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THE HEAT CAPACITIES OF SELECTED INORGANIC ALKALI METAL COMPOUNDS

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Abstract

The heat capacities of selected inorganic binary and ternary alkali metal compounds are determined using differential scanning calorimetry (DSC). As part of an ongoing research program at Battelle Memorial Institute since 1983, the heat capacities of cesium and rubidium chalcogenides, aluminates, silicates and uranates in the temperature range 310 to 800 K have been added to the series of compounds. The measured data is to be combined with the standard enthalpies of formation and low temperature heat capacities to obtain reliable thermodynamic data on the alkali metal compounds to high temperatures.

Keywords: alkali metal compounds, DSC, heat capacity, high temperature, thermodynamic data

Introduction

The alkali metals find numerous industrial applications in electrochemical energy storage (primary cells and storage batteries) and in energy generation (fission and fusion reactors, space power plants using the Rankine cycle, solar energy, thermionic converters, and magnetohydrodynamics) [1].

Because the alkali metals are very reactive, it is the chemical reactions forming complex binary and ternary compounds that need to be considered in analyzing these multicomponent systems. For example, 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 [2, 3].

The addition of aluminum and silicon can getter fission product cesium and rubidium in nuclear reactor fuel by forming the respective aluminates and silicates. At the same time, the complex aluminosilicates are being considered for immobilizing the long-lived alkali fission products in the overall process of radioactive waste disposal [4].

Cesium and rubidium form a number of very stable compounds with the fuel and the other fission products in the strongly oxidizing atmosphere in nuclear reactor fuel rods [5, 6]. This suggests that the chemical activity of other volatile, aggressive fission products, such as the chalcogens and the halogens, may well be determined by cesium and rubidium during irradiation.

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The ternary compounds of cesium and rubidium with silicon and aluminum also serve as model substances to understand the structural properties and phase behavior of alkali glasses and ionic conductors [7, 8].

The reactions of the alkali metals occur at high temperatures. To understand these complex interactions, reliable high-temperature thermodynamic data are needed for relevant compounds in each system. Fortunately, the thermodynamic properties of the alkali metal systems are amenable to calculation by available estimation methods [9], which yield surprisingly reliable thermodynamic properties at high temperatures. Therefore, it is often only necessary to measure a key property, such as the heat capacity, of a representative compound in each system over a useful temperature range. To this end, an experimental research program has been under way for several years now to obtain reliable thermodynamic data on various binary and ternary alkali metal compounds to 1500 K. Heat capacity measurements to 800 K have been reported to date on cesium and rubidium chromates, dichromates, molybdates, dimolybdates and halides, as well as on rubidium zirconate [10–15]. Preliminary data on the heat capacity of Cs and Rb chalcogenides, aluminates and silicates have also been presented [4].

Heat capacity measurements have recently been completed on rubidium uranate and diuranate, potassium diuranate, rubidium tellurate and selenate, cesium selenate, rubidium and lithium metaborates, and rubidium ruthenate, as well as on cesium and potassium zirconates. Measurements on several other lithium, sodium, and potassium compounds are in progress. The measured specific heat data are being combined with available enthalpy and entropy values to obtain a complete set of thermodynamic properties for these compounds to 800 K.

Materials

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 glove box 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.

Sample preparation and calorimetric techniques

The salts are compacted to form small pellets to fit into gas-tight aluminum or gold pans. This is necessary to avoid any reaction between the sample material and the atmosphere, and to render a high sample-to-pan mass ratio. A special pellet press and pan crimping tool have been designed for this purpose [16].

The pellets are heated at 673 K for 1 h in order to anneal out stored energy from compaction and, after cooling to room temperature, are hermetically sealed by crimping the pans. The tightness of all filled pans is checked by heating them in a furnace at slightly higher than the maximum temperature used in the DSC instrument. All preparation of the samples is carried out in the glove box.

Heat capacity measurements are carried out in a DSC from 310 to 800 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 NIST-sapphire, sealed in a gas-tight pan is used; its mass is chosen to render a heat capacity similar to those of the samples.

The heat capacity is determined in the usual way by measuring an empty pan (baseline), the sample, and the reference material against an empty pan. The heat capacities are calculated from the expression:

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

where $[m]$ is the mass of the sample being measured, $[d]$ is the recorded thermal effect, and $[C_p^o]$ is the heat capacity in J $K^{-1}mol^{-1}$.

The method of least squares is used to fit the measured heat capacity values to obtain a polynomial expression for the heat capacity in the temperature range of the measurements.

Solution calorimetry is used to obtain standard enthalpies of formation, while enthalpy increments are determined from 750 to 1500 K in a drop calorimeter. To date, very few measurements have been made by solution calorimetry or with the drop calorimeter. Entropy, $S^o(T)$/J K^{-1} mol^{-1}, and enthalpy increments, $H^o(T)-H^o(298)$ /kJ mol^{-1}, for each compound are calculated from appropriate integrals of the least squares polynomial fit of the measured heat capacities.

In parallel with the experimental program, existing methods for estimating the thermodynamic properties of these compounds are being evaluated and new, improved methods are being explored. The agreement between the measured and estimated values has generally been excellent.

Results

Zirconates

A method to estimate standard enthalpy of formation values, $\Delta H_f^o(298)$, for alkali metal zirconates had been proposed previously as part of the present research program [17]. Unfortunately, this method consistently yielded estimated values which are 13 to 160 kJ mol^{-1} higher than the measured values [17]. The parameters in the estimation equations have now been revised to yield $\Delta H_f^o(298)$ values that agree with the measured values to within ±5 kJ mol^{-1} [1].

Cordfunke *et al.* [19] have reported the standard enthalpy of formation of Cs_2ZrO_3, –1584.80 kJ mol^{-1}, which is in serious disagreement with our preliminary measured value from solution calorimetry of –1712.93 kJ mol^{-1} [18]. The reason for this disagreement is not evident at this time. However, we are performing new measurements that may resolve the discrepancy and establish the more reliable value for the standard enthalpy of formation of Cs_2ZrO_3.

The complete thermodynamic properties of Rb_2ZrO_3 from 298 to 800 K have been reported [12]. With this new thermodynamic data on Rb_2ZrO_3, as well as the published data on Rb_2MoO_4 [10] and Rb_2UO_4 [20], we have reanalyzed the chemical interactions involved in light water reactor (LWR) fuel rod cladding failures due to halogen stress corrosion cracking (SCC) [6]. Only the following reactions

$$2RbI(s) + Zr(s) + 3/2O_2(g) = Rb_2ZrO_3(s) + 2I(g) \tag{2}$$

$$2RbBr(s) + Zr(s) + 3/2O_2(g) = Rb_2ZrO_3(s) + 2Br(g), \tag{3}$$

involving the formation of Rb_2ZrO_3, generate partial pressures of iodine (10^{-5} MPa) or bromine (10^{-7} MPa), greater than the minimum pressure (10^{-8} MPa) required for iodine SCC of zircaloy cladding in LWRs. We now have a thermodynamic justification for halogen SCC of zircaloy.

Chalcogenides

The thermodynamic properties of Cs_2Te have been reported [5]. The results of the measurements on the other binary chalcogenides can be represented by the following expressions for the heat capacity from 310 to 800 K:

$$Rb_2Te\text{: } (69.174\pm0.117)+(2.439\pm0.021)\times10^{-2}\times T \tag{4}$$

$$Rb_2Se\text{: } (66.801\pm0.498)+(2.585\pm0.068)\times10^{-2}\times T+(0.129\pm0.038)\times10^{5}\times T^{-2} \tag{5}$$

$$Cs_2Se\text{: } (67.975\pm0.498)+(2.649\pm0.064)\times10^{-2}\times T+(0.143\pm0.036)\times10^{5}\times T^{-2} \tag{6}$$

By combining these data with published and estimated values for the standard enthalpies of formation and the entropy, the complete thermochemical properties of these chalcogenides are expected to be published shortly.

Cordfunke *et al.* [5] have reported selected thermodynamic properties of Cs_2TeO_3, $Cs_2Te_2O_5$, $Cs_2Te_4O_9$, Cs_2TeO_4, and $Cs_2Te_4O_{12}$.

Uranates

The Cs-U-O system has been reviewed in detail [5, 21]. Except for a value for the standard enthalpy of formation of Rb_2UO_4 [20] and $RbUO_3$ [22], no thermodynamic data for any other Rb–U–O compounds have been reported.

Heat capacity measurements on $Rb_2U_2O_7$ have been completed. The data from 310–800 K can be represented by the following equation:

$$C_p^o(\text{J K}^{-1}\text{ mol}^{-1})=(221.673\pm2.219)+(6.684\pm0.281)\times10^{-2}\times T+$$
$$+(14.792\pm0.165)\times10^{5}\times T^{-2} \tag{7}$$

Silicates and aluminates

As mentioned earlier, cesium and rubidium silicates and aluminates can serve as model glasses to understand the structural properties and phase behavior of alkali glasses. To this end, heat capacity measurements have been completed on cesium and rubidium aluminates and silicates. The results can be represented by the following expressions for the heat capacity from 310 to 800 K:

$$Cs_2SiO_3\text{: } (133.638\pm0.774)+(4.050\pm0.099)\times10^{-2}\times T$$
$$-(2.016\pm0.056)\times10^{6}\times T^{-2} \tag{8}$$

$$Rb_2SiO_3\text{: } (126.479\pm0.322)+(4.759\pm0.042)\times10^{-2}\times T$$
$$-(1.786\pm0.023)\times10^{6}\times T^{-2} \tag{9}$$

$$CsAlO_2\text{: } (103.963\pm0.812)+(1.587\pm0.105)\times10^{-2}\times T$$
$$-(2.572\pm0.059)\times10^{6}\times T^{-2} \tag{10}$$

$$RbAlO_2\text{: } (89.974\pm0.686)+(2.953\pm0.088)\times10^{-2}\times T$$
$$-(1.908\pm0.050)\times10^{6}\times T^{-2} \tag{11}$$

Borates

Boron carbide is used in control rods in LWRs. Under the chemical conditions prevailing in a reactor accident, the formation of cesium and rubidium borates is possible. The other alkali borates are of interest in the chemical industry and for fusion reactor technology. The previously published heat capacity data on $CsBO_2$ [23, 24] were in serious disagreement with recent high temperature heat capacity measurements on high purity samples [5]. By analogy, the thermodynamic properties of the other alkali borates, published by Wagman *et al.* [23] and Chase *et al.* [24] based on older heat capacity measurements, could also be in error. We have recently measured the heat capacities of $LiBO_2$, $NaBO_2$, KBO_2 and $RbBO_2$. The preliminary analysis of the data suggests that the previously published values for the other alkali metaborates will also need to be revised.

Summary of compounds in the present research program

The thermodynamic properties of the following compounds in the present research program have either been reported in the temperature range 298 to 800 K, or these properties are in the process of publication. The literature citations are provided for readers with common interests.

1. $Cs_2Mo_2O_7$, $Rb_2Mo_2O_7$	[5, 10, 14]
2. $Cs_2Cr_2O_7$, $Rb_2Cr_2O_7$	[5, 11, 13)
3. Cs_2ZrO_3, Rb_2ZrO_3	[12, 17, 19, 20, this work]
4. Rb_2Te, Cs_2Se, Rb_2Se	[this work]
5. CsBr, RbI, RbBr	[5, 15]
6. Rb_2UO_4, $Rb_2U_2O_7$	[20, 22, this work]
7. $CsAlO_2$, $RbAlO_2$, Cs_2SiO_3, Rb_2SiO_3	[this work]
8. K_2ZrO_3 and $K_2U_2O_7$	[in process]

9.	$RbBO_2$, $NaBO_2$ and $LiBO_2$	[in process]
10.	Rb_2SeO_3, Rb_2TeO_3, Cs_2SeO_3	[in process]
11.	Rb_2RuO_4	[in process]
12.	$CsAlSi_2O_6$	[in process]

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