

the formation of appreciable quantities of an intermediate, probably chloroformic acid. If excess chlorine is present or if the reaction vessel is heated to destroy any residual intermediate, the

products are solely carbon dioxide and hydrogen chloride. A mechanism which will account for the observations has been presented.

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

The Heat Capacity and Entropy of Potassium Permanganate from 15 to 300° Absolute. The Entropy and Free Energy of Permanganate Ion

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As part of a general program for the evaluation of the entropies of the common inorganic ions, the entropy of potassium permanganate has been determined.

Material.—Kahlbaum "For analysis with guarantee" grade potassium permanganate was used in the first series of heat capacity runs. These measurements demonstrated that the sample contained water. The material was removed from the calorimeter, ground in a mortar, and dried over sulfuric acid in a darkened desiccator. The sample was then analyzed by titration with sodium oxalate solution. Within experimental error ($\pm 0.1\%$) the sample was 100% potassium permanganate.

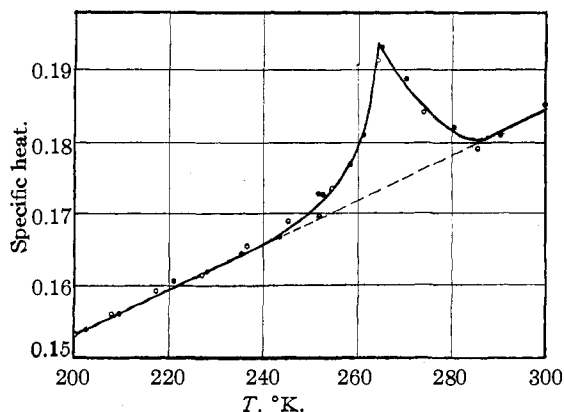


Fig. 1.—Specific heat of wet sample of potassium permanganate.

Heat Capacity Measurements.—The heat capacities were determined by the experimental method used by Latimer and Greensfelder.¹ One calorie was assumed equal to 4.1833 int. joules. The molecular weight of potassium permanganate was taken as 158.03. Measurements on Series I were made on a sample of 133.034 g. (weight *in vacuo*). An anomaly was found in the heat capacities, which appeared to be due to the presence of considerable water included in the sample. On removing the sample from the calorimeter the crystals were found to decrepitate upon heating, confirming the presence of water. The specific heats of the sample in the neighborhood of the melting point of water are presented in Table I and

(1) Latimer and Greensfelder, *THIS JOURNAL*, **50**, 2202 (1928).

TABLE I

SPECIFIC HEAT OF SERIES I (WET SAMPLE)

Run	T , °K.	C_p , cal./gram/deg.	ΔT
1	202.67	0.1539	6.426
2	209.69	.1561	6.176
3	221.15	.1605	6.898
4	228.15	.1619	6.678
5	235.37	.1643	7.542
6	243.53	.1667	8.417
7	251.76	.1696	8.060
8	251.69	.1727	7.538
9	258.37	.1768	7.236
10	265.00	.1931	7.573
11	252.58	.1726	9.776
12	261.24	.1809	9.162
13	270.26	.1887	9.460
14	280.40	.1819	9.640
15	290.41	.1808	10.520
16	300.04	.1851	11.149
17	200.34	.1532	7.234
18	208.12	.1560	9.132
19	217.34	.1592	10.281
20	227.06	.1614	9.836
21	236.47	.1654	9.320
22	245.35	.1689	8.898
23	254.39	.1732	9.586
24	264.14	.1912	9.720
25	274.10	.1840	10.885
26	285.55	.1789	11.895

plotted as a function of temperature in Fig. 1. The half filled circles represent runs 1-7 (Oct. 14, 1933), the filled circles runs 8-16 (March 28-29, 1934), the open circles runs 17-26 (April 4, 1934). The area between the dotted curve and the solid curve corresponds to 0.28 cal., and after subtracting 0.02 cal. for the heat absorbed by the solution of potassium permanganate in the liquid water formed, corresponds to the melting of 0.0033 g. of water in each gram of sample. Although the eutectic of ice and potassium permanganate occurs at about 272.5°K., the maximum of the observed "hump" occurs at 265°K. and the abnormal specific heats persist even down to about 245°K. In view of the large amount of water present it was decided to dry the sample as described above, and repeat the entire series of measurements, even though it appeared reasonable that the heat capacity of dry potas-

sium permanganate could be calculated by correcting these measurements for the amount of water present.

Series II (made on the dry sample) is shown in Table II and plotted as a function of temperature in Fig. 2. The measurements on series I, after being corrected for 0.33% of water,³ are shown in Table III. A few of these measurements selected at random are plotted as filled circles in Fig. 2. The measurements on the wet sample were not used in computing the entropy, but the excellent concordance of these two sets of data indicates that it is

TABLE II
MOLAL HEAT CAPACITY OF POTASSIUM PERMANGANATE

$T, ^\circ\text{K.}$	$C_p,$ cal./mole/deg.	$T, ^\circ\text{K.}$	$C_p,$ cal./mole/deg.
14.79	1.55	138.11	20.12
16.49	2.01	145.07	20.59
18.03	2.43	152.22	21.11
20.20	3.01	158.93	21.55
22.76	3.70	166.09	21.98
25.13	4.39	173.62	22.45
27.62	5.00	181.51	22.77
35.57	7.26	189.59	23.33
39.13	8.06	198.42	23.89
42.25	8.85	204.45	24.37
46.73	9.69	206.81	24.40
51.36	10.67	209.80	24.51
55.92	11.52	214.69	24.83
61.20	12.33	218.53	25.03
72.77	13.91	222.21	25.14
78.87	14.64	226.43	25.38
84.24	15.22	229.90	25.66
90.31	15.86	238.67	25.91
94.27	16.21	247.12	26.07
101.34	16.98	255.44	26.82
108.59	17.67	264.87	27.18
116.77	18.30	272.74	27.14
123.28	18.89	283.87	27.53
130.78	19.56	295.24	28.42

TABLE III
MOLAL HEAT CAPACITY OF SERIES I (WET SAMPLE) OF KMnO_4

$T, ^\circ\text{K.}$	$C_p,$ cal./mole/deg.	$T, ^\circ\text{K.}$	$C_p,$ cal./mole/deg.
37.56	7.77	136.01	19.90
41.89	8.82	141.36	20.29
46.69	9.85	147.12	20.68
51.52	10.82	153.36	21.14
56.80	11.66	160.29	21.64
62.12	12.49	165.72	22.12
72.06	13.89	177.78	22.73
77.52	14.52	184.01	23.13
83.42	15.10	190.10	23.53
88.82	15.83	196.27	23.77
94.67	16.54	202.67	24.19
100.86	16.97	209.68	24.59
106.70	17.50	221.15	25.22
112.60	18.03	228.15	25.44
118.69	18.54	235.37	25.82
124.64	18.97	243.53	26.19
130.44	19.55	251.76	26.63

(2) Giauque and Stout, *THIS JOURNAL*, **58**, 1144 (1936).

quite feasible to correct for water impurity in a salt crystal by assuming the water present as ice. This conclusion is important in cases where the instability of the substance under investigation precludes rigorous drying, although working with wet samples is not recommended as a general practice.

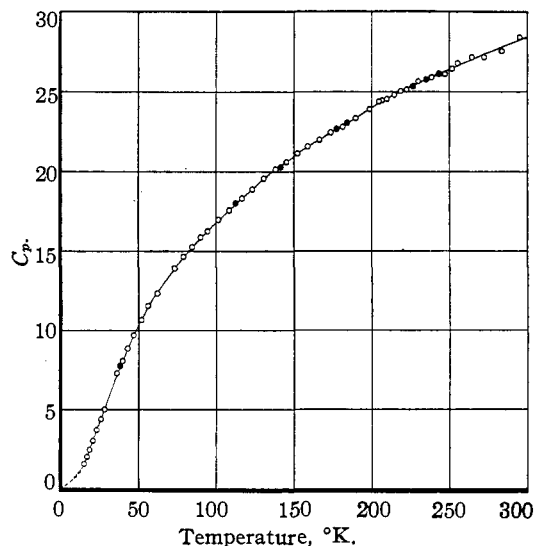


Fig. 2.—Molal heat capacity of potassium permanganate.

Entropy of Potassium Permanganate.—The entropy was calculated by graphical integration of the integral $S = \int_0^T C_p d \ln T$ combined with an extrapolation using the Debye specific heat equation. A summary of the entropy calculation is given in Table IV.

TABLE IV MOLAL ENTROPY OF POTASSIUM PERMANGANATE		
0–14.79°K.	Debye extrapolation	0.53
14.79–298.1°K.	Graphical from data	40.51 ± 0.1
Entropy at 298.1°K.		41.04 E. U.

Heat and Free Energy of Solution.—Roth and Becker³ have measured the integral heats of solution of potassium permanganate at several different temperatures and concentrations. Heats of dilution to very low concentrations have been determined⁴ for the similar salt, potassium perchlorate, but not for potassium permanganate. Since the heats of dilution calculated from the measurements of Roth and Becker are almost identical with those for potassium perchlorate over the same range of concentration, we may assume that the heats of dilution remain the same down to very low concentrations. The heat of

(3) Roth and Becker, *Z. physik. Chem.*, **A159**, 27 (1932).

(4) Andauer and Lange, *ibid.*, **A165**, 89 (1933).

solution of potassium permanganate in an infinite amount of water is, then, 10,620 cal. per mole at 298.1°K.

The solubility⁵ of potassium permanganate in water at 298.1°K. is 0.482 *M*. By extrapolation of the activity coefficients of potassium permanganate obtained from freezing point lowering,⁶ γ at 0.482 *M* is 0.49. The free energy change when potassium permanganate dissolves to form a hypothetical one molal solution is, therefore

$$\Delta F_{298.1}^0 = -1363.8 \log (0.482 \times 0.49)^2 = 1710 \text{ cal./mole}$$

Entropy of Solution.—Substituting the above values in the equation $\Delta S^0 = (\Delta H^0 - \Delta F^0)/T$ we have for the reaction $\text{KMnO}_4(\text{s}) = \text{K}^+ + \text{MnO}_4^-$ (hypothetical one molal solution); $\Delta S_{298.1}^0 = 29.9 \text{ E. U.}$

Entropy of Permanganate Ion.—The entropy of potassium ion has previously been taken⁷ as 24.6 E. U. as an average of the values obtained from the entropies of solution of potassium chloride and potassium bromide, and the entropy change of the potassium electrode reaction. Since the time that this value was calculated, improved data for the first two reactions have become available, so that we now regard the entropy change of the potassium electrode as inferior in accuracy to the values 24.3 E. U. and 24.1 E. U. calculated from the entropies of solution of potassium chloride and potassium bromide, respectively.^{7b} As an average we shall adopt 24.2 E. U. as the entropy of potassium ion. The entropy of permanganate ion is given by the expression

$$S_{\text{MnO}_4^-}^0 = \Delta S^0 + S_{\text{KMnO}_4} - S_{\text{K}^+} = 29.9 + 41.0 - 24.2 = 46.7 \text{ E. U.}$$

This value, as well as the value of the entropy of potassium permanganate, may be somewhat in error due to the possibility that the paramagnetic nature of potassium permanganate may contribute to the heat capacity below the lowest temperatures obtained in this investigation. No trace of this behavior was found, and the heat capacity

(5) Flöttmann, *Z. anal. Chem.*, **73**, 1 (1928).

(6) Landolt-Börnstein, "Physikalisch-chemische Tabellen," Eg. Iib, p. 1122.

(7) (a) Latimer, Schutz and Hicks, *J. Chem. Phys.*, **2**, 82 (1934); (b) Latimer, *Chem. Rev.*, **18**, 349 (1936). These references contain complete summaries of all previous work in this field.

appeared to be rapidly approaching the limiting T^3 law. The paramagnetism of potassium permanganate is without temperature coefficient, and no theory has yet been proposed which adequately accounts for this type of magnetic behavior. Further work on the entropies of paramagnetic ions, and particularly the study of reactions in which the products have a different magnetic behavior than the reactants, should help to settle this difficult question of magnetic entropy.

Free Energy of Potassium Permanganate and Permanganate Ion.—Bichowsky and Rossini⁸ have selected -192,900 cal. as the ΔH of formation of solid potassium permanganate at 18°. Since the correction to 25° amounts to only 14 cal. it may be neglected. Using the entropies of potassium, manganese and oxygen as given by Kelley⁹ we find ΔS of formation to be -79.5 E. U., from which the free energy of formation of solid potassium permanganate is -169,200 cal. per mole. Combining this value with the free energy of solution computed above, and subtracting the free energy of potassium ion¹⁰ (-67,431), the free energy of formation of permanganate ion is found to be -100,060 cal./mole.

The authors wish to thank Dr. Philip W. Schutz of this Laboratory for assistance in the experimental work and calculations on Series I.

Summary

The heat capacity of potassium permanganate has been measured from 15 to 300°K., and the entropy of the salt determined by graphical integration to be 41.04 E. U. Coupling this value with the entropy of solution, and the entropy of potassium ion herein adopted, the entropy of permanganate ion has been determined to be 46.7 E. U.

The free energy of formation of potassium permanganate and of permanganate ion have been computed from the known entropies and heat of formation.

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(8) Bichowsky and Rossini, "The Thermochemistry of the Chemical Substances," Reinhold Publishing Co., New York, 1936, p. 162.

(9) Kelley, Bull. 350, Bureau of Mines, 1932.

(10) Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., Inc., New York, 1923, p. 434.