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THE THERMODYNAMIC PROPERTIES OF ALKALI METAL COMPOUNDS AT HIGH TEMPERATURES

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Abstract

A research program has been in progress to obtain reliable thermodynamic data on various binary and ternary alkali metal compounds in the temperature range of 300 to 1500 K. To date, heat capacity measurements have been made on cesium and rubidium chromates, dichromates, zirconates, molybdates, dimolybdates, and halides in the temperature range of 300 to 800 K. In addition, measurements are planned or are currently in progress on cesium and rubidium chalcogenides, aluminates, uranates, silicates, and several other lithium, sodium, and potassium compounds. The status of the research program is discussed.

Keywords: alkali metal compounds, high temperature, thermodynamic properties

Introduction

The alkali metals lithium, sodium, potassium, rubidium, and cesium, along with their compounds, are used extensively in a variety of industrial applications such as electrochemical energy storage (primary cells and storage batteries) and energy generation (fusion and fission reactors, space power plants using the Rankine cycle, solar energy, thermionic converters, and magnetohydrodynamic power generators). Also, cesium and rubidium are volatile high-yield fission products in light water reactor (LWR) fuel rods. Since the alkali metals are also chemically very reactive, their thermochemistry is of fundamental and practical interest. To understand the reaction behaviour of these elements in complex chemical processes involving multicomponent systems most of which occur at high temperatures, reliable high temperature thermodynamic data are needed for several binary and ternary alkali compounds. In particular, cesium and rubidium form a number of very stable compounds with the fuel and other fission products in reactor fuel rods. This suggests that the chemical activity of other volatile, aggressive fission products such as the halogens (iodine and bromine) and the chalcogens (tellurium and selenium) may well be determined by cesium and rubidium during irradiation. In addition, the long half lives of cesium and rubidium isotopes require that the reactions of these ele-

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ments be considered for subsequent long-term storage of irradiated fuel in a nuclear waste repository.

An experimental research program has been in progress to obtain reliable thermodynamic data on various binary and ternary alkali metal compounds in the temperature range of 300 to 1500 K. To date, heat capacity measurements have been made on cesium and rubidium chromates, dichromates, zirconates, molybdates, dimolybdates, and halides in the temperature range of 300 to 800 K. In addition, measurements are planned or are currently in progress on cesium and rubidium chalcogenides, aluminates, uranates, silicates, and several other lithium, sodium, and potassium compounds. The measured heat capacity data has been combined with published enthalpy and entropy values to obtain a complete set of thermal functions for several of these compounds to 800 K. In parallel with the experimental measurements, thermodynamic functions for several of these compounds have been estimated by a variety of methods.

Experimental

Materials and characterization

The following compounds are presently included in this program.

1. $Cs_2Mo_2O_7$, $Rb_2Mo_2O_7$
2. $Cs_2Cr_2O_7$, $Rb_2Cr_2O_7$
3. Cs_2ZrO_3, Rb_2ZrO_3
4. Rb_2Te, Cs_2Se, Rb_2Se
5. CsBr, RbI, RbBr
6. Rb_2UO_4, $Rb_2U_2O_7$
7. $CsAlO_2$, $RbAlO_2$, Cs_2SiO_3, Rb_2SiO_3

The compounds are either purchased from commercial sources and purified for calorimetry; or they are synthesized from high-purity starting materials. All air or moisture-sensitive materials are handled in an argon or helium-atmosphere glovebox in which the H_2O and O_2 levels are customarily below 2 ppm by volume. X-ray, chemical and spectroscopic analyses are used to determine the purity of the samples prior to calorimetric measurements.

Calorimetric techniques

Solution calorimetry is used to obtain standard enthalpies of formation. Heat capacity measurements are carried out in a differential scanning calorimeter (DSC) from 310–780 K, while enthalpy increments are determined from 750–

1500 K in a drop calorimeter system. To date, very few measurements have been made with the drop calorimeter.

Data presentation

Entropy and enthalpy values for each compound are calculated from appropriate integrals of the least squares polynomial fit of the measured heat capacities. These values are combined with published or measured data to obtain a complete set of thermodynamic properties at 50 degree intervals to 800 K. For each compound, the following functions are tabulated:

- Heat capacity, C_p° / J·mol^{-1}·K^{-1}
- Entropy, $S^\circ(T)$ / J·mol^{-1}·K^{-1}
- Enthalpy increments, $H^\circ(T)$–$H^\circ(298)$ / kJ·mol^{-1}
- Free energy function, $G^\circ(T)$–$H^\circ(298)/T$ / J·mol^{-1}·K^{-1}
- Enthalpy of formation, ΔH_f° / kJ·mol^{-1}
- Free energy of formation, ΔG_f° / kJ·mol^{-1}

Results

$Cs_2Mo_2O_7$ and $Rb_2Mo_2O_7$

Heat capacity measurements to 800 K for these compounds have been completed and the complete thermochemical properties are expected to be published shortly.

$Cs_2Cr_2O_7$ and $Rb_2Cr_2O_7$

Heat capacity measurements to 650 K on both solid dichromates have been completed. These data will be combined with published enthalpy and entropy values to obtain a complete set of thermal functions to the melting point. The heat capacity data for $Cs_2Cr_2O_7$(s) merge smoothly with the low temperature (5–350 K) data of Lyon *et al.* [1], as well as with the enthalpy increments of Venugopal *et al.* [2] in the liquid phase (662–826 K).

Cs_2ZrO_3

A method to estimate $\Delta H_f^\circ(298)$ values for alkali metal zirconates has been proposed as part of the present research program. The estimated values for the alkali zirconates are listed in Table 1 along with the experimental values for these compounds [3–9]. Except for Cs_2ZrO_3, the agreement is very good, espe-

cially if one considers the very large absolute values of the enthalpies of formation.

Table 1 Comparison of measured and estimated values for the standard enthalpies of formation of the alkali metal zirconates

Zirconate	$-\Delta H_f^\circ(298)$ / kJ·mol^{-1}		Reference
	Estimated	Measured	
Li_2ZrO_3	1768.91	1755.70	3
		1755.61	4
		1742.81	5
Na_2ZrO_3	1700.08	1686.30	6
		1667.80	7
		1654.90	8
K_2ZrO_3	1732.05	1699.18*	
Rb_2ZrO_3	1730.34	1698.37*	
Cs_2ZrO_3	1748.20	1584.80	9

*Our preliminary measured value

Rb_2ZrO_3

Heat capacity measurements have been made on Rb_2ZrO_3 in the present study. These values have been combined with published values for the standard enthalpy and entropy to obtain a complete set of thermodynamic functions for Rb_2ZrO_3 to 800 K. This data has been used to reanalyze the chemical interactions involved in LWR fuel rod cladding failure due to halogen stress corrosion cracking (SCC).

For fission-product rubidium, the principal chemical reactions that can lead to halogen SCC of the Zircaloy cladding are

$$2RbI(s) + Zr(s) + \frac{3}{2}O_2(g) = Rb_2ZrO_3(s) + 2I(g) \quad (1)$$

$$2RbBr(s) + Zr(s) + \frac{3}{2}O_2(g) = Rb_2ZrO_3(s) + 2Br(g) \quad (2)$$

The temperature of the cladding is approximately 650 K in the fuel-clad gap. Using the available thermodynamic data at 650 K for Rb_2ZrO_3, RbI, RbBr, Zr, I, and Br [10–12], the partial pressures of I and Br are calculated to be 10^{-5} and 10^{-7} MPa for reactions (1) and (2), respectively, for a typical oxygen potential of −420 kJ·mol^{-1}, greater than the 10^{-8} MPa minimum pressure required for

iodine SCC of Zircaloy [13]. This is a very important conclusion since it provides thermodynamic justification for halogen SCC of Zircaloy.

Rb_2Te, Cs_2Se and Rb_2Se

Heat capacity measurements have been started and are expected to be completed shortly.

CsBr

Heat capacity measurements on CsBr are expected to be completed in the near future. The data will be combined with the published enthalpy and entropy values to obtain a complete set of thermodynamic data to 800 K.

RbI and RbBr

Heat capacity measurements on these compounds have been completed and a complete set of thermochemical values to 800 K will be available in the near future.

Rb_2UO_4 and $Rb_2U_2O_7$

Except for a value for the standard enthalpy of formation of Rb_2UO_4 [14] and $RbUO_3$ [15], no thermodynamic data for any other Rb–U–O compounds have been reported. Heat capacity measurements for Rb_2UO_4 and $Rb_2U_2O_7$ are in progress.

$CsAlO_2$, Cs_2SiO_3, $RbAlO_2$ and Rb_2SiO_3

No heat capacity measurements have been reported for these compounds. Preparation of the compounds for calorimetry is completed and heat capacity measurements have been started.

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Zusammenfassung — Im Rahmen eines Forschungsprogrammes werden im Temperaturintervall 300 bis 1500 K zuverlässige thermodynamische Angaben verschiedener binärer und ternärer Alkalimetallverbindungen ermittelt. In vorliegendem Falle wurden Messungen der Wärmekapazität von Cäsium- und Rubidiumchromaten, -dichromaten, -zirkonaten, -molybdaten, -dimolybdaten und -halogeniden im Temperaturbereich 300 bis 800 K vorgenommen. Zusätzlich sind Messungen an Cäsium- und Rubidiumchalkogenaten, -aluminaten, -uranaten, -silikaten und an verschiedenen anderen Lithium-, Natrium- und Kaliumverbindungen geplant oder bereits im Gange. Der Stand des Forschungsprogrammes wird diskutiert.