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Thermodynamic Properties of Ferric Oxychloride and Low-Temperature Heat Capacity of Ferric Trichloride

By J. M. Stuve, M. J. Ferrante, D. W. Richardson,
and R. R. Brown



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THERMODYNAMIC PROPERTIES OF FERRIC OXYCHLORIDE
AND LOW-TEMPERATURE HEAT CAPACITY
OF FERRIC TRICHLORIDE

by

J. M. Stuve,¹ M. J. Ferrante,¹ D. W. Richardson,² and R. R. Brown¹

ABSTRACT

This Bureau of Mines investigation measured the low-temperature heat capacities of FeOCl(c) and FeCl₃(c) in the temperature ranges of 6 to 305 K and 4.6 to 300 K, respectively. The standard entropies (S°, 298.15 K) of FeOCl(c) and FeCl₃(c) were derived as 19.73±0.03 cal/deg-mole and 35.33±0.07 cal/deg-mole. A large lambda transition was observed in the heat capacity of FeCl₃(c) at 8.4 K.

The standard enthalpy of formation (ΔH°_f , 298.15 K) of FeOCl(c) was determined to be -98.23±0.22 kcal/mole by HCl solution calorimetry. High-temperature enthalpy measurements ($H_{298.15} - H_{700}$) of FeOCl(c) were determined to 700 K by precision drop calorimetry. Standard thermodynamic formation data and related functions were tabulated at various temperatures for FeOCl(c) and FeCl₃(c).

INTRODUCTION

This Bureau of Mines investigation is part of a program designed to provide basic data in support of technology for mineral recovery and processing, and for environmental preservation. Depletion of high-grade ore deposits, as well as environmental and energy considerations, has renewed interest in the application of leaching techniques for economical recovery of metals from low-grade ore deposits. Recent Bureau investigations (3-4, 10-11)³ have focused on using soluble iron salts, particularly FeCl₃ solutions, as effective leachants of sulfidic ores and concentrates.

There has been a continuing interest in high-temperature chlorination as a separation technique for various transition metals, exploiting the widely varying chloride vapor pressures. Iron chloride and oxychloride are often present as reaction intermediates due to the wide lithospheric distribution of iron compounds.

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³Underlined numbers in parentheses refer to items in list of references at the end of this report.

The chemical literature contains many physiochemical investigations of FeCl_3 and FeOCl , including solubility studies, vapor phase equilibria, electromotive force methods, spectroscopic evaluations, and incomplete calorimetric results. Generally, data derived from these methods are in wide disagreement, resulting in a conflicting and incomplete picture of the thermodynamic properties of these important iron compounds. The Bureau has previously reported the following properties of FeCl_3 . Vapor pressure (9); heat capacity, 52 to 300 K (16); standard enthalpy of formation (8); and enthalpy increments to 592 K, relative to 298.15 K (16). The present investigation extended heat capacity measurements of $\text{FeCl}_3(\text{c})$ down to 4.6 K which allows an accurate calorimetric evaluation of its standard entropy. A complete calorimetric investigation of $\text{FeOCl}(\text{c})$ was made over its entire range of thermal stability using adiabatic calorimetry for low-temperature heat capacities, solution calorimetry for ΔH°_f at 298.15 K, and drop calorimetry for enthalpy measurements to temperatures up to 700 K. The results of these determinations are discussed in relation to selected published studies most relevant to precision calorimetric methods.

MATERIALS

Ferric oxychloride was prepared from a reagent-grade sample of ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$). The hydrated chloride was uniformly heated to produce a crude FeOCl mixture by thermal decomposition and hydrolysis. This material was placed in a furnace tube and heated at 200° C in a stream of anhydrous HCl gas, diluted with argon, to remove residual water. The resulting FeOCl mixture contained a small quantity of hydroxyl material.

Subliming $\text{FeCl}_3(\text{g})$ through the mixture at 240° C with an argon carrier produced a final product of nearly pure FeOCl that analyzed 52.02 pct iron (theoretical = 52.05 pct). Chlorine analyses averaged 33.07 pct (theoretical = 33.04 pct). Oxygen was analyzed by a gas technique based on hydrogen reduction and weighing the H_2O and HCl formed. The resulting oxygen content was 14.91 pct, the same as theoretical. Spectrographic and X-ray analyses indicated the FeOCl has less than 0.01-pct metallic impurities and was single-phase material corresponding to the American Society for Testing and Materials indexed pattern for $\text{FeOCl}(\text{c})$.

The synthesis of anhydrous FeCl_3 was started by dehydration and subliming $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ in a stream of dry chlorine gas. The sublimation step was repeated at a final temperature of 350° C for 6 hours. The resulting sublimed FeCl_3 was sealed in the receiver vessel and transferred to a dry, argon-filled vacuum glove box. A representative portion of the FeCl_3 was divided among smaller sample bottles for chemical analyses. Gravimetric iron determinations resulted in an average value of 34.46 pct iron (34.43 pct theoretical). The chlorine content analyzed 62.50 ± 0.2 pct by the gravimetric silver method (theoretical = 65.57 pct). This low chloride result was probably owing to an observed slight loss of Cl_2 or HCl when the samples were dissolved. Spectrographic emission analysis indicated the presence of 0.005 pct Cu and 0.05 pct Mn, the only significant metallic impurities detected. Powder X-ray diffraction analysis detected only lines corresponding to the normal hexagonal structure.

LOW-TEMPERATURE CALORIMETRY

The heat capacities of $\text{FeCl}_3(\text{c})$ and $\text{FeOCl}(\text{c})$ were determined by an adiabatic calorimeter positioned within a helium cryostat. Details of the design and operation of this apparatus were previously reported by Stuve, Richardson, and King (15). Sample temperatures in the range of 15 to 310 K were determined with a platinum resistance thermometer calibrated by the National Bureau of Standards. The potentiometric measurement system was capable of resolving temperatures to about 0.0001 K throughout this range with deviations of less than ± 0.01 K from the International Practical Temperature Scale of 1968. Temperatures below 15 K were determined with a germanium resistance thermometer calibrated by the National Bureau of Standards, for better resolution in this range. Both thermometers and a resistance heater were mounted in a reentrant well located at the bottom of a 90-ml, copper sample container. Sample masses of $\text{FeCl}_3(\text{c})$ and $\text{FeOCl}(\text{c})$ were 91.951 g and 121.263 g; with mole weights corresponding to 162.206 and 107.299. The later values were calculated from the International Union of Pure and Applied Science 1974 Table of Atomic Weights. The heat capacity of the empty sample vessel ranged from about 0.0046 cal/deg at 5 K to approximately 9.5 cal/deg at 300 K.

The experimental heat capacity data for $\text{FeCl}_3(\text{c})$ and $\text{FeOCl}(\text{c})$ are tabulated in tables 1 and 2. Energy units are in terms of the defined thermochemical calorie (1 calorie = 4.1840 joules). Curvature corrections were applied to the experimental data when significant, and these data are plotted in figures 1 and 2. Heat capacities were determined by the method of discrete heating periods, preceded and followed by temperature rating (equilibration) periods. In each case, the next heating period was not initiated until sample temperature drifts approached a zero rate. Near the transition peak of $\text{FeCl}_3(\text{c})$ at 8.4 K, heating periods were shortened to provide smaller temperature increments, thus giving better definition of heat capacities in this zone. This sharp lambda-type anomaly was not within the measurement range of a previous Bureau investigation (16).

TABLE 1. - Experimental heat capacities of $\text{FeCl}_3(\text{c})$

T, K	C_p° , cal/deg-mole	T, K	C_p° , cal/deg-mole	T, K	C_p° , cal/deg-mole
4.68	1.051	8.18	6.885	56.42	7.607
4.69	1.052	8.23	6.819	60.33	8.274
4.70	1.053	8.26	6.604	65.20	9.087
4.72	1.079	8.29	7.118	71.09	10.030
4.76	1.080	8.32	9.038	79.15	11.239
4.78	1.092	8.34	11.403	83.52	11.874
4.82	1.106	8.36	6.925	88.92	12.607
4.89	1.126	8.40	4.642	95.17	13.404
4.98	1.164	8.45	3.647	102.54	14.271
5.11	1.204	8.54	3.044	111.06	15.19
5.25	1.258	8.67	2.507	120.51	16.09
5.27	1.326	8.87	2.152	131.45	17.01
5.73	1.430	9.13	2.122	143.81	17.92
6.11	1.589	9.28	1.999	157.51	18.76
6.62	1.853	10.14	1.864	171.89	19.53
7.21	2.253	10.41	1.863	185.99	20.17
7.31	2.358	12.20	1.695	201.75	20.77
7.48	2.549	14.24	1.672	217.22	21.28
7.62	2.736	18.12	1.820	230.64	21.68
7.73	2.922	20.89	2.043	243.90	22.02
7.82	3.135	24.25	2.404	257.48	22.34
7.84	3.263	28.37	2.933	267.36	22.55
7.94	3.403	33.05	3.608	277.50	22.76
8.03	3.747	38.57	4.546	287.58	22.95
8.11	4.381	46.49	5.854	297.55	23.17
8.16	5.678	51.30	6.687	307.56	23.36

TABLE 2. - Experimental heat capacities of $\text{FeOCl}(\text{c})$

T, K	C_p° , cal/deg-mole	T, K	C_p° , cal/deg-mole	T, K	C_p° , cal/deg-mole
6.07	0.023	39.29	2.106	156.60	12.470
6.72	.029	43.16	2.523	166.47	12.990
7.45	.037	47.37	2.962	176.45	13.471
8.43	.049	51.96	3.457	187.49	13.965
9.71	.070	57.10	4.034	198.84	14.418
11.25	.099	62.69	4.650	209.86	14.808
12.91	.140	68.56	5.294	220.66	15.19
14.65	.196	74.70	5.950	231.32	15.47
16.56	.271	81.15	6.905	241.83	15.78
18.53	.367	89.08	7.609	252.22	16.03
20.70	.497	93.60	7.964	262.85	16.25
23.17	.652	99.51	8.436	273.38	16.45
26.27	.870	106.79	9.016	283.84	16.61
28.53	1.020	124.50	10.392	294.43	16.77
32.08	1.382	134.69	11.129	304.75	16.94
35.60	1.734	145.85	11.839	313.10	17.08

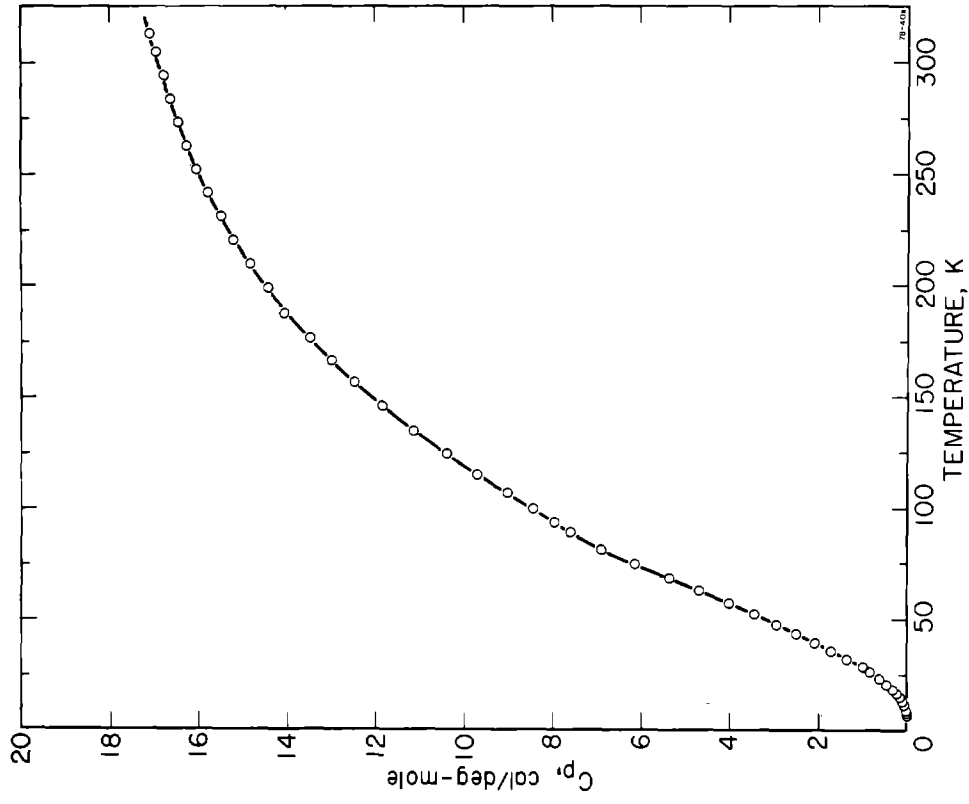


FIGURE 2. - Low-temperature heat capacities of $\text{FeOCl}(c)$.

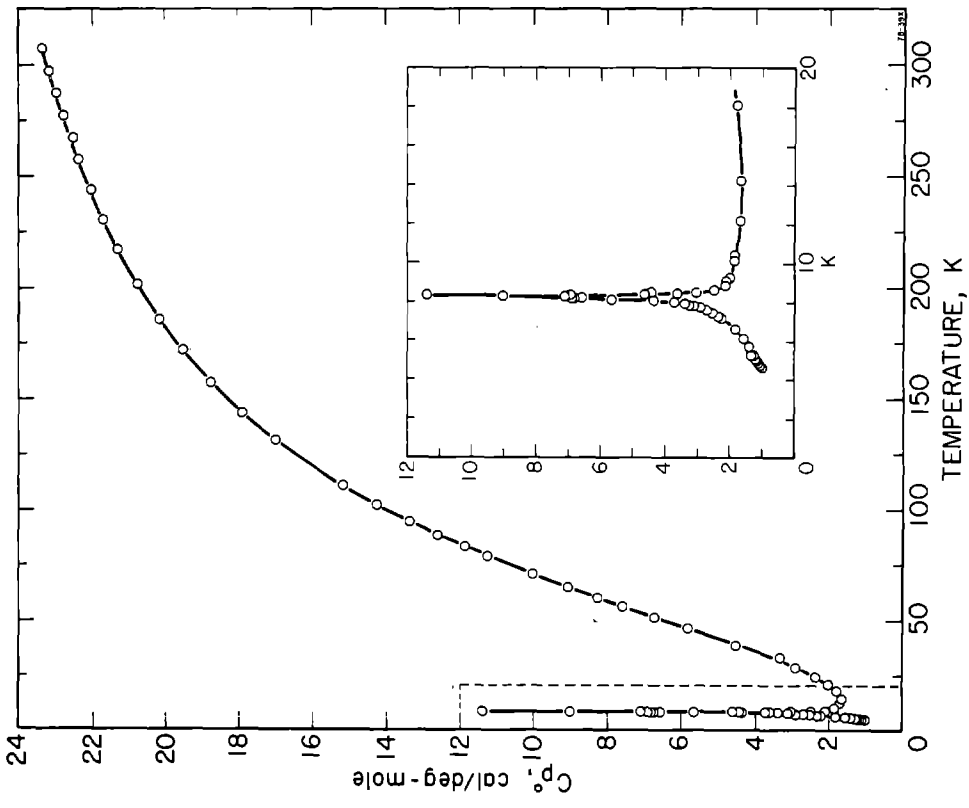


FIGURE 1. - Low-temperature heat capacities of $\text{FeCl}_3(c)$.

The low-temperature heat capacities of FeOCl(c) had no unusual properties. Smooth lines drawn through the experimental data in figures 1 and 2 represent the loci of heat capacities derived from a least-squares fitting of the respective experimental data sets, using orthogonal polynomials. Transition zone data of FeCl₃(c) were fitted and computed manually. These smooth data are tabulated in tables 3 and 4 at even temperature intervals. Standard state values of heat capacity at constant pressure, entropy, and enthalpy relative to 0 K correspond to C_p° , S° , and $H^\circ - H_0^\circ$. The Gibbs energy function, $(G^\circ - H_0^\circ)/T$, was calculated from corresponding entropy and enthalpy values. The entropies of FeOCl(c) and FeCl₃(c) were assumed to be zero at 0 K. Extrapolation of C_p° to 0 K was accomplished by using the function C_p/T versus T^2 for FeOCl(c). In the case of FeCl₃(c), the heat capacity curve below the transition was smoothly joined to 0 K and graphical interpolations were made.

TABLE 3. - Low-temperature thermodynamic properties of FeCl₃(c)

T, K	cal/deg-mole			$H^\circ - H_0^\circ$, cal/mole
	C_p°	S°	$-(G^\circ - H_0^\circ)/T$	
5	1.195	0.885	0.394	2.453
10	1.920	2.767	1.064	17.031
15	1.689	3.479	1.761	25.769
20	1.971	3.998	2.257	34.830
25	2.476	4.488	2.654	45.856
30	3.162	4.998	3.002	59.89
35	3.948	5.544	3.326	77.64
40	4.769	6.125	3.639	99.43
45	5.602	6.734	3.948	125.35
50	6.473	7.369	4.259	155.49
60	8.214	8.704	4.888	228.98
70	9.858	10.095	5.532	319.43
80	11.374	11.512	6.191	425.71
90	12.748	12.932	6.861	546.4
100	13.980	14.340	7.538	680.2
110	15.07	15.72	8.215	825.6
120	16.04	17.08	8.903	981.3
130	16.90	18.40	9.584	1,146.1
140	17.65	19.68	10.259	1,318.9
150	18.32	20.92	10.928	1,498.8
160	18.91	22.12	11.589	1,684.9
170	19.43	23.28	12.241	1,876.7
180	19.90	24.41	12.891	2,073.4
190	20.33	25.49	13.518	2,274.6
200	20.71	26.55	14.151	2,479.8
210	21.06	27.57	14.767	2,688.7
220	22.37	28.55	15.36	2,900.8
230	21.66	29.51	15.96	3,116.0
240	21.92	30.44	16.55	3,333.9
250	21.17	31.34	17.12	3,554.4
260	22.39	32.21	17.68	3,777.2
270	22.60	33.06	18.24	4,002.2
273.15	22.67	33.32	18.41	4,073.5
280	22.80	33.89	18.79	4,229.2
290	23.00	34.69	19.32	4,458.3
298.15	23.17	35.33	19.75	4,646.4
300	23.21	35.47	19.84	4,689.3

TABLE 4. - Low-temperature thermodynamic properties of FeOCl(c)

T, K	cal/deg-mole			$H^\circ - H_0^\circ$, cal/mole
	C_p°	S°	$-(G^\circ - H_0^\circ)/T$	
5	0.016	0.010	0.004	0.031
10	.074	.035	.012	.231
15	.188	.088	.028	.905
20	.457	.178	.053	2.510
25	.755	.310	.090	5.497
30	1.173	.483	.141	10.269
35	1.655	.700	.205	17.333
40	2.136	.952	.282	26.809
45	2.672	1.234	.372	38.783
50	3.268	1.548	.474	53.70
60	4.356	2.238	.710	91.70
70	5.452	2.992	.981	140.77
80	6.505	3.789	1.282	200.59
90	7.499	4.613	1.606	270.66
100	8.428	5.452	1.949	350.35
110	9.288	6.296	2.305	438.98
120	10.081	7.139	2.673	535.9
130	10.809	7.975	3.049	640.4
140	11.478	8.801	3.430	751.9
150	12.090	9.614	3.815	869.8
160	12.651	10.412	4.203	993.5
170	13.164	11.195	4.591	1,122.6
180	13.633	11.960	4.979	1,256.6
190	14.062	12.709	5.366	1,395.1
200	14.455	13.441	5.753	1,537.7
210	14.814	14.155	6.135	1,684.1
220	15.14	14.852	6.516	1,833.9
230	15.44	15.53	6.891	1,986.9
240	15.71	16.19	7.263	2,142.6
250	15.96	16.84	7.636	2,301.1
260	16.19	17.47	8.002	2,461.8
270	16.39	18.09	8.369	2,624.7
273.15	16.45	18.28	8.482	2,676.4
280	16.57	18.69	8.728	2,789.5
290	16.53	19.27	9.077	2,956.0
298.15	16.85	19.73	9.357	3,092.8
300	16.87	19.84	9.427	3,124.0

FORMATION ENTHALPY OF FeOCl(c)

Solution enthalpies of the various components of the reaction scheme for FeOCl(c) were measured with a precision HCl reaction calorimeter. This apparatus incorporates a 2-liter dewar reaction vessel thermostated to ± 0.002 K in a constant-temperature bath. The operation and construction details were previously given by Southard (13) and Ko, Stuve, and Brown (7). The enthalpies of all solution reactions were obtained by using an initial 2131.1-g mass of aqueous 4.360-molal hydrochloric acid. Table 5 gives the calorimetric reaction

scheme used to calculate the standard enthalpy of formation of FeOCl(c). The sample masses of the various solutes were in accordance with strict stoichiometric requirements using 10 millimoles of FeOCl(c) as a basis. The enthalpy changes at 298.15 K for the first three reactions in table 5 were determined experimentally by using five samples of each solute. Enthalpies for reactions 5 through 7 were taken from published sources (8, 17). Reaction 8 represents the standard formation enthalpy of FeOCl(c), which results in a rounded value of -98.23 ± 0.22 kcal/mole at 298.15 K.

TABLE 5. - Calorimetric reaction scheme for FeOCl(c) at 298.15 K

Reaction	H _f ^o , cal	Uncertainty, cal
(1) FeOCl(c) + 2(HCl+12.731H ₂ O)(sol) = FeCl ₃ (sol) + 26.462H ₂ O(sol).....	-14,650	16
(2) FeCl ₃ (c) = FeCl ₃ (sol).....	-24,696	8
(3) 26.462H ₂ O(l) = 26.462H ₂ O(sol).....	-2,027	7
(4) 2(HCl+12.731H ₂ O)(l) = 2(HCl+12.731H ₂ O)(sol).....	0	0
(5) Fe(c) + 1.5Cl ₂ (g) = FeCl ₃ (c).....	-95,480	200
(6) H ₂ (g) + 0.5O ₂ (g) = H ₂ O(l).....	-68,315	10
(7) H ₂ (g) + Cl ₂ (g) + 25.462H ₂ O(l) = 2(HCl+12.731H ₂ O)(l)	-77,640	80
(8) Fe(c) + 0.5O ₂ (g) + 0.5Cl ₂ (g) = FeOCl(c).....	-98,230	±220
$\Delta H_8 = -\Delta H_1 + \Delta H_2 + \Delta H_3 - \Delta H_4 + \Delta H_5 + \Delta H_6 - \Delta H_7$		

Assigned uncertainties for individual reactions measured were twice the standard deviation of each group of five determinations. The standard Gibbs energy of formation ($\Delta G^{\circ f}$) and related high-temperature formation data are given later in table 8. No impurity corrections were applied to the FeOCl(c) solution enthalpy determined by reaction 1.

HIGH-TEMPERATURE ENTHALPY

Enthalpy measurements of FeOCl(c) in the temperature range 403 to 716 K were accomplished with a precision drop calorimeter. The receiver calorimeter was a copper-block type enclosed in an isothermal jacket. The receiver calorimeter temperature was measured with a resistance bridge thermometer in conjunction with six-dial, microvolt potentiometer using a galvanometer sensitivity of ± 0.02 microvolt. The approximate heat capacity of the receiver calorimeter at 298 K was 3.7 cal/ μ v in terms of the bridge thermometer signal. Periodic comparative accuracy checks of the calorimetric apparatus were made using a standard sample of MgO. A detailed description of this apparatus was given by Douglas and King (1).

A FeOCl(c) mass corresponding to 0.08496 g mole was sealed in a platinum-10-pct rhodium capsule for enthalpy determinations. The enthalpy of the empty capsule was determined in a series of separate measurements and averaged about 20 pct of the total measured enthalpy in the temperature range 300 to 700 K.

The results of enthalpy determinations for FeOCl(c) are listed in table 6 for temperatures in the range 403 to 716 K. Determinations at 691.9 and 716.2 K were not used in the final fitting of the experimental data because they showed signs of thermal decomposition. A second capsule was filled with FeOCl(c) and measured at 601.9 K, heated to 716.1 K for an additional measurement. The results of this measurement and X-ray analysis confirmed that an appreciable irreversible sample change had occurred at the highest temperature. The experimental enthalpy data are presented in figure 3 as the function $(H_T^\circ - H_{298.15}^\circ)/T - 298.15$ versus temperature. The smooth line through the data points represents the polynomial function fitted to the experimental data for calculation of high-temperature relative enthalpies and related functions. This curve was fitted to the low-temperature heat capacity at 298.15 K.

TABLE 6. - Experimental enthalpies
of FeOCl(c)

T, K	$H^\circ - H_{298}^\circ$, kcal/mole	T, K	$H^\circ - H_{298}^\circ$, kcal/mole
403.2	1.846	¹ 601.9	5.625
427.3	2.284	^{2,3} 602.0	5.756
451.3	2.730	611.3	5.810
477.5	3.226	639.3	6.375
503.3	3.707	662.1	6.845
529.3	4.198	³ 691.9	7.779
555.8	4.714	^{1,3} 716.1	8.869
579.8	5.186	³ 716.2	9.421

¹2nd sample.

²Measurements at 691.9 and 716.2 K caused partial sample decomposition before final measurement at 602.0 K with first sample.

³Partial sample decomposition, and not used in computer fit.

The results of these computations are presented in table 7. Heat capacities and standard entropies were evaluated from the appropriate analytic functions derived from the selected polynomial.

TABLE 7. - Thermodynamic properties of FeOCl(c) to 700 K

T, K	cal/deg-mole			$H^\circ - H_{298}^\circ$, kcal/mole
	C_p°	S°	$-(G^\circ - H_{298}^\circ)/T$	
298.15	16.85	19.73	19.73	0
300	16.87	19.84	19.74	.031
350	17.56	22.50	19.94	.893
400	18.10	24.88	20.41	1.785
450	18.56	27.04	21.04	2.702
500	19.00	29.02	21.74	3.641
550	19.44	30.85	22.48	4.602
600	19.90	32.56	23.25	5.586
650	20.40	34.17	24.03	6.594
700	(20.95)	(35.70)	(24.80)	(7.626)

NOTE.--Values in parentheses are extrapolations.

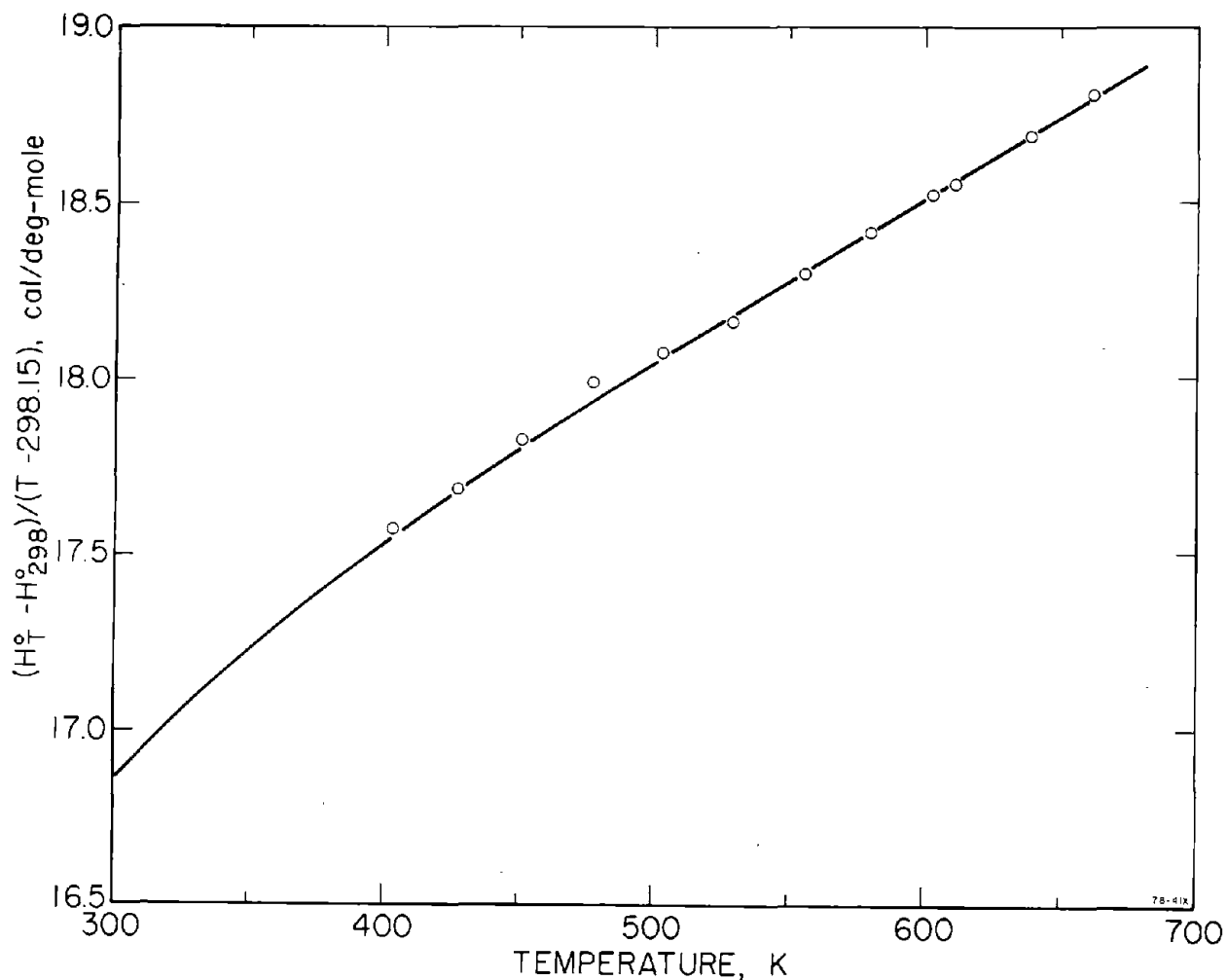


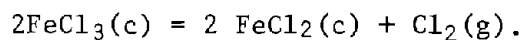
FIGURE 3. - High-temperature enthalpy function of FeOCl(c).

SUMMARY OF RESULTS

Evidence of abnormal thermal behavior for FeOCl(c) was not observed in the range of low-temperature measurements. The heat capacity of this substance exhibits a normal sigmoid-shaped curve as shown in figure 2.

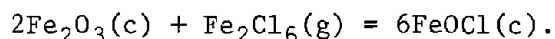
No previously reported low-temperature data for FeOCl(c) were found in the literature. The observed C_p° at 298.15 K of 16.85 cal/deg-mole agrees within 5 pct of the estimated value using a Kopp's rule approximation.

In contrast, a large thermal anomaly was discovered in the heat capacity of FeCl₃(c) below 10 K. A maximum C_p° of approximately 11.4 cal/deg-mole at 8.34 ± 0.05 K was observed. The entropy effect of this transition was about 2.8 cal/deg-mole above the estimated normal lattice contribution. The resulting standard entropy at 298.15 K was evaluated as 35.33 ± 0.07 cal/deg-mole. This value was expectedly larger than 32.2 ± 0.4 cal/deg-mole, previously reported by Todd and Coughlin (16), which excluded a magnetic spin contribution. Kangro and Peterson (6) reported an entropy of 36.99 ± 0.07 cal/deg-mole, based on equilibrium measurements in the range 525 to 575 K of the reaction



Because the vaporization of FeCl₃(c) is complex, the latter entropy value may be subject to uncertainty from interpretation of experimental data.

Reported formation enthalpies of FeOCl(c) from different sources of thermochemical data, have varied by nearly 9 kcal. Wagman (18) has reported a value of -90.1 kcal/mole. Stirnemann (14) investigated the FeCl₃-H₂O system at moderately high temperatures, using vapor pressure equilibrium methods. He evaluated an enthalpy change of -26.0 kcal at 298 K for the reaction



Using JANAF (2) values for ΔH°_f of Fe₂O₃(c) and Fe₂Cl₆(g), results in a formation enthalpy of -96.2 kcal/mole for FeOCl(c). More recently, Schaefer, Wittig, and Jori (12) measured the formation enthalpy of FeOCl(c) calorimetrically, obtaining a result of -99.0 kcal/mole at 298 K. Both of these latter values are in fairly good agreement with the value -98.23 ± 0.22 kcal/mole determined in the present investigation. Schaefer used a slightly larger formation enthalpy for FeCl₃ in his calorimetric reaction scheme, which accounts for the difference. Unfortunately, there is not a well-characterized iron compound suitable as a solution calorimetric standard, and accordingly, the major source of experimental error in these calorimetric schemes is the formation enthalpy of FeCl₃(c).

The high-temperature enthalpy of FeOCl(c) has not previously been reported. Heat capacities derived from this investigation were used to extend the formation properties of FeOCl(c) to 700 K. These values are listed in tables 7 and 8. The S° , (298) value of Fe(α) was taken from Hultgren (5).

TABLE 8. - High-temperature formation data of FeOCl(c)

T, K	kcal/mole		Log Kf	T, K	kcal/mole		Log Kf
	ΔH°_f	ΔG°_f			ΔH°_f	ΔG°_f	
0	-98.11	-98.11	0	400	-97.87	-83.11	45.411
100	-98.56	-94.63	206.818	500	-97.48	-79.47	34.736
200	-98.51	-90.70	91.109	600	-97.08	-75.09	27.647
298.15	-98.23	-86.92	63.715	700	-96.67	-72.40	22.604
300	-98.22	-86.85	63.271				

Although the Gibbs formation energies indicate that FeOCl(c) is very stable with respect to its component elements, it was found to decompose partially to Fe₂O₃(c) and Fe₂Cl₆(g) at about 690 K. While analyzing the capsule contents from the higher temperature enthalpy determinations, an abnormally high concentration of an Fe₂O₃ phase was detected on the surface of the FeOCl particles by X-ray analysis. However, there were no indications of substantial FeCl₃ formation or capsule leaks. A chemical analysis of the capsule contents revealed substantially FeOCl stoichiometry, suggesting that FeCl₃(g) formation at the FeOCl(c) surface is diffusion controlled.

The following equation was derived to express the relative enthalpy of FeOCl(c) in kilocalories per mole as a function of temperature, valid in the temperature interval 298 to 700 K:

$$H^\circ_f - H^\circ_{298} = 16.021 \times 10^{-3}T + 3.470 \times 10^{-6}T^2 + 1.104 \times 10^2T^{-1} - 5.455.$$

This equation fits the experimental data within ± 0.1 pct.

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⁴Title enclosed in parentheses are translations from the language in which the item was published.

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