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

Silver Chlorite: Its Heat Capacity from 15 to 300°K., Free Energy and Heat of Solution and Entropy. The Entropy of Chlorite Ion

BY WENDELL V. SMITH, KENNETH S. PITZER AND WENDELL M. LATIMER

In gaining a further insight into the nature of the interactions between water molecules and ions in solution it is important to have entropies of a series of ions such as the oxy-halogen ions. The series with chlorine as the halogen is complete except for the entropies of hypochlorite and chlorite ions. The necessary data are already available for the calculation of the entropy of hypochlorite and the present measurements provide the means of calculating the entropy of chlorite ion.

Preparation of Sample.—A barium chlorite solution was first prepared by the method used by Bray and Barnett.[1] Potassium chlorate, oxalic acid and a small amount of water were heated together at 60°. The evolved carbon dioxide and chlorine dioxide were passed through a dilute sodium hydroxide solution to remove chlorine, and the chlorine dioxide was absorbed in water cooled to 0°. Treating the cold solution with excess solid barium peroxide converted the dissolved chlorine dioxide into a solution of barium chlorite. The solution, being slightly alkaline, was made just neutral by the addition of dilute sulfuric acid. A small amount of dilute silver nitrate solution was added, and the precipitated barium sulfate and silver chloride allowed to settle overnight, after which the solution was filtered. Excess concentrated silver nitrate solution was then used to precipitate the silver chlorite.

The sample was analyzed for its silver content by conversion to silver chloride and weighing as such. The analysis showed it to contain 99.8% of the theoretical amount of silver. The slightly high heat capacity through the ice point indicated the presence of approximately 0.1% water.

Heat Capacity Measurements.—A calorimeter and cryostat similar to that described by Latimer and Greensfelder[2] was employed in the measurements. Some slight modifications were required due to the explosive character of the salt. It appeared unlikely that it would be possible to seal the thermocouple in its well on the bottom of the filled calorimeter without heating it up enough to explode the salt, consequently the resistance thermometer-heater on the calorimeter was relied upon to determine the temperature scale. This resistance thermometer was calibrated against the thermocouple at numerous temperatures, both before and after the silver chlorite measurements, also during the course of these measurements it was calibrated at 14, 66 and 293°K. by bringing the calorimeter and surrounding block to the same temperature. All these various calibrations were in satisfactory agreement.

A relatively small sample of the salt, 56.63 g. (*in vacuo*), was used in the measurements in order that none of the salt in the calorimeter would be too close to the lid while it was being soldered with Wood's metal.

In the calculations one calorie was taken equal to 4.1833 int. joules and the temperature of the ice point assumed to be 273.10°K.

The accuracy of the heat capacities of silver chlorite is necessarily less than that of most of the other salts run in these investigations due to the smaller sample and greater uncertainties in the temperature scale. The results are given in Table I and shown as a function of temperature in Fig. 1.

TABLE I

MOLAL HEAT CAPACITY OF SILVER CHLORITE

T, °K.	C_p, cal./deg.	T, °K.	C_p, cal./deg.
14.15	1.21	140.48	16.18
16.79	1.61	146.22	16.28
19.04	2.05	152.03	16.67
21.79	2.59	157.99	16.84
26.40	3.55	163.69	17.05
30.96	4.67	169.87	17.34
34.85	5.59	176.45	17.56
49.12	7.81	182.86	17.86
53.43	8.64	189.05	18.09
57.76	9.07	195.10	18.34
61.95	9.71	207.07	18.71
66.45	10.29	213.67	18.86
70.78	10.82	220.37	19.09
75.01	11.28	226.59	19.55
79.78	11.83	233.65	19.80
85.24	12.41	240.71	19.90
90.83	12.96	247.56	20.00
98.33	13.66	254.42	20.23
104.16	14.10	261.76	20.30
109.10	14.64	268.52	20.41
114.25	14.89	275.40	20.51
119.48	15.19	282.43	20.57
124.74	15.52	289.95	20.83
129.77	15.83	297.10	20.81
135.02	16.08		

Entropy of Silver Chlorite.—The entropy at 298.1°K. was obtained by graphical integration

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(1) Barnett, Ph.D. Dissertation, University of California, 1935; Bray, *Z. physik. Chem.*, **54**, 569 (1906).

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

between 14.13 and 298.1°K., combined with an extrapolation from 14.13 to 0°K. using the Debye specific heat equation. The calculation is summarized in Table II.

TABLE II

MOLAL ENTROPY OF SILVER CHLORITE

14.13–298.1°K. Graphical from data	31.73
0–14.13°K. Debye extrapolation	0.43
Entropy in cal./deg. mole	32.16 ± 0.2

Free Energy of Solution.—The free energy of solution was determined from the solubility of the salt in water. In order to investigate whether or not silver forms a complex ion with chlorite similar to the one with nitrite,[3] Mr. J. W. Aubry and Mr. W. R. Kong of this Laboratory have determined the solubility of silver chlorite in solutions containing various concentrations of chlorite ion. Their measurements are given in Table III.

TABLE III

SOLUBILITY OF SILVER CHLORITE IN PRESENCE OF CHLORITE ION AND SILVER ION

Ag^+, moles per liter	ClO_2^-, moles per liter	Other ions	t, °C.
0.211	0.00733	NO_3^-	22.5
.0295	.0299		24.1
.00751	.1832	K^+	24.1
.0047	.3760	K^+	22.5

These data were corrected to 25° by making use of the heat of solution described later. These corrected results are given in Table IV. The first column gives the ionic strength, μ, the second column gives Kc, the product of the silver ion concentration and the chlorite ion concentration, the third column gives the square of the activity coefficient of silver nitrate[4] in a solution of ionic strength μ, and the fourth column gives the thermodynamic equilibrium constant, assuming that the activity coefficient of silver chlorite is the same as that of silver nitrate.

TABLE IV

SOLUBILITY PRODUCT OF SILVER CHLORITE

μ	Kc, 25°	γ^2 $AgNO_3$	K, 25°	Added salt
0.21	1.70×10^{-3}	0.42	0.71×10^{-3}	$AgNO_3$
.03	0.914	.68	.62	
.18	1.43	.44	.63	$KClO_2$
.38	1.95	.32	.62	$KClO_2$

The constancy of K calculated in this manner indicates that there is no complex ion found in solutions up to 0.4 M chlorite and that the activity coefficient of silver chlorite is very nearly the same as that for silver nitrate. Using the value of K calculated for the solution in pure water, where the assumption that the activity coefficient is the same as for silver nitrate must be the best, the free energy change at 298.1°K. is $\Delta F^\circ = -1{,}364 \log (0.62 \times 10^{-3}) = 4380 \pm 100$ cal.

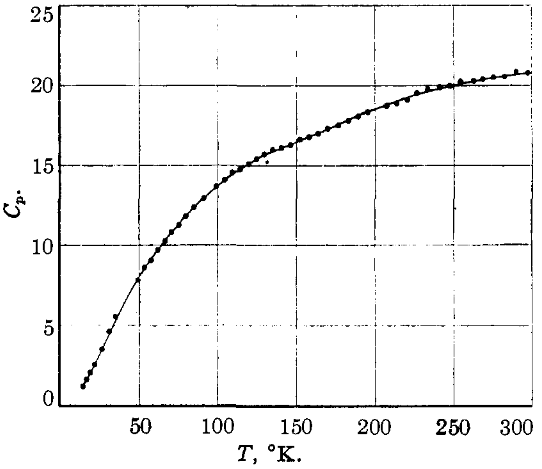

Fig. 1.—Molal heat capacity of silver chlorite in cal. per degree per mole.

The Heat of Solution.—The rate of solution in pure water was found to be too slow to get satisfactory results. This difficulty was overcome by first wetting the sample thoroughly and then measuring its heat of solution in dilute aqueous ammonia. It was thus necessary to determine the amount of salt which dissolved by analysis of the resulting solution rather than by following the usual technique of weighing out the sample to be dissolved. In this case the total amount of salt dissolved was determined by analyzing for the chlorite concentration iodimetrically. It was found that the reaction between chlorite ion and aqueous ammonia was slow enough to be disregarded in these measurements, since the chlorite concentration of a solution 0.01 M in silver chlorite and 0.14 M in ammonia decreased by only 7% in twenty-four days. The heat of solution of silver chlorite in aqueous ammonia (0.01 M silver chlorite and 0.14 M ammonium hydroxide) was found to be $\Delta H^0 = -6180 \pm 80$ cal. per mole at 25°. To obtain the desired heat of solution at infinite dilution in water we subtract from the above quantity the heat of solution of silver nitrate in the ammonia solution[5] and add the heat of solution at infinite dilution of silver nitrate in water,[5] obtaining

$$AgClO_2 = Ag^+ + ClO_2^- \quad \Delta H^0 = 7200 \pm 100 \text{ cal.}$$

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[3] Abegg and Pick, *Z. anorg. Chem.*, **51**, 1 (1906).

[4] Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., Inc., New York, 1923, p. 362.

[5] Smith, Brown and Pitzer, THIS JOURNAL, **59**, 1213 (1937).

Entropy of Chlorite Ion.—From the above free energy and heat of solution the entropy of solution at 25° is found to be $\Delta S = 9.5 \pm 0.5$ cal./deg. mole. Combining this with the entropy of silver ion[6] and the entropy of silver chlorite, the entropy of chlorite ion at 25° is found to be $S^0_{ClO_2^-} = 9.5 + 32.16 - 17.54 = 24.1 \pm 0.5$ cal./deg. mole.

Summary

The heat capacity of silver chlorite has been measured from 15 to 300°K. and its entropy at 298.1°K. found to be 32.2 cal./deg. mole. Its free energy and heat of solution have been determined. The entropy of chlorite ion has been calculated to be 24.1 cal./deg.

BERKELEY, CALIF. RECEIVED SEPTEMBER 29, 1937

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[6] Pitzer and Smith, THIS JOURNAL, **59**, 2633 (1937).

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

Silver Chromate: Its Heat Capacity, Entropy and Free Energy of Formation. The Entropy and Free Energy of Formation of Chromate Ion

BY WENDELL V. SMITH, KENNETH S. PITZER AND WENDELL M. LATIMER

A determination of the entropy and free energy of formation of chromate ion is an important step in extending the thermodynamics of chromium compounds. Silver chromate was chosen as the substance on which to base the calculation because the necessary heat and free energy data are most readily obtained from it. The experimental part of this investigation is concerned with measuring the heat capacity and heat of solution of silver chromate.

Preparation of Sample.—Part of the sample was obtained by repeatedly washing a sample of red "chemically pure" silver chromate with hot water until the wash water no longer contained chromic acid. The remainder of the sample was prepared from silver chromate precipitated from chromic acid solution by adding silver oxide; this precipitated silver chromate was treated in the same manner as the above sample. The product consisted of small dark green crystals which were dried at 130° for three days. This was analyzed for silver content gravimetrically by precipitating the silver as silver chloride, the oxidizing power was determined iodimetrically. The results of the analysis showed the silver content to be 100.0% of the theoretical and the chromate content to be 100.2% of the theoretical.

Heat Capacity Measurements.—The measurements were made in a calorimeter and cryostat similar to those described by Latimer and Greensfelder.[1] In calculating the heat capacities and the heat of solution one calorie was taken equal to 4.1833 int. joules, and the absolute temperature of the ice-point was assumed to be 273.10°K. Measurements were made on a sample of 207.95 g. (weight *in vacuo*) of the silver chromate. The results are given in Table I and shown as a function of temperature in Fig. 1.

TABLE I

MOLAL HEAT CAPACITY OF SILVER CHROMATE

T, °K.	C_p, cal./deg. mole	T, °K.	C_p, cal./deg. mole
15.85	2.96	141.45	25.52
19.06	4.01	146.93	26.04
21.84	5.01	152.16	26.44
24.77	5.94	157.28	26.89
27.86	6.93	162.16	27.29
31.69	8.15	167.34	27.67
36.29	9.58	172.70	28.09
41.02	10.78	178.22	28.46
46.65	12.08	182.81	28.89
52.59	13.34	189.88	29.27
57.39	14.37	195.80	29.68
72.54	17.10	202.15	30.04
77.42	17.87	208.56	30.46
82.77	18.68	215.17	30.84
88.34	19.50	221.62	31.19
93.44	20.23	228.33	31.45
95.62	20.51	235.15	31.78
99.92	21.10	242.10	32.31
105.01	21.74	248.99	32.58
110.33	22.38	256.14	32.95
115.28	22.95	263.06	33.01
120.52	23.49	270.11	33.30
126.02	24.08	278.28	33.44
131.23	24.55	287.10	33.66
136.20	25.06	294.75	33.90

Entropy of Silver Chromate.—The entropy was calculated by the graphical integration of a plot of C_p *vs.* log T, combined with an extrapolation to 0°K., using the Debye specific heat equation. The calculation is summarized in Table II.

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