values obtained for the heat of solution of silver nitrate, mercuric cyanide, lead bromide and lead nitrate. These are all salts of metals that have a marked tendency to form stable complexes with ammonia. The heat effects in the case of the lead salts are particularly high. The value of 29,100 for lead iodide is close to that found by Kraus and Ridderhof for lead bromide, 29,600 cal.

Summary

Some improvements to the liquid ammonia calorimeter of Kraus and Ridderhof are described.

The heats of solution of silver nitrate, mercuric cyanide, lead iodide, lead nitrate, sodium chlorate and sodium bromide have been determined.

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

The Heat Capacity and Entropy of Potassium Chlorate from 13 to 300°K. The Entropy of Chlorate Ion

BY WENDELL M. LATIMER, PHILIP W. SCHUTZ AND J. F. G. HICKS, JR.

This determination of the entropy of potassium chlorate completes the data on the entropy of the halogenate[1] ions.

Material.—Potassium chlorate of C. P. quality was recrystallized from distilled water three times and dried at 110° for sixty-five hours. The sample showed only very slight traces of chloride with acid silver nitrate. We are indebted to Dr. J. E. Ahlberg for the preparation of the sample. Specific heat measurements were made on a sample weighing 118.867 g. *in vacuo* (0.9699 mole).

TABLE I

HEAT CAPACITY OF POTASSIUM CHLORATE

MOLECULAR WEIGHT OF $KClO_3$ = 122.55

T, °K.	Molal C_p	T, °K.	Molal C_p
13.95	0.44	122.64	16.53
15.84	0.77	128.23	16.81
18.48	1.28	133.94	17.13
22.35	2.01	139.75	17.43
24.66	2.62	145.79	17.75
27.79	3.53	151.83	18.07
32.60	4.67	157.89	18.37
37.31	5.84	164.00	18.65
41.16	6.80	169.83	18.89
44.78	7.65	175.89	19.20
48.92	8.52	181.35	19.40
53.30	9.41	182.23	19.46
58.11	10.28	189.02	19.89
63.23	11.13	196.71	20.18
67.91	11.82	204.38	20.51
72.60	12.40	212.30	20.79
74.04	12.59	220.76	21.12
79.07	13.15	229.13	21.47
84.51	13.77	236.81	21.84
89.52	14.23	245.50	22.04
94.86	14.68	254.21	22.57
100.26	15.06	262.95	22.84
105.92	15.49	272.28	23.33
111.69	15.90	283.85	23.39
117.17	16.22	293.35	23.84

Measurements.—The molal heat capacity values fall on a smooth curve and are presented in Table I and graphically as a function of log T in Fig. 1. The heating intervals employed in various temperature regions are 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.

Entropy of Potassium Chlorate.—The entropy of $KClO_3$ was obtained by graphical integration of the equation $S^\circ_{298.1} = \int_0^{298.1} C_p \, d \ln T$ from a larger scale plot of the curve shown in Fig. 1. The curve was extrapolated graphically to 10°K. and by means of the T^3 law below that. A summary of the entropy calculation is given in Table II.

TABLE II

0—10°K.	T^3 extrapolation	0.054 E. U.
10—298.1°K.	Graphical	34.116 E. U.
S° at 298.1° of $KClO_3$ =		34.17 E. U.

The relative accuracy of 34.17 E. U. is estimated at ±0.05 per cent.

Heat and Free Energy of Solution.—Stackelberg[2] gives 10,500 cal. for ΔH° at 16° for the reaction

$KClO_3(s) = (K^+ + ClO_3^-)$ (hypothetical one molal)

Correcting this figure to 25° gives $\Delta H^\circ_{298.1}$ = 10,120 cal.

(1) (a) $Ba(BrO_3)_2 \cdot H_2O$, Greensfelder and Latimer, THIS JOURNAL, **50**, 3286 (1928); (b) $AgIO_3$, G. and L., *ibid.*, **53**, 3813 (1931); (c) $KBrO_3$ and KIO_3, Ahlberg and Latimer, *ibid.*, to be published.

(2) Stackelberg, *Z. physik. Chem.*, **26**, 540 (1898).

The activity coefficient of potassium chlorate in a saturated solution at 25° (0.715 *m*)[3] has been taken as 0.476 because of the close agreement between the activity of potassium nitrate and potassium chlorate solutions[4] below 0.1 *m*. Experimental activity coefficients of potassium chlorate are not available up to saturation. However, 0.476 cannot be far from the true value. The free energy change involved in the transfer of one mole of solid potassium chlorate to the aqueous ions at unit activity is $-1363.8 \log (0.476 \times 0.715)^2 = 1277$ cal. as compared with the older value of 1570.[5]

Entropy of Chlorate Ion.—Substituting $\Delta H° = 10{,}120$ cal. and $\Delta F° = 1277$ in the expression for the first and second laws, we have for the entropy of solution, $\Delta S°_{298.1} = 29.7$ E. U. $= S_{K^+} + S_{ClO_3^-} - S_{KClO_3}$. For the entropy of K^+ we shall use 24.6 E. U.[6] We then obtain, employing this value and our entropy for potassium chlorate at 298.1°K, $S°_{ClO_3^-} = 39.3$ E. U.

Free Energy of Chlorate Ion.—For the reaction

$$\frac{1}{2} Cl_2 + \frac{3}{2} O_2 + \frac{1}{2} H_2 = ClO_3^- + H^+; \quad \Delta H = -19{,}100^{7} \text{ cal.} \quad \Delta S = -76.5^{8}$$

From these data we calculate the free energy of formation of chlorate ion at unit activity to be +3700 cal. From earlier data Lewis and Randall[5] find −250 cal. However, it is quite possible that the error in the ΔH term is as large as this discrepancy.

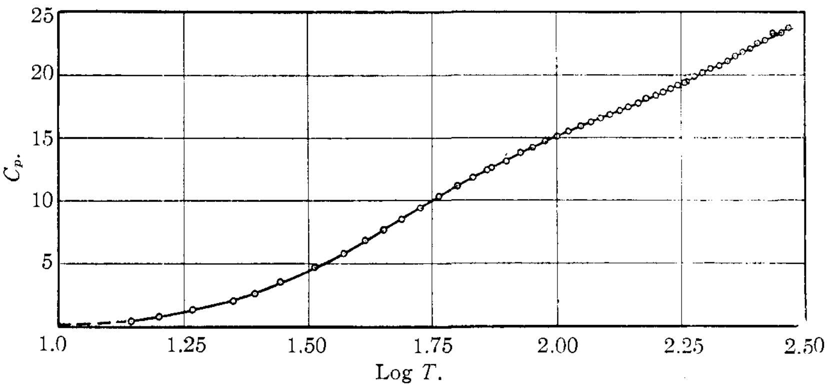

Fig. 1.—Molal heat capacity of $KClO_3$.

Summary

The heat capacity of potassium chlorate has been measured from 13 to 300°K. and the curve of C_p *vs.* log T integrated graphically. The entropy at 298.1° of the salt has been evaluated at 34.17 E. U.

The entropy of ClO_3^- has been calculated to be 39.3 E. U. and the free energy of formation 3700 cal., both at 25°.

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(3) Seidell, "Solubilities," D. von Nostrand Co., New York, 1919, p. 512.
(4) Landolt-Börnstein, "Tabellen," II Ergänzungsband, p. 1122.
(5) Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., Inc., New York, 1923, p. 511.
(6) The details of this calculation will be published shortly by Latimer, Schutz and Hicks in a complete revision of the ionic entropy values.
(7) "International Critical Tables," Vol. V.
(8) $S°_{298.1}$ used are $\frac{1}{2}Cl_2 = 26.7$, $\frac{3}{2}O_2 = 73.5$, $\frac{1}{2}H_2 = 15.6$, $ClO_3^- = 39.3$, $H^+ = 0$.