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Heat capacity and thermodynamic properties of alkali metal compounds.
Part 6. Cesium and rubidium dichromates

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Abstract

The heat capacities of cesium and rubidium dichromates have been measured by differential scanning calorimetry (DSC) in the temperature range 310–610 K. These values have been combined with measured and estimated values for the standard entropy and enthalpy of formation of $Cs_2Cr_2O_7$ and $Rb_2Cr_2O_7$ to obtain thermodynamic functions up to 600 K.

INTRODUCTION

The formation of cesium chromates has been implicated in chemical interactions of the fuel cladding in stainless steel-clad nuclear reactor fuel rods [1, 2]. In post-irradiation examination of nuclear reactor fuel rods, fission product cesium and rubidium have been observed at the inner surface of the cladding [2, 3]. Also, nuclear decay of the krypton isotope Kr-85 produces rubidium. The presence of impurity oxygen in the recovered gas, as well as adsorbed water vapor inside the container, may cause corrosion, stress corrosion and liquid metal embrittlement of the stainless steel krypton containers [4, 5].

In the Cs–Cr–O system, the compounds most likely to form will be Cs_2CrO_4, Cs_3CrO_4, Cs_4CrO_4 and, possibly, Cs_5CrO_4 and $Cs_2Cr_2O_7$ at the conditions of oxygen potential and temperature which exist in the fuel rods [2, 6]. Although the Rb–Cr–O system is not as well characterized as the Cs–Cr–O system, the formation of analogous compounds has been observed [7]. In fact, Rb_2CrO_4, Rb_4CrO_4, and $Rb_2Cr_2O_7$ are known to be relatively stable.

To define the thermochemical conditions under which such interactions will occur, high temperature thermodynamic data on the alkali metal chromates are needed. Cordfunke and Konings [8] have assessed the measured and estimated thermodynamic properties of the cesium chro-

TABLE 1

Measured molar heat capacity of $Cs_2Cr_2O_7$. Molar mass of $Cs_2Cr_2O_7 = 481.799\ g\ mol^{-1}$

Temperature/K	$C_p^\circ/(J\ K^{-1}\ mol^{-1})$	Temperature/K	$C_p^\circ/(J\ K^{-1}\ mol^{-1})$
310	243.13	500	287.46
350	256.23	530	292.84
380	263.90	550	295.17
400	269.01	580	300.67
430	275.33	600	302.03
450	278.11	610	303.47
480	284.77	620	305.15

mates. Although the heat capacity of solid $Cs_2Cr_2O_7$ has been measured in the range 5–350 K [9], there are no heat capacity measurements for the solid above 350 K. For solid $Rb_2Cr_2O_7$, however, there are no experimental thermodynamic data. This paper, which is the sixth in a series on the thermodynamic properties of alkali metal compounds, presents the results of heat capacity measurements on solid $Cs_2Cr_2O_7$ and $Rb_2Cr_2O_7$.

EXPERIMENTAL

Sample preparation and characterization

The dichromates were purchased from Electronic Space Products, Anaheim, California. The salts were purified by successive dissolution and recrystallization from distilled water. Each material was dried in vacuum at 400 K for 50 h and stored in a glove box until further use. Chemical and spectrographic analyses gave the Cs:Cr and the Rb:Cr ratios as 1.008 ± 0.007 and 1.007 ± 0.008 for $Cs_2Cr_2O_7$ and $Rb_2Cr_2O_7$, respectively.

Calorimetric technique

The experimental techniques employed have been described previously [10]. All handling of the samples was carried out in an argon-filled glove box. The measurements were carried out on a Perkin-Elmer DSC II instrument from 310 to 610 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 gas-tight pan; its mass was so chosen as to provide a heat capacity similar to those of the samples.

The heat capacity was determined in the usual way by measurements on an empty pan (baseline), the samples, and the reference material against an

TABLE 2

Thermodynamic properties of Cesium dichromate to 600 K

Temperature/ K	C_p° /(J K^{-1} mol^{-1})	$S^\circ(T)$ /(J K^{-1} mol^{-1})	$H^\circ(T) - H^\circ(298)$ /(kJ mol^{-1})	$-[G^\circ(T) - H^\circ(298)]/T$ /(J K^{-1} mol^{-1})	$-\Delta H_f^\circ$ /(kJ mol^{-1})	$-\Delta G_f^\circ$ /(kJ mol^{-1})
298.15	231.54	330.06	0	330.06	2091.12	1910.718
300	233.744	331.503	0.432	330.064	2091.084	1909.599
350	254.308	369.182	12.666	332.993	2093.866	1878.782
400	268.769	404.135	25.762	339.730	2091.817	1848.189
450	279.683	436.448	39.485	348.704	2089.301	1817.883
500	288.393	466.382	53.694	358.994	2086.432	1787.876
550	295.664	494.219	68.300	370.037	2083.284	1758.171
600	301.954	520.221	83.244	381.480	2079.906	1728.762

empty pan. The heat capacities were calculated from the expression

$$[C_p^\circ]_{\text{sample}} = [C_p^\circ]_{\text{sapphire}} \times \frac{[m]_{\text{sapphire}} \cdot [d]_{\text{sample}}}{[m]_{\text{sapphire}} \cdot [d]_{\text{sample}}} \qquad (1)$$

where $[m]$ = mass, $[d]$ = recorded thermal effect and $[C_p^\circ]$ = heat capacity.

RESULTS AND DISCUSSION

Cesium dichromate

The experimental heat capacity values are given in Table 1 for each temperature. The method of least squares was used to fit these values to the following polynomial for the heat capacity from 310–620 K

$$C_p^\circ/(\text{J K}^{-1}\text{ mol}^{-1}) = 254.702 + 9.832 \times 10^{-2}T - 4.04122 \times 106 \times T^{-2} \qquad (2)$$

Equation (2) was combined with the low-temperature data of Lyon et al. [9] and the experimental value of the standard enthalpy of formation [11] to

TABLE 3

Measured molar heat capacity of $Rb_2Cr_2O_7$. Molar mass of $Rb_2Cr_2O_7$ = 386.992 g mol^{-1}

Temperature/K	C_p°/(J K^{-1} mol^{-1})	Temperature/K	C_p°/(J K^{-1} mol^{-1})
310	234.80	500	281.07
350	248.37	530	287.63
380	256.41	550	290.96
400	260.14	580	294.11
430	268.78	600	299.02
450	273.91	610	301.35
480	278.56	620	301.94

TABLE 4

Thermodynamic properties of Rubidium dichromate to 600 K

Temperature/ K	C_p° /(J K^{-1} mol^{-1})	$S^\circ(T)$ /(J K^{-1} mol^{-1})	$H^\circ(T) - H^\circ(298)$ /(kJ mol^{-1})	$-[G^\circ(T) - H^\circ(298)]/T$ /(J K^{-1} mol^{-1})	$-\Delta H_f^\circ$ /(kJ mol^{-1})	$-\Delta G_f^\circ$ /(kJ mol^{-1})
298.15	227.45 [a]	306.60	0	306.60	2060.94 [a]	1878.529
300	228.712	308.012	0.422	306.604	2060.909	1877.397
350	247.365	344.748	12.350	309.463	2064.184	1846.365
400	261.377	378.732	25.083	316.025	2062.497	1815.357
450	272.690	410.191	38.443	324.762	2060.343	1784.589
500	282.328	439.432	52.324	334.784	2057.803	1754.082
550	290.871	466.749	66.658	345.553	2054.927	1723.847
600	298.668	492.397	81.399	356.732	2051.753	1693.887

[a] Estimated value.

obtain the thermodynamic properties of $Cs_2Cr_2O_7$ listed in Table 2 at selected temperatures up to the melting point. The thermodynamic properties of cesium, oxygen, and chromium used in the present calculations were taken from published data [8, 12–15].

Rubidium dichromate

Table 3 lists the experimental values for the heat capacity. These values were fitted to a polynomial by the method of least squares to obtain the following expression for the heat capacity of $Rb_2Cr_2O_7$ in the temperature range 310–620 K

$$C_p^\circ/(\mathrm{J\,K^{-1}\,mol^{-1}}) = 236.500 + 12.141 \times 10^{-2}T - 3.78034 \times 10^{6} \times T^{-2} \qquad (3)$$

As noted earlier, no heat capacity measurements are available for solid $Rb_2Cr_2O_7$. We have estimated the entropy and the standard enthalpy of formation at 298.15 K based on the experimental values for other alkali dichromates.

Entropy and enthalpy values for solid $Rb_2Cr_2O_7$ were calculated from appropriate integrals of eqn. (3), which was constrained by the estimated value for the entropy of $Rb_2Cr_2O_7$ at 298.15 K. These values were combined with the thermodynamic properties of rubidium, oxygen, and chromium from refs. 12–15 to obtain the thermochemical functions for $Rb_2Cr_2O_7$ listed in Table 4.

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