

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 ion⁶ and the entropy of silver chlorite, the entropy of chlorite ion at 25° is found to be $S^0_{\text{ClO}_2^-} = 9.5 + 32.16 - 17.54 = 24.1 \pm 0.5$ cal./deg. mole.

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

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.

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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.

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

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

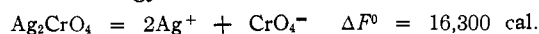
Entropy of Silver Chromate.—The entropy was calculated by the graphical integration of a plot of C_p vs. $\log T$, combined with an extrapolation to 0°K., using the Debye specific heat equation. The calculation is summarized in Table II.

TABLE II

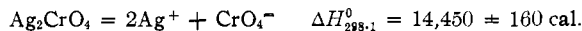
MOLAL ENTROPY OF SILVER CHROMATE

0-15.85°K. Debye extrapolation	1.17
15.85-298.1°K. Graphical from data	50.65
Entropy at 298.1°K. in cal./deg. mole	51.82 ± 0.2

Free Energy of Solution.—The free energy obtained from electrode potential measurements, even though they involve a liquid junction potential correction, is to be preferred to direct measurements of the solubility due to the fact that it is very difficult to prepare the solid without its having a slight excess of chromium trioxide. In preparing the present sample even after repeated washings with boiling water it apparently contained a slight excess of chromium trioxide. The latest work on the silver, silver chromate, chromate ion electrode potential is that of Cann and Mueller,² who give references to the previous work. They measured the potential of this electrode against the silver, silver chloride, chloride ion electrode and corrected for the liquid junction between the potassium chloride and potassium chromate solutions. Their data yield for the free energy of solution at 25°



Heat of Solution.—The heat of solution measurements were carried out in the calorimeter described by one of the authors.³ The solvent used in the measurements was an aqueous solution of ammonia of concentration 0.14 *M*, while the final concentration of silver chromate was 0.007 *M*. The heat of solution at 25° in this solvent which corresponds to the heat of forming silver ammonia complex ion and chromate ion from silver chromate was found to be $-12,310 \pm 100$ cal. To obtain the desired heat of solution at infinite dilution of silver chromate in water we subtract from the above quantity twice the heat of solution of silver nitrate in the ammoniacal solution⁴ and add twice the heat of solution at infinite dilution of silver nitrate in water,⁴ obtaining



Entropy of Chromate Ion.—The above values for the heat and free energy of solution give -6.2 cal. per deg. mole for the entropy of solution at 25°. Combining this with the entropy of silver chromate given above and the entropy of silver ion,⁵ we obtain for the entropy of chromate ion at 25°

$$S_{\text{CrO}_4}^0 = 51.82 - 2 \times 17.54 - 6.20 = 10.5 = 1.0 \text{ cal./deg. mole}$$

In the entropy of chromate ion as well as silver chromate there arises the same uncertainty that exists in the entropy of potassium permanganate⁶ due to the presence of paramagnetism. Here again the paramagnetism is without appreciable temperature coefficient so is of a different nature from that which is known to produce a considerable entropy in the case of gadolinium salts.⁷ And again the heat capacity curve throughout the whole temperature region appears to be quite normal, in fact, approaching very closely to the curve of silver sulfate in the lower temperature region.

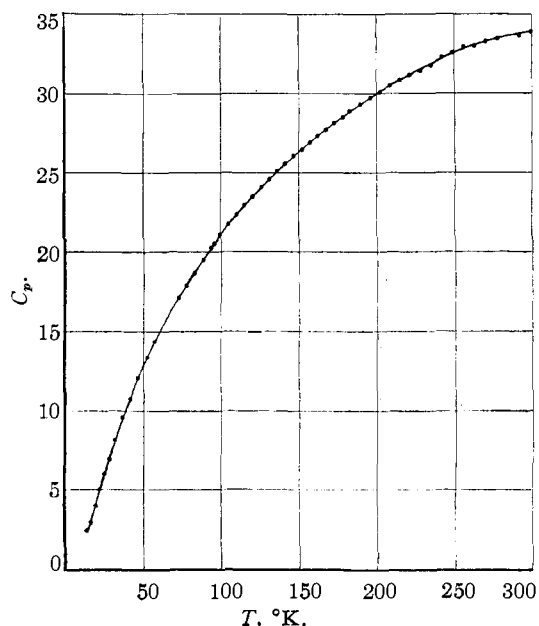


Fig. 1.—Molal heat capacity of silver chromate in cal. per degree per mole.

Free Energy of Formation of Chromate Ion.—The heat of formation at 18° is given as $\Delta H^0 = -207,900$ cal. by Bichowsky and Rossini.⁸ Applying an estimated correction for the change in heat content with temperature, the heat of formation at 25° may be taken to be $-208,500$ cal. The entropy of formation involves the entropies of chromate ion, hydrogen ion, chromium,⁹ oxygen⁹ and hydrogen.⁹

It is

$$\Delta S^0 = 10.5 - 5.68 - 2 \times 49.03 - 31.23 = -124.5 \pm 1.0$$

(6) Brown, Smith and Latimer, *ibid.*, **58**, 2144 (1936).

(7) Giauque and MacDougall, *Phys. Rev.*, **44**, 235 (1933).

(8) Bichowsky and Rossini, "Thermochemistry of Chemical Substances," Reinhold Publishing Co., New York, N. Y., 1936, p. 95.

(9) Kelley, *Bur. of Mines Bull.*, 394 (1935).

(2) Cann and Mueller, *This Journal*, **57**, 2525 (1935).

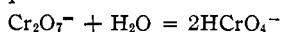
(3) K. S. Pitzer, *ibid.*, **59**, 2365 (1937).

(4) Smith, Brown and Pitzer, *ibid.*, **59**, 1213 (1937).

(5) Pitzer and Smith, *ibid.*, **59**, 2633 (1937).

The free energy of formation of chromate ion from its elements at 25° is, therefore, $\Delta F^0 = -171,400$ cal.

The free energies of formation of other substances whose equilibria with chromate ion have been measured, immediately follow, and their values will be included for the sake of completeness. The most recent determination of the second ionization constant of chromic acid¹⁰ gives 3.2×10^{-7} at 25° or $\Delta F^0 = 8740$ cal. so that the free energy of formation of HCrO_4^- ion is $-180,140$ cal. Neuss and Riemann¹⁰ also have determined the equilibrium constant for the reaction



finding $K = 0.023$ or $\Delta F = 2210$ cal. The free energy of formation of water⁵ is $-56,690$ cal., so that the free energy of formation of dichromate

(10) Neuss and Riemann, *THIS JOURNAL*, **56**, 2238 (1934).

ion at 25° is $-305,800$ cal. The free energy of formation of solid silver chromate involves the free energies of formation of silver ion,¹¹ $18,450$ cal. chromate ion and the free energy of solution of silver chromate.² It is found to be $-150,800$ cal.

Summary

The heat capacity of silver chromate has been measured from 15 to 300°K. and its entropy at 298.1°K. calculated to be 51.8 cal./deg. mole. Its heat of solution has been determined to be 14,450 cal. The entropy of chromate ion has been calculated to be 10.5 cal./deg. mole. The free energies of formation of chromate and several related ions and of solid silver chromate have been obtained.

(11) Gerke, *Chem. Rev.*, **1**, 377 (1925).

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The Rate and Mechanism of Hydrolysis and Alcoholysis of Tertiary Butyl Chloride. An Application to the Transition State Theory of Solvent Effects

BY A. R. OLSON AND R. S. HALFORD¹

Ingold and his collaborators² have postulated that two types of mechanism may operate in typical organic substitution reactions. One of these is identical with the mechanism discussed by Polanyi³ and Olson.⁴ It can be characterized as a one-step bimolecular reaction, resulting in inversion of configuration. In the second mechanism, a primary ionization of one of the reactants would occur as the slow rate determining step and this would be followed by a rapid addition reaction. Such a reaction would be unimolecular, its rate would be independent of the substituting agent, and in the case of an optically active reactant, presumably would result in racemization. It was just this type of reaction which Olson and Voge⁵ had in mind when they stated: "We therefore conclude that in the absence of large resonance effects any reaction mechanism which involves primary breaking of strong bonds at ordinary temperatures is erroneous."

Hughes⁶ in studying the hydrolysis of *t*-butyl chloride in aqueous ethanol solvents found that the reaction was first order with respect to the halide and independent of the concentration of hydroxide ions. The specific reaction constant increased 750-fold as the solvent was changed from 90% ethanol by volume to 40% ethanol by volume. Since the reaction was not catalyzed by hydrogen or hydroxide ions, Hughes and Ingold⁷ state that this reaction occurs by primary ionization and that water acts "as solvent alone." The tremendous change in rate constant which accompanied the change in composition of the solvent was ascribed to the superior properties of water over alcohol as an ionizing medium. It was decided therefore to reinvestigate this reaction, bearing in mind the role of nonionized water as the substituting agent. In general, Hughes' procedure was adopted. Aqueous methanol was employed as a solvent and methyl red was substituted for lacmoid as indicator.

A preliminary qualitative experiment, in which 25 cc. of *t*-butyl chloride was shaken for several

(1) Shell Research Fellow in Chemistry, 1937-1938.

(2) Hughes, Ingold and Patel, *J. Chem. Soc.*, 526 (1933).

(3) Polanyi, *Z. physik. Chem.*, **B19**, 164 (1932).

(4) Olson, *J. Chem. Phys.*, **1**, 418 (1933).

(5) Olson and Voge, *THIS JOURNAL*, **56**, 1690 (1934).

(6) Hughes, *J. Chem. Soc.*, 255 (1935).

(7) Hughes and Ingold, *ibid.*, 244 (1935).