Available online at www.sciencedirect.com

ScienceDirect

J. Chem. Thermodynamics 39 (2007) 1474–1492

JCT

www.elsevier.com/locate/jct

Thermodynamics of Cr_2O_3, $FeCr_2O_4$, $ZnCr_2O_4$, and $CoCr_2O_4$

Stephen E. Ziemniak [a,*], Lawrence M. Anovitz [b], Roy A. Castelli [a], Wallace D. Porter [b]

[a] Lockheed Martin Corp., P.O. Box 1072, Schenectady, NY 12301-1072, United States
[b] Oak Ridge National Laboratory, P.O. Box 2008, Oak Ridge, TN 37831-6110, United States

Received 13 January 2007; received in revised form 1 March 2007; accepted 1 March 2007

Abstract

High-temperature heat capacity measurements were obtained for Cr_2O_3, $FeCr_2O_4$, $ZnCr_2O_4$, and $CoCr_2O_4$ using a differential scanning calorimeter. These data were combined with previously available, overlapping heat capacity data at temperatures up to 400 K and fitted to 5-parameter Maier–Kelley $C_p(T)$ equations. Expressions for molar entropy were then derived by suitable integration of the Maier–Kelley equations in combination with recent $S^\circ(298)$ evaluations. Finally, a database of high-temperature equilibrium measurements on the formation of these oxides was constructed and critically evaluated. Gibbs free energies of Cr_2O_3, $FeCr_2O_4$, and $CoCr_2O_4$ were referenced by averaging the most reliable results at reference temperatures of (1100, 1400, and 1373) K, respectively, while Gibbs free energies for $ZnCr_2O_4$ were referenced to the results of Jacob [K.T. Jacob, Thermochim. Acta 15 (1976) 79–87] at $T = 1100$ K. Thermodynamic extrapolations from the high-temperature reference points to $T = 298.15$ K by application of the heat capacity correlations gave $\Delta_f G^\circ(298) = (-1049.96, -1339.40, -1428.35, \text{and } -1326.75)\ \text{kJ} \cdot \text{mol}^{-1}$ for Cr_2O_3, $FeCr_2O_4$, $ZnCr_2O_4$, and $CoCr_2O_4$, respectively.

Keywords: Magnetic materials; Oxides; Differential scanning calorimetry; Specific heat; Thermodynamic properties

1. Introduction

The family of transition metal chromites, MCr_2O_4, where M = Fe, Ni and Co and Zn represent ideal constituents of the metal oxide ‘skins’ that form on iron and nickel base FeNiCr alloys exposed to hydrothermal environments typical of light water nuclear reactors. Presently available compilations of Gibbs free energies ($\Delta_f G^\circ$) for Cr_2O_3 and the family of MCr_2O_4 oxides are based on extrapolations of both high-temperature data ($\Delta G^\circ, \Delta H^\circ$) and low-temperature data (S°) to room temperature. Unfortunately, most of these extrapolations have been conducted in the absence of experimentally determined heat capacities, using estimates of uncertain validity.

Tabulated Gibbs free energies, for example, for Cr_2O_3, $FeCr_2O_4$, and $CoCr_2O_4$ in Barin [1] rely on estimated, super-ambient heat capacities for these oxide phases; no entry is provided for $ZnCr_2O_4$. Furthermore, the chromium(III) ion-based spinel oxides undergo magnetic transitions at very low temperatures, and additional phenomena associated with the presence of transition metal ions (*i.e.*, Schottky effect) may also contribute to heat capacity anomalies in this low-temperature region. Therefore, any low-temperature extrapolation of C_p to absolute zero based on application of the Debye equation ($C_p \propto T^3$) will be inappropriate and lead to significant underestimation of standard molar entropy, $S^\circ(298)$.

Recent results, obtained within the past decade, have considerably improved the state of knowledge regarding the thermodynamic properties of Cr_2O_3: emf studies (ΔG°, ΔH°; Holzheid and O’Neill [2]) and low-temperature C_p studies (down to $T = 1.5$ K; Klemme *et al.* [3]). New C_p measurements for $FeCr_2O_4$, which extended the temperature range down to 2.5 K [3], confirmed the presence of a magnetic anomaly (at $T = 36.5$ K) that had been predicted earlier based on neutron diffraction measurements [4]. Similarly, C_p measurements for $NiCr_2O_4$ [5], $ZnCr_2O_4$ [6], and $CoCr_2O_4$ [7] are now available in the temperature range 0.5 K to 400 K. This work has also revealed thermal anom-

---

[*] Corresponding author. Tel.: +1 518 395 6887; fax: +1 518 395 7298. *E-mail address:* ziemnia@kapl.gov (S.E. Ziemniak).

0021-9614/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jct.2007.03.001

alies, indicative of magnetic transitions in $NiCr_2O_4$ (at $T = 29$ K), $ZnCr_2O_4$ (at $T = 12.3$ K) and $CoCr_2O_4$ (at $T = 24$ K).

Due to these encouraging results, improved estimates for standard molar entropies are now available for Cr_2O_3, $FeCr_2O_4$, $ZnCr_2O_4$, and $CoCr_2O_4$. The present work was undertaken to eliminate the remaining source of uncertainty in extrapolating available super-ambient temperature reaction equilibria to $T = 298.15$ K by performing high-temperature heat capacity measurements for the above four oxides. Then, by combining the new results with a critical evaluation of the existing database of high-temperature reaction equilibria for formation of these oxides, recommended thermodynamic properties are determined for Cr_2O_3, $FeCr_2O_4$, $ZnCr_2O_4$, and $CoCr_2O_4$ at $T = 298.15$ K (S°, C_p°, $\Delta_f H^\circ$, and $\Delta_f G^\circ$).

2. High-temperature heat capacity measurements

2.1. Experimental methodology

The metal oxides examined were synthesized ceramically from high purity single metal oxide powders. Portions of these materials have also been used in solubility studies; see Wesolowski *et al.* [8] and references cited therein. Descriptions of oxide preparation and characterization are included in individual publications reporting their solubility behaviour (cf. Ziemniak *et al.* [9]). For completeness, a summary of their crystallographic features is given in table 1.

The super-ambient heat capacities of Cr_2O_3, $FeCr_2O_4$, $ZnCr_2O_4$, and $CoCr_2O_4$ were measured using a Netzsch differential scanning calorimeter (d.s.c.). In order to prevent oxidation of the materials during the measurement, an inert atmosphere was maintained in the calorimeter by first evacuating it, backfilling three times with Ar gas, and then performing the measurement under a slowing flowing Ar stream. The argon used was first deoxygenated using a high-temperature Zr oxygen getter to further reduce any potential for sample oxidation.

The same measurement procedure was used for all materials. Each sample was first ground by hand to a powder in an agate mortar. During test runs these powders were pressed into the Pt sample pan by hand. Initially, each sample was dried by heating to $T = 573$ K in an Ar stream in a thermal gravimeter for a few minutes. However, examination of several samples processed in this manner showed that no weight changes occurred during this time. As this implied that the amount of water adsorbed onto the powder was too small to affect the C_p results this procedure was discontinued.

TABLE 1
Crystallographic features of the metal oxides tested

Oxide	Crystal symmetry	Lattice parameter/nm
Cr_2O_3	Rhombohedral	$a_o = 0.49589(3)$ $c_o = 1.35930(9)$
$FeCr_2O_4$	Cubic	$a_o = 0.83780(5)$
$ZnCr_2O_4$	Cubic	$a_o = 0.83276(1)$
$CoCr_2O_4$	Cubic	$a_o = 0.83320(1)$

Data were first obtained for each phase up to $T = 1323$ K using both heating and cooling cycles at a rate of $10\ K \cdot min^{-1}$ with 30 min isothermal holds at $T = (673, 973, \text{and } 1323)$ K. An empty Pt pan was used on the reference side, and this pan was not moved between cycles. Each measurement required five heating/cooling cycles. In the first, the empty sample pan was run to serve as a standard. In the second, third and fifth, a sapphire disc was run to serve as a standard. The repetition of this measurement was performed in order to obtain an estimate of the repeatability of the measurement. Initially, this was done without running the sample multiple times, which it was thought, might adversely affect its composition or structure. Later tests, however, showed that these materials were stable under the measurement conditions and sample repetitions were also performed.

Once the first set of runs was completed, a second set was initiated to obtain C_p data at higher temperatures. These were expected to be more difficult, as the d.s.c. is less stable above $T = 1273$ K, and thus were run separately. Again, both heating and cooling cycles were used, with the sample heated at $10\ K \cdot min^{-1}$, and isothermal holds imposed at $T = (1323, 1673, \text{and } 1873)$ K. As the temperature range from room temperature to 1323 K had to again be traversed for these measurements, additional repetitions of the measurements below $T = 1323$ K were performed to further refine the experimental statistics. Data above $T = 1323$ K were not obtained for $ZnCr_2O_4$, as the temperatures of the available experiments constraining its Gibbs free energy do not exceed $T = 1273$ K.

2.2. Data pre-processing

The aforementioned experiments provided a number of repetitive measurements of C_p for each material. To process these data, the results of each run were first calculated using each of three measurements with the sapphire standard. The results of the heating and cooling cycles for each run were then averaged, and the results compared. An example of this comparison is shown in figure 1, which shows the raw data for Cr_2O_3. In all cases, results from sapphire 3, which was run after the sample itself, were somewhat different from the remainder. This was probably caused by deformation of the sample pan during sample removal, and the sapphire 3 calculations were therefore not used for further calculations. The remaining results were again averaged, and the standard deviations of this average calculated as a function of temperature. The resultant curves were then compared to the low-temperature C_p data in the literature. Finally, the data were extrapolated by hand to $T = 2273$ K (2000 K for the chromites). This was done to place a high-temperature constraint on the fitted C_p curve, which tended to deviate from a reasonable extrapolation unless such a constraint was employed.

Prior to fitting it was necessary to “clean up” the data set by removing certain data points. This was done for several reasons. First, because heating is slower than normal