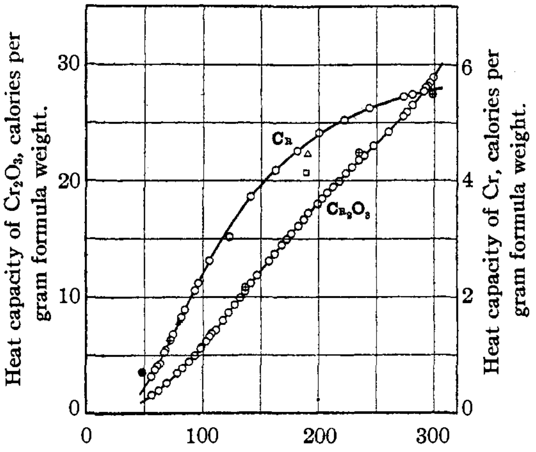
[Contribution from the Metallurgical Division, U. S. Bureau of Mines]

The Heat Capacities of Chromium, Chromic Oxide, Chromous Chloride and Chromic Chloride at Low Temperatures[1]

By C. Travis Anderson[2]

The work presented in this paper is a part of the program for a systematic thermodynamic study of chromium and some of its compounds that the U. S. Bureau of Mines has been conducting for a number of years. This report deals with the heat capacities and entropies of chromium, chromic oxide, chromous chloride and chromic chloride. A manuscript, the "Chemistry of the Anhydrous Chlorides of Chromium," is in course of publication as a Bureau bulletin.

The methods, apparatus and accuracy have been described previously.[3]



○, Anderson; ●, Dewar; □, Richards and Jackson; △, Nordmeyer and Bernoulli; +, Simon and Ruhemann; ⊕, Russell.

Fig. 1.—The heat capacities of chromium and chromic oxide, in calories per gram formula weight.

Materials

The sample of chromium metal, which was prepared electrolytically, was obtained for this Laboratory through the courtesy of Dr. John Chipman, who obtained it from Mr. Marsh of the Hoskins Manufacturing Company. It was carefully hand-picked to obtain particles of uniform color without a coating of chromic oxide. The selected particles were placed in a silica flask, evacuated and heated to 1100° to remove any hydrogen that might have been present. An analysis of the sample, after this treatment, by Dr. Chipman showed it to contain 0.65% oxygen and no nitrogen. This oxygen was assumed to be present in the form of chromic oxide and was corrected for in the heat capacity of the chromium. The calorimeter was filled with 401.6 g.

The chromic oxide was Kahlbaum highest quality, containing no detectable impurity. It was compressed into pellets, placed in a silica flask, evacuated and heated. Measurements were made on a 145.6-g. sample.

The author is indebted to H. A. Doerner and W. C. McGavock for the preparation of the anhydrous chlorides of chromium. The chromic chloride was prepared by passing chlorine gas through a mixture of chromic oxide and carbon at about 800°. The resulting vapor was condensed, removed from the condenser and redistilled in an atmosphere of dry chlorine containing small amounts of carbon tetrachloride vapor. The product consisted of brilliant violet, flat, thin flakes about 2 mm. in diameter. It was compressed into pellets, broken to size and dried by passing dry chlorine containing a little carbon tetrachloride through the chromic chloride at about 300°. It was finally evacuated to remove any excess chlorine, after which a 113.6-g. sample was transferred to the calorimeter out of contact with air.

The chromous chloride used in this investigation was prepared from a portion of the pure chromic chloride described above by reduction with hydrogen containing a small amount of hydrogen chloride to prevent reduction of the chloride to metal. The resulting chloride was grayish-white and extremely hygroscopic. The material was transferred from the reaction flask to the calorimeter out of contact with air; 111.8 g. of this sample was used in the specific heat measurements.

The Specific Heats

A number of investigators[4] have made specific heat measurements on chromium metal. With the exception of those of Simon and Ruhemann, these determinations are mean specific heats. The various values obtained by these investigators on chromium are shown in Fig. 1.

Russell[5] has made measurements on the specific heat of chromic oxide ranging from 137 to 299°K. These values are also shown in Fig. 1.

Trapeznikowa, Schubnikow and Miljutin[6] have recently measured the specific heat of chromic chloride from 12 to 130°K. Their results are definitely higher than those of the present work.

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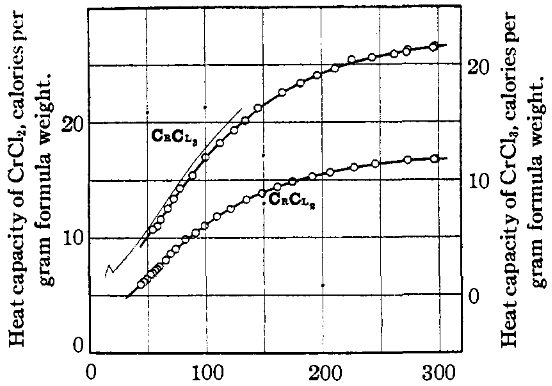
[3] Anderson, This Journal, **52**, 2296, 2712 (1930); **54**, 107 (1932); **55**, 3621 (1933).

[4] Dewar, *Proc. Roy. Soc.* (London), **A89**, 158 (1913); Richards and Jackson, *Z. physik. Chem.*, **70**, 414 (1910); Nordmeyer and Bernoulli, *Verhand. deut. physik. Ges.*, **9**, 175 (1907); Simon and Ruhemann, *Z. physik. Chem.*, **129**, 321 (1927).

[5] Russell, *Physik. Z.*, **13**, 59 (1912).

[6] Trapeznikowa, Schubnikow and Miljutin, *Phys. Z. Sowjetunion*, **9**, 237 (1936).

Over the range of 56 to 112°K. they average 0.82 cal./deg. higher. These values are represented graphically in Fig. 2. From the description of their apparatus it appears that their measurements have been sufficiently accurate and their temperature scale should not be in error. However, the sample they used might have contained water, as the apparently insoluble chromic chloride is capable of absorbing up to 3% water in sixty minutes of contact with laboratory air as shown by Crespi.[7] It appears probable, since the difference between these two curves is constant over the range of 56 to 112°K., that some systematic error is the cause of the discrepancy.



-o-, Anderson; —— $CrCl_3$, Trapeznikowa, Schubnikow and Miljutin.

Fig. 2.—The heat capacities of chromous chloride and chromic chloride, in calories per gram formula weight.

No previous low temperature measurements have been reported on chromous chloride. The results obtained in this Laboratory on the heat capacities of chromium and chromic oxide expressed in gram calories (15°) per gram formula weight are shown graphically in Fig. 1 and the values for chromous and chromic chlorides are represented graphically in Fig. 2. The experimental determinations of the heat capacities for chromium are given in Table I, the values for chromic oxide up to about 270°K. are given in Table II, while Table III shows the values for the heat capacities from about 270° to 340°K. with the temperature rise (ΔT) of the determinations. This table is represented graphically in the upper figure in Fig. 3. The experimental values for the chromous and chromic chlorides are given in Tables IV and V. The calculations were made on the basis of Cr = 52.01, O = 16.00 and Cl = 35.457.

TABLE I

HEAT CAPACITY PER GRAM ATOMIC WEIGHT OF CHROMIUM

T, °K.	C_p	T, °K.	C_p	T, °K.	C_p
56.1	0.634	81.6	1.646	162.9	4.180
59.5	.752	84.8	1.776	181.6	4.508
61.1	.811	93.2	2.114	200.1	4.816
63.5	.851	96.1	2.237	222.1	5.043
66.9	1.042	105.8	2.623	244.1	5.244
68.0	1.087	123.1	3.027	274.0	5.442
72.4	1.256	141.6	3.715	281.5	5.479
74.2	1.357			291.1	5.542

After calculating and plotting the heat capacity curve for chromic oxide it was noted that the points above the ice point appeared to deviate from the smooth curve which was drawn through the lower points. Further measurements were made which showed this deviation was due to an anomaly. The peak of the curve appears at about 305°K. No measurements were made on the energy necessary to heat the chromic

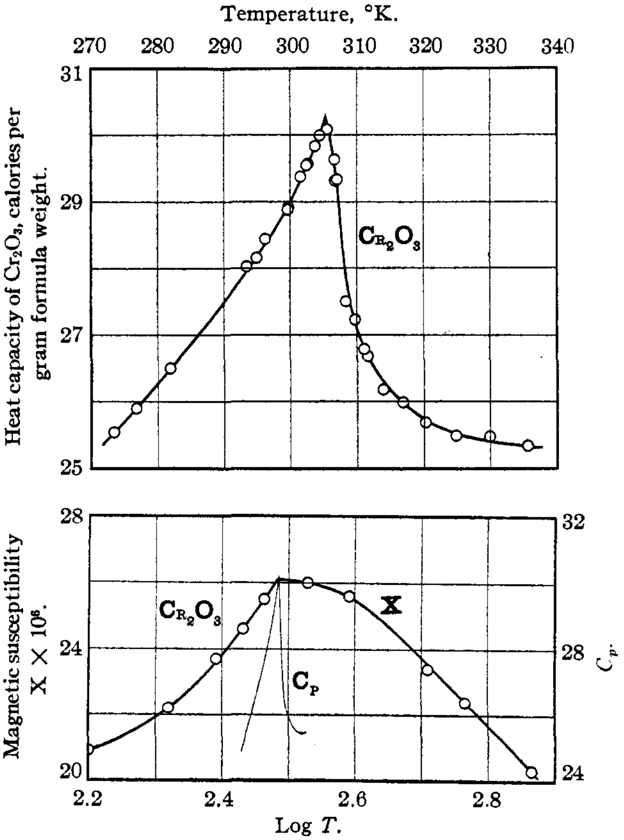


Fig. 3.—The heat capacity and magnetic susceptibility of chromic oxide.

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[7] Crespi, *Anales soc. españ. fís. quím.*, **26**, 152 (1928).

TABLE II

HEAT CAPACITY PER GRAM FORMULA WEIGHT OF CHROMIC OXIDE

T, °K.	C_p	*T*, °K.	C_p	*T*, °K.	C_p
56.3	1.504	117.2	7.951	187.4	16.62
62.5	1.958	122.2	8.625	192.1	17.20
69.4	2.577	127.4	9.312	199.6	17.98
78.5	3.417	132.1	9.903	203.6	18.43
83.0	3.866	136.4	10.45	207.9	18.94
88.1	4.410	141.7	11.16	212.6	19.43
93.0	4.962	147.0	11.83	217.9	19.94
98.1	5.562	157.4	13.07	223.7	20.61
98.6	5.629	162.2	13.69	229.0	21.14
102.9	6.169	168.5	14.45	234.9	21.75
105.9	6.587	172.7	14.93	239.7	22.15
107.4	6.729	176.6	15.41	247.6	23.00
111.1	7.131	182.6	16.09	260.4	24.20

TABLE III

HEAT CAPACITY PER GRAM FORMULA WEIGHT OF CHROMIC OXIDE

T, °K.	ΔT	C_p	*T*, °K.	ΔT	C_p
273.3	3.610	25.54	306.6	4.518	29.63
276.7	4.907	25.90	306.7	3.954	29.31
281.8	4.727	26.50	307.0	2.419	29.33
293.4	3.161	28.03	308.3	2.579	27.50
294.9	3.004	28.16	309.7	2.537	27.23
296.2	3.829	28.44	311.1	2.607	26.79
299.6	2.632	28.88	311.6	4.736	26.68
299.7	2.563	28.92	313.9	2.629	26.18
301.5	4.017	29.37	316.8	2.612	25.99
302.4	2.547	29.54	320.2	5.204	25.69
302.6	2.496	29.56	324.8	5.163	25.47
303.7	2.554	29.83	329.9	4.996	25.48
304.4	2.399	29.99	335.6	3.892	25.34
305.5	2.436	30.08			

TABLE IV

HEAT CAPACITY PER GRAM FORMULA WEIGHT OF CHROMOUS CHLORIDE

T, °K.	C_p	*T*, °K.	C_p	*T*, °K.	C_p
43.6	5.987	70.0	8.620	162.4	14.41
46.4	6.207	74.3	9.010	174.3	14.89
49.5	6.430	82.5	9.857	191.2	15.29
52.9	6.847	91.1	10.42	206.8	15.65
54.7	6.958	99.0	11.04	227.3	16.08
56.7	7.184	109.8	11.85	245.3	16.37
58.2	7.320	121.8	12.50	273.5	16.67
60.2	7.518	134.9	13.30	295.1	16.73
65.9	8.098	148.3	13.89	296.1	16.76

TABLE V

HEAT CAPACITY PER GRAM FORMULA WEIGHT OF CHROMIC CHLORIDE

T, °K.	C_p	*T*, °K.	C_p	*T*, °K.	C_p
54.4	5.705	112.0	13.21	211.2	19.64
58.4	6.020	123.3	14.31	225.6	20.42
61.2	6.597	132.8	15.14	243.0	20.60
67.4	7.521	144.9	16.24	261.9	20.90
72.4	8.398	165.9	17.58	272.6	21.04
77.7	9.300	181.6	18.40	273.5	21.24
88.4	10.41	195.7	19.06	295.4	21.46
99.8	11.99			296.9	21.59

oxide through this transition. Honda and Sone[8] measured the magnetic susceptibility of chromic oxide over a wide temperature range. A graphical representation of a portion of their results is shown in the lower figure of Fig. 3. The magnetic susceptibility is plotted against the logarithm of the absolute temperature. The temperature of the break in their curve approximates very closely the peak in the specific heat curve which is drawn in for comparison.

The calorimeter was cooled to below 300°K. five times, after which measurements were made both below and above the transition temperature. The curve was found to be perfectly reproducible.

Calculation of Entropies

The entropies were calculated by the usual graphical method of plotting the heat capacity against the logarithm of the temperature. In the case of the chromic chloride the results of Trapeznikowa, Schubnikow and Miljutin were used on the lower portion of the curve. Since there appeared to be a constant difference of 0.82 cal. over the range of 56 to 112°K. between their measurements and those presented in this report, it was assumed that this difference would exist below 56°K. Accordingly, their results were used on the lower end of the curve to attempt to obtain a more reliable value for the entropy than if they had not been used. If their data are extrapolated to room temperature from their highest point, assuming a 1.0 calorie difference between the two curves over this region, an entropy value of 31.2 units is obtained.

The experimental heat capacity curves coincided at low temperature with Debye functions having the following parameters (Θ): for chromium, 488; chromic oxide, 362; chromous chloride, 82; and chromic chloride, 100. Simon and Ruhemann gave a value for $\Theta = 486 \pm 8$, after correcting the 92% chromium they used for the impurities it contained. This is in excellent accord with the value of 488 obtained in this work.

Obviously, no combination of Debye and Einstein functions can be made to fit the experimental curve for the heat capacity of chromic chloride. Similarly, the function sum cannot be expected to fit the chromic oxide near room temperature as the transition begins to have an influence on the heat capacity even as low as

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(8) Honda and Sone, *Science Rep. Tôhoku Imp. Univ.*, **3**, 223 (1914).

200°. For this reason one may expect the function sum in this case to give a considerably lower entropy value than that obtained by the more accurate graphical method.

The following combinations were found to fit the experimental data on chromic oxide and chromous chloride to above 100°.

$$C_{Cr_2O_3} = D\left(\frac{362}{T}\right) + 2E\left(\frac{470}{T}\right) + 2E\left(\frac{780}{T}\right)$$

$$C_{CrCl_2} = D\left(\frac{82}{T}\right) + E\left(\frac{226}{T}\right) + E\left(\frac{444}{T}\right)$$

TABLE VI

ENTROPY DATA

	Cr	Cr_2O_3	$CrCl_3$
Extrap. (0–56.2), °K.	0.22	0.53	3.96
Graph (56.2–298.1), °K.	5.46	18.84	24.24
$S°_{298.1}$ graphical	5.68 ± 0.05	19.4 ± 0.2	28.2 ± 1.0
$S°_{298.1}$ calcd. from functions		18.0	
		$CrCl_2$	
Extrap. (0–44.7), °K.		5.05	
Graph (44.7–298.1), °K.		22.36	
$S°_{298.1}$ graphical		27.4 ± 0.7	
$S°_{298.1}$ calcd. from functions		27.6	

Table VI gives the results of the entropy calculations.

Related Thermal Data

Thermal data relating to these materials and the source are given in Table VII.

TABLE VII

THERMAL DATA

	$\Delta H_{298.1}$	$\Delta F°_{298.1}$	$S_{298.1}$ This report	$S_{298.1}$
Cr			5.68	
Cr_2O_3	−288,900[a]	−269,400[c]	19.4	
$CrCl_2$	− 92,750[b]	− 84,008[b]	27.4	29.7[b]
$CrCl_3$	−129,565[b]	−113,253	28.2	31.0[b], 31.2[d]

[a] Roth and Becker, *Z. physik. Chem.*, **A145**, 467 (1930).

[b] Doerner, U. S. Bureau of Mines (in press).

[c] Calculated from $\Delta H_{298.1}$ and entropies.

[d] Trapeznikowa, Schubnikow and Miljutin, *Physik. Z. Sowjetunion*, 9, 237 (1936).

Summary

The heat capacities of chromium, chromic oxide and chromous and chromic chlorides at low temperatures have been determined and their corresponding entropies calculated as 5.68, 19.4, 27.4 and 28.2, respectively.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NEW YORK UNIVERSITY]

The Ternary Systems $KClO_3$–K_2SO_4–H_2O and $NaClO_3$–Na_2SO_4–H_2O[1]

BY JOHN E. RICCI AND NICHOLAS S. YANICK

Introduction

This study is part of a systematic investigation of ternary systems involving sodium and potassium chlorates, a series of systems of which several examples are already to be found in the literature. No double salts containing sodium chlorate have yet been reported, the only ternary systems studied being $NaClO_3$–Na_2CO_3–H_2O, $NaClO_3$–$NaCl$–H_2O and $NaClO_3$–$KClO_3$–H_2O.[2] Similarly, in the systems involving potassium chlorate that have been investigated, no compounds are found (-H_2O + KCl, K_2CO_3, $NaClO_3$[2]; also +KBr and KI[3]); potassium chlorate however is found to form solid solutions in the systems $KClO_3$–KNO_3–H_2O and $KClO_3$–$TlClO_3$–H_2O.[2]

As for the sulfates in the present systems, while sodium sulfate is known to form both various double compounds and solid solutions with other sodium salts, potassium sulfate, in systems so far studied, forms no double salts with other potassium salts, but does form solid solutions with potassium chromate and potassium molybdate.[2]

In the present investigation potassium chlorate and potassium sulfate show no complex formation, while the sodium salt system forms one double salt, $NaClO_3 \cdot 3Na_2SO_4$. As for the other sodium halogenates, sodium sulfate forms similar compounds with sodium iodate, namely, $NaIO_3 \cdot 3Na_2SO_4$ and $NaIO_3 \cdot 4Na_2SO_4$,[4] while with sodium bromate it forms no definite compound but a solid solution.[5]

Experimental Methods

The experimental procedure was that usually described for similar investigations. Weighed complexes of known composition were brought to equilibrium by stirring in a

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(1) Presented at the Pittsburgh meeting of the American Chemical Society, September, 1936.

(2) "International Critical Tables," Vol. IV, 1928.

(3) Author's unpublished data.

(4) Foote and Vance, *Am. J. Sci.*, **19**, 203 (1930).

(5) Ricci, THIS JOURNAL, **57**, 805 (1935).