[CONTRIBUTION FROM THE PACIFIC EXPERIMENT STATION, BUREAU OF MINES, UNITED STATES DEPARTMENT OF THE INTERIOR]

Low-temperature Heat Capacity, Entropy at 298.16°K., and High-temperature Heat Content of Ferric Chloride[1]

BY S. S. TODD AND J. P. COUGHLIN

The heat capacity of crystalline ferric chloride was measured throughout the temperature range from 51 to 298°K. The entropy is $S^0_{298.16} = 32.2 \pm 0.4$ cal./deg./mole. The high-temperature heat content was determined at several points between 298°K. and the melting point, 577°K. Heat content and entropy increments above 298.16°K. are listed and an equation for the heat content of the crystals is given.

Introduction

Thermodynamic calculations pertaining to ferric chloride have been hampered by lack of entropy and heat capacity values. The present paper supplies some of these data—heat capacities between 51 and 298.16°K., entropy at 298.16°K., and heat content and entropy increments between 298.16°K. and the melting point, 577°K.

Material

Ferric chloride was prepared from high-grade sponge iron (from reduction of specular hematite) and commercial chlorine.[2] Chlorine, dried by concentrated sulfuric acid and magnesium perchlorate, was passed over the sponge iron in a Pyrex tube at temperatures below 350°. The ferric chloride sublimed from the charge in the hot zone and recondensed downstream on the cooler parts of the tube wall. The product was removed and resublimed three times in a stream of dry chlorine, after which it was thoroughly evacuated at 100° to remove adsorbed chlorine. Analysis gave 34.48% iron and 65.52% chlorine, as compared with the theoretical 34.43 and 65.57%, respectively. Tests for ferrous iron indicated 0.03%, corresponding to 0.07% ferrous chloride.

Measurements and Results

Measurements of low-temperature heat capacity and high-temperature heat content were conducted with previously described apparatus,[3] using samples of 91.128 and 4.323 g. mass, respectively. The defined calorie (1 cal. = 4.1833 int. joules) is used throughout, and all results are reported upon a molal basis (mol. wt. of $FeCl_3$ 162.22 g., in accordance with the 1949 International Atomic Weights).

The measured low-temperature heat-capacity values are listed in Table I. These data follow an entirely normal course with increasing temperature, and no discussion appears necessary.

The entropy increase between 51 and 298.16°K. was obtained by Simpson-rule integration of a C_p *vs.* log T plot, as 27.69 ± 0.09 cal./deg./mole. The entropy increment below 51°K. was obtained from the empirical Debye and Einstein function sum, $D(108.5/T) + 2E(263/T) + E(447/T)$, which was found to fit the heat capacity data between 51 and 125°K. to within 0.4%, and to fit the data up to 298°K. to within 2.9%. The extrapolated entropy is 4.50 ± 0.30 cal./deg./mole, making $S^0_{298.16} = 32.2 \pm 0.4$. Of necessity, no allowance has been made in the value for possible unextracted magnetic entropy remaining at 51°K.

TABLE I

LOW-TEMPERATURE HEAT CAPACITY OF $FeCl_3(c)$

T, °K.	C_p, cal./deg./mole	T, °K.	C_p, cal./deg./mole	T, °K.	C_p, cal./deg./mole
52.92	7.064	114.79	15.50	216.28	21.12
57.33	7.795	124.85	16.40	226.33	21.29
61.73	8.516	135.96	17.34	236.13	21.59
66.71	9.326	146.33	18.05	245.97	21.76
71.53	10.09	156.13	18.67	256.17	22.06
76.20	10.81	166.18	19.22	265.90	22.22
80.62	11.43	176.24	19.71	275.38	22.34
85.36	12.08	186.22	20.09	286.56	22.52
95.08	13.32	196.00	20.47	296.79	22.68
105.13	14.51	206.50	20.82	298.16	(22.69)

The measured high-temperature heat-content values are in Table II. Premelting was evident only in the determinations labeled (a), at 549.1 and 560.9°K. Attempts to carry the measurements into the liquid range were unsuccessful because of rapid attack of the platinum–rhodium container capsule by the fused chloride. No evidence of attack appeared as long as the chloride was in the crystalline state. Although measurements in the liquid range were inadequate for obtaining the heat of fusion, and therefore not reported, they did indicate C_p = 32 cal./deg./mole as the approximate value of the heat capacity of the liquid between 577 and 670°K.

TABLE II

HEAT-CONTENT VALUES ABOVE 298.16°K.

T, °K.	$H_T - H_{298.16}$, cal./mole	T, °K.	$H_T - H_{298.16}$, cal./mole	T, °K.	$H_T - H_{298.16}$, cal./mole
339.6	1025	466.4	4240	549.1	6710[a]
374.4	1835	467.6	4290	560.9	7375[a]
413.8	2860	536.2	6105		

[a] These values include premelting effects.

Table III contains smooth values of the heat-content and entropy increments above 298.16°K. The heat content for the crystals up to the melting point.

TABLE III

HEAT-CONTENT AND ENTROPY INCREMENTS ABOVE 298.16° K.

T, °K.	$H_T - H_{298.16}$, cal./mole	$S_T - S_{298.16}$, cal./deg./mole	T, °K.	$H_T - H_{298.16}$, cal./mole	$S_T - S_{298.16}$, cal./deg./mole
350	1220	3.77	577	7,250 (c)	17.00
400	2500	7.18	577	17,550 (l)	34.85
450	3810	10.27	592	18,030 (l)	35.67
500	5140	13.07	592	24,050 (g)	45.84
550	6490	15.65			

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(1) Article not copyrighted.

(2) Preparation and analysis were conducted by K. R. Bonnickson and R. E. Lorenson, Pacific Experiment Station, Bureau of Mines.

(3) Kelley, Naylor and Shomate, *U. S. Bur. Mines Tech. Paper* 686 (1946).

577°K., is represented to within an average deviation of 0.3% by the equation

$$H_T - H_{298.16} = 29.56T + 6.11 \times 10^5T^{-1} - 10,863$$

In Table III also are values for the liquid at the melting and boiling points, 577 and 592°K., respectively, and for the gas (in terms of 0.5 mole Fe_2Cl_6) at the boiling point. These values were obtained by supplementing the present data with the heat of fusion and vaporization values from the N. B. S. Tables.[4]

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[4] National Bureau of Standards, Tables of Selected Values of Chemical Thermodynamic Properties, Ser. II, Table 47-2 (Sept. 30. 1949).

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Periodate Oxidation of the Formyl Esters of Starch[1]

BY OWEN A. MOE, SIDNEY E. MILLER AND MARJORIE IWEN BUCKLEY

The formyl esters and the 2-cyanoethyl ethers of diverse starches have been subjected to periodate oxidations and it has been found that the consumption of oxidant is dependent on a number of variants. The results of the current study show that the selectivity of the periodate is dependent on the concentration of the oxidant and the *p*H of the media.

In connection with some of the periodate oxidation studies[2] underway in this Laboratory, it became of interest to investigate the oxidation of the formyl esters of starch by periodate. Previous investigators[3] observed that the periodate oxidation of the formyl esters of corn starch (essentially a monoformate, degree of substitution approximately 1.1) proceeded in the same general course as that observed with the original starch although the reaction was slower for the formate ester. They found that approximately 1 mole of periodate had been consumed per mole (substituted anhydropyranose unit) of derivative after a reaction period of one hundred twenty hours. The results of the periodate oxidation studies indicated that the formyl group was located primarily in the C_6-position.

In view of our previous observations[2a] relative to the importance of the *p*H of the oxidation medium and the temperature at which the oxidation was carried out, it was considered possible that considerable hydrolysis accompanied oxidations of this type when the proper conditions were not imposed. This assumption was verified by the experimental evidence presented in this paper.

In agreement with Gottlieb, Caldwell and Hixon,[3] it was found that formyl esters of starch were slightly in excess of monoformates. The formyl content of the esters was usually within the range 16.3–16.8%.

When the oxidations involving the starch formates were carried out in buffered (0.05 *M*)[2a] media (*p*H 4.2–4.3) approximately 0.6–0.7 mole of oxidant had been consumed per mole of derivative after a 96-hour period as shown in Table I. This proved to be so with the formates of either cereal or tuber starches.

TABLE I

PERIODATE OXIDATIONS OF STARCH FORMATES IN BUFFERED (0.05 *M*) MEDIA, 19°

Source	Formyl, %	Degree of substitution	Reaction time in hours	Mole periodate consumed/mole derivative
Wheat	16.8	1.13	24	0.58
			48	.60
			96	.61
Potato	16.5	1.10	24	.60
			48	.62
			96	.66
Corn	16.8	1.13	24	.60
			48	.66
			96	.69

However, when the oxidations with periodate were carried out in unbuffered media, completely different results were obtained, and the final values were in all cases at least twice as high as those obtained when the oxidations were carried out in buffered media. The results of the oxidations in unbuffered media are presented in Table II.

TABLE II

PERIODATE OXIDATIONS OF STARCH FORMATES IN UNBUFFERED MEDIA, 23°

Source	Degree substitution	Molar concentration of HIO_4	Reaction time in hours	Moles periodate consumed/mole derivative
Wheat	1.15	0.5	24	1.08
			96	1.64
		.05	24	0.99
			48	1.19
			96	1.32
Potato	1.10	.5	24	1.19
			96	1.77
		.05	24	1.09
			48	1.21
			96	1.34

The molar concentration of the aqueous periodic acid employed appeared to have an appreciable effect and substantially higher values were obtained as the molar concentration was increased. From the tables, it becomes apparent that the oxidations carried out in buffered media were substantially complete after 24 hours and an increase of only 0.06 ± 0.03 mole of periodate per mole of derivative occurred during the next 72-hour period. However, when the oxidations were carried out in unbuffered media, the increase

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[1] Paper No. 99, Journal Series, General Mills, Inc., Research Dept.

[2] (a) O. A. Moe, S. E. Miller and Marjorie H. Iwen, THIS JOURNAL, **69**, 2621 (1947); (b) H. Wittcoff, O. A. Moe and M. H. Iwen, *ibid.*, **70**, 742 (1948).

[3] D. Gottlieb, C. G. Caldwell and R. M. Hixon, *ibid.*, **62**, 3342 (1940).