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HEAT CAPACITY AND THERMODYNAMIC PROPERTIES OF ALKALI METAL COMPOUNDS. IV. CESIUM AND RUBIDIUM CHROMATES

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ABSTRACT

The heat capacities of cesium and rubidium chromates have been measured by differential scanning calorimetry (DSC) in the temperature range 350–780 K. These values have been combined with measured and estimated values for the standard entropy and enthalpy of formation for Cs_2CrO_4 and Rb_2CrO_4 to obtain thermodynamic functions to 800 K.

INTRODUCTION

The alkali metals cesium and rubidium are known to play a significant role in the corrosion of the stainless-steel cladding of nuclear reactor fuel pins [1,2]. To define the thermochemical conditions under which such interactions will occur, high-temperature thermodynamic data on the alkali metal chromates Cs_2CrO_4 and Rb_2CrO_4 are needed. Lyon et al. [3] measured the heat capacity of Cs_2CrO_4 from 5 to 350 K, while Danielou et al. [4] and Frederickson et al. [5] used drop calorimetry to measure enthalpy increments and to derive heat capacities to 1500 K. For Rb_2CrO_4, on the other hand, there are no thermodynamic data at high temperatures.

This paper, which is the fourth in series on the thermodynamic properties of alkali metal compounds [6–8], presents the results of heat capacity measurements on Cs_2CrO_4 and Rb_2CrO_4.

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EXPERIMENTAL

Sample preparation and characterization

The salts were purchased from Cerac/Pure, Wisconsin. They were prepared for calorimetry by the methods described by Lyon et al. [3] and O'Hare and Boerio [9]. X-ray, chemical, and spectrographic analyses showed the samples to be better than 99.95% purity.

Calorimetric technique

The experimental techniques employed have been described previously [6]. The salts were compacted to form small pellets to fit into gastight aluminum pans. This was necessary to avoid any reaction between the sample material and the atmosphere and to render a high sample-to-pan mass ratio. The pellets were heated at 673 K for 1 h in order to anneal out stored energy from compaction, and, after cooling to room temperature, were hermetically sealed in the pans. The tightness of all filled pans was checked by heating them in a furnace at a temperature slightly higher than the maximum used in the DSC instrument. All handling of the samples was carried out in an argon-filled glove box.

The measurements were carried out in a Perkin-Elmer DSC II from 310 to 780 K with a heating rate of 10 K min^{-1} and a sensitivity of 5 mcal s^{-1} full-scale deflection. As reference material ground NBS-sapphire was sealed in a gastight pan—its mass was chosen to render a heat capacity similar to those of the samples.

The heat capacity was determined in the usual way by measuring an empty pan (baseline), the samples, and the reference material against an empty pan. The heat capacities were calculated from the expression

$$\left[C_p^0\right]_{\text{sample}} = \left[C_p^0\right]_{\text{sapphire}} \frac{[m]_{\text{sapphire}}[d]_{\text{sample}}}{[m]_{\text{sample}}[d]_{\text{sapphire}}} \tag{1}$$

where $[m]$ is the mass, $[d]$ is the recorded thermal effect, and $[C_p^0]$ is the heat capacity.

RESULTS AND DISCUSSION

Cesium chromate

The experimental heat capacities are listed in Table 1 for each temperature. The method of least squares was used to fit these values to the

TABLE 1

Molar heat capacity of Cs_2CrO_4 (molar mass of Cs_2CrO_4 = 381.804 g mol^{-1})

Temperature (K)	C_p^0 ($J\,K^{-1}\,mol^{-1}$)	Temperature (K)	C_p^0 ($J\,K^{-1}\,mol^{-1}$)
350	152.36	580	177.70
370	155.75	600	180.47
380	157.79	630	181.47
400	159.38	650	183.21
430	162.82	680	186.58
450	165.44	700	188.96
480	169.81	730	192.73
500	171.57	750	196.02
530	173.17	770	198.31
550	174.84		

following polynomial for the heat capacity from 350 to 800 K

$$C_p^0(J\,K^{-1}\,mol^{-1}) = 128.4593 + 9.002 \times 10^{-2}T - 8.126 \times 10^5 \times T^{-2} \quad (2)$$

These values are in excellent agreement with the recent data of Frederickson et al. [5], as shown in Fig. 1. Equation (2) was combined with the low-temperature data of Lyon et al. [3] to obtain the thermodynamic properties of Cs_2CrO_4. These values are listed in Table 2 at selected temperatures. The thermodynamic properties of cesium, oxygen, and chromium used in the present calculations were taken from published data [10–12].

Rubidium chromate

The experimental values for the heat capacity are listed in Table 3. These values were fitted to a polynomial by the method of least squares to obtain

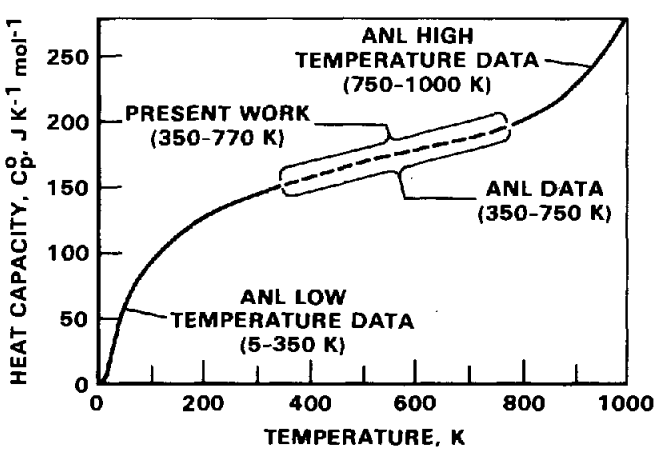

Fig. 1. Heat capacity of Cs_2CrO_4 as a function of temperature. ANL data are from Frederickson et al. [5].

TABLE 2

Thermodynamic properties of cesium chromate to 800 K

T (K)	C_p^0 (J K^{-1} mol^{-1})	$S^0(T)$ (J K^{-1} mol^{-1})	$H^0(T)-H^0(298)$ (kJ mol^{-1})	$-[G^0(T)-H^0(298)]/T$ (J K^{-1} mol^{-1})	$-\Delta H_f^0$ (kJ mol^{-1})	$-\Delta G_f^0$ (kJ mol^{-1})
298.15	146.06	228.59	0	228.59	1430.01	1318.02
300	146.44	229.49	0.27	228.59	1430.01	1317.45
350	153.33	252.60	7.77	230.40	1429.88	1298.89
400	159.39	273.48	15.59	234.51	1430.02	1279.95
450	164.96	292.58	23.70	239.91	1429.99	1261.64
500	170.22	310.23	32.08	246.07	1429.58	1242.45
550	175.28	326.69	40.72	252.65	1429.19	1224.07
600	180.21	342.16	49.61	259.48	1428.59	1205.11
650	185.05	356.77	58.74	266.40	1427.90	1186.79
700	189.81	370.66	68.11	273.36	1426.68	1167.67
750	194.53	383.92	77.72	280.29	1425.96	1149.76
800	199.21	396.62	87.56	287.17	1423.72	1130.13

TABLE 3

Molar heat capacity of Rb_2CrO_4 (molar mass of Rb_2CrO_4 = 286.928 g mol^{-1})

Temperature (K)	C_p^0 ($J\,K^{-1}\,mol^{-1}$)	Temperature (K)	C_p^0 ($J\,K^{-1}\,mol^{-1}$)
350	150.06	600	178.88
380	154.87	610	180.08
400	156.07	640	182.48
410	158.47	670	183.65
440	162.07	700	187.28
470	165.67	710	188.48
500	168.08	740	189.68
510	169.26	750	191.28
540	172.87	780	194.49
570	175.26		

the following expression for the heat capacity of Rb_2CrO_4 in the temperature range 350–800 K (also shown in Fig. 2)

$$C_p^0(J\,K^{-1}\,mol^{-1}) = 129.7861 + 8.502 \times 10^{-2}T - 1.0084 \times 10^6\,T^{-2} \quad (3)$$

Recently, O'Hare [13] measured the heat of solution of Rb_2CrO_4 using solution calorimetry from which he calculated the heat of formation to be -1411.0 ± 1.9 kJ mol^{-1}. In addition, the heat capacity and entropy at 298.15 K have been estimated as 143.79 and 217.60 J K^{-1} mol^{-1}, respectively, based on experimental values for other alkali chromates and sulfates.

Entropy and enthalpy values for Rb_2CrO_4 were calculated from appropriate integrals of eqn. (3). These values were combined with the other estimated values given above to obtain the thermal functions listed in Table 4. The thermodynamic properties of rubidium used in the calculations were taken from Barin et al. [11], while those for oxygen and chromium were obtained from refs. 10–12.

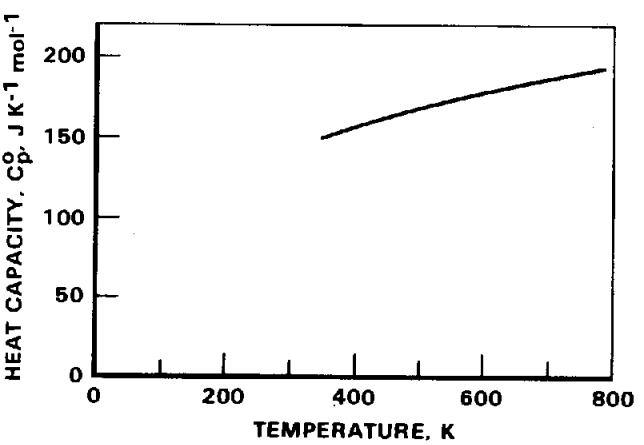

Fig. 2. Heat capacity of Rb_2CrO_4 as a function of temperature.

TABLE 4

Thermodynamic properties of rubidium chromate to 800 K

T (K)	C_p^0 (J K^{-1} mol^{-1})	$S^0(T)$ (J K^{-1} mol^{-1})	$H^0(T)-H^0(298)$ (kJ mol^{-1})	$-[G^0(T)-H^0(298)]/T$ (J K^{-1} mol^{-1})	$-\Delta H_f^0$ (kJ mol^{-1})	$-\Delta G_f^0$ (kJ mol^{-1})
298.15	143.79 [a]	217.60 [a]	0	217.60	1411.00 [b]	1300.86
300	144.09	218.49	0.27	217.59	1411.00	1300.17
350	151.31	241.26	7.66	219.37	1415.59	1286.28
400	157.49	261.88	15.38	223.43	1415.33	1262.02
450	163.07	280.75	23.40	228.75	1415.31	1243.57
500	168.26	298.21	31.68	234.85	1414.17	1223.96
550	173.21	314.48	40.22	241.35	1413.15	1205.04
600	178.00	329.76	49.00	248.09	1412.09	1186.15
650	182.66	344.19	58.02	254.93	1411.16	1167.74
700	187.24	357.89	67.26	261.80	1409.19	1148.74
750	191.76	370.96	76.74	268.64	1407.55	1130.40
800	196.23	383.48	86.44	275.43	1405.52	1111.81

[a] Estimated values.

[b] Unpublished value obtained by O'Hare [13] from solution calorimetry.

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