value of Southard and Shomate¹⁰ is employed. Values computed from other considerations by Kelley,¹¹ in his survey of thermal properties of sulfur-containing compounds, are shown in column 5.

TABLE III
FREE ENERGIES OF FORMATION AT 298.16°K. CAL./MOLE

Substance	$\Delta H_{298.16}$	$\Delta S_{298.16}$	$\Delta F_{298.16}^{\circ}$ (T.L.)	$\Delta F_{298.16}^{\circ}$ (misc.)
FeSO ₄	-221,300	-86.5	-195,500	...
MgSO ₄	-304,950	-91.6	-277,640	-285,180
MnSO ₄	-254,180	-86.5	-228,380	-228,020
K ₂ SO ₄	-342,660	-94.1	-314,600	-314,580

Except for magnesium sulfate, the values are in good agreement. In this instance there exists a rather gross discrepancy between the third law and decomposition pressure results. At present the authors prefer the third-law value for this substance.

Summary

Specific heat measurements of anhydrous sulfates of iron, magnesium, manganese and potassium are reported in the temperature range 51 to 298°K.

The entropies at 298.16°K. were computed to be 25.7 ± 0.3 for FeSO₄, 21.9 ± 0.2 for MgSO₄, 26.8 ± 0.3 for MnSO₄, and 42.0 ± 0.6 for K₂SO₄.

Free-energy-of-formation values based upon the third law of thermodynamics are computed and compared with results from other data.

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- (8) Kelley, Bureau of Mines Bulletin, 434, 1941, 115 pp.
 (9) Bichowsky and Rossini, "Thermochemistry of Chemical Substances," Reinhold Publishing Co., New York, N. Y., 1936.
 (10) Southard and Shomate, THIS JOURNAL, 64, 1770 (1942).
 (11) Kelley, Bureau of Mines Bulletin 408, 1937, 154 pp.