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Note

HEAT CAPACITY AND THERMODYNAMIC PROPERTIES OF ALKALI METAL COMPOUNDS. V. RUBIDIUM ZIRCONATE

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Previous papers in this series have reported measurements on the high-temperature heat capacities of cesium and rubidium molybdates [1] and chromates [2], and estimated values for the thermodynamic properties of alkali metal zirconates [3] and chalcogenides [4]. This is part of a larger experimental program on high-temperature heat capacity measurements of alkali metal compounds. The results of these measurements have been combined with published standard entropies and enthalpies of formation to obtain thermodynamic properties of cesium and rubidium compounds to 800 K. These data can, in turn, be used to deduce the chemical thermodynamic conditions under which specific reactions of these compounds will occur.

In the case of the relatively abundant alkali fission products, cesium and rubidium, the presence of the respective zirconates, Cs_2ZrO_3 and Rb_2ZrO_3, in the fuel-clad gap in light water reactor (LWR) fuel rods has enormous implications for the halogen activity in the gap [3,5]. As shown previously [3], sufficiently large halogen activities can be generated in the presence of the alkali zirconates to cause failure of the zircaloy cladding by stress corrosion cracking (SCC). This conclusion was based on calculations using data at 298.15 K extrapolated to the zircaloy cladding temperature of 650 K in the fuel-clad gap. To make accurate predictions, however, thermodynamic data at 650 K are needed.

Except for lithium zirconate [6] and sodium zirconate [7], there are no experimental heat capacities available on any of the other alkali metal zirconates. For that matter, the existence of Cs_2ZrO_3 is still uncertain [3]. Rb_2ZrO_3, on the other hand, has been successfully prepared and characterized [8]. In the present work, differential scanning calorimetry (DSC) has been used to measure the heat capacities of Rb_2ZrO_3 in the temperature

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range 350–750 K. The measured values have been combined with other literature data to obtain thermodynamic functions for Rb_2ZrO_3 to 800 K. This paper, which is the fifth in the series on the thermodynamic properties of alkali metal compounds, presents the results for Rb_2ZrO_3.

EXPERIMENTAL

Sample preparation and characterization

The sample of Rb_2ZrO_3 for calorimetry was prepared and characterized according to the methods described by Hoppe and Seeger [8]. The X-ray diffraction pattern very closely matched that obtained by Hoppe and Seeger [8]. Chemical and spectrographic analyses gave the following values: Rb = 170.879 g mol^{-1}; Zr = 91.170 g mol^{-1}. Based on these results, the sample was judged to be better than 99.95% purity.

Calorimetric techniques

The experimental techniques employed in the present work have been described previously [1]. All operations involved in handling the sample were carried out in an argon-filled, dry glove box, since Rb_2ZrO_3 is hygroscopic.

The measurements were carried out in a Perkin-Elmer DSC II from 310 up 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

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

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

RESULTS AND DISCUSSION

The experimental values of the heat capacity for Rb_2ZrO_3 from 350 to 750 K are given in Table 1. These values can be represented by the following least-squares polynomial expression for the heat capacity

$$C_p^0 = 149.6024 + 6.4050 \times 10^{-2}T - 3.1243 \times 10^{6}T^{-2} \tag{2}$$

TABLE 1

Molar heat capacity of Rb_2ZrO_3 (molar mass of Rb_2ZrO_3 = 310.179 g mol^{-1})

Temp. (K)	C_p^0 (J K^{-1} mol^{-1})	Temp. (K)	C_p^0 (J K^{-1} mol^{-1})
350	146.78	550	176.63
380	152.10	580	177.73
400	157.94	600	179.09
420	158.63	620	181.69
450	161.06	650	182.08
480	166.36	680	184.29
500	170.27	700	186.36
520	171.17	720	187.66
		750	194.93

As noted earlier, there are no measured low-temperature C_p^0 data for Rb_2ZrO_3. The heat capacity at 298.15 K was estimated by addition of the appropriate C_p^0 values for the component oxides, Rb_2O (77.34 J K^{-1} mol^{-1}) and ZrO_2 (56.05 J K^{-1} mol^{-1}), taken from ref. 9. The estimated C_p^0 value for Rb_2ZrO_3 is listed in Table 2 along with estimated values for the other alkali zirconates. Table 2 also lists measured C_p^0 values for Li_2ZrO_3 and Na_2ZrO_3. As can be seen, there is excellent agreement between the estimated and measured heat capacities of Li_2ZrO_3 and Na_2ZrO_3. Hence, the estimated value for Rb_2ZrO_3 in Table 2 is considered reliable. This value was combined with eqn. (2) to obtain the heat capacities listed in Table 3 at selected temperatures in the range 298–800 K. The enthalpy increments and the entropies were derived from appropriate integrations of eqn. (2). The free energy function

$$\frac{G^0(T) - H^0(298)}{T} = \frac{H^0(T) - H^0(298)}{T} - S^0(T) \tag{3}$$

was also calculated. Finally, the standard enthalpy, ΔH_f^0, and the standard

TABLE 2

Comparison of measured and estimated values for the heat capacity of the alkali metal zirconates at 298.15 K

Compound	Heat capacity, C_p^0 (J K^{-1} mol^{-1})		
	Measured	Ref.	Estimated
Li_2ZrO_3	110.236	6,9	109.537
Na_2ZrO_3	125.880	7	125.089
K_2ZrO_3	–	–	139.905
Rb_2ZrO_3	–	–	133.394
Cs_2ZrO_3	–	–	132.051

TABLE 3

Thermodynamic properties of rubidium zirconate 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	133.39	183.31	0	183.31	1730.34	1635.91
300	134.10	184.14	0.25	183.31	1730.33	1635.32
350	146.52	205.80	7.28	185.00	1734.64	1622.64
400	155.70	225.99	14.85	188.87	1733.87	1602.55
450	162.99	244.76	22.82	194.05	1732.86	1586.51
500	169.13	262.26	31.13	200.01	1731.32	1570.14
550	174.50	278.64	39.72	206.42	1729.69	1554.31
600	179.35	294.03	48.57	213.08	1727.63	1538.28
650	183.84	308.57	57.65	219.88	1725.54	1522.78
700	188.06	322.35	66.95	226.71	1723.06	1507.10
750	192.09	335.46	76.45	233.52	1720.60	1491.95
800	195.96	347.98	86.15	240.29	1717.78	1476.64

Gibbs energy of formation, ΔG_f^0, were calculated for each temperature and are given in Table 3. The thermodynamic properties of rubidium, oxygen and zirconium used in the present calculations were taken from refs. 9 and 10, while those for Rb_2ZrO_3 were taken from ref. 3.

Application to LWR cladding failure

As noted earlier, the high-temperature thermodynamic properties of Rb_2ZrO_3 can be used to analyze the chemical interactions involved in LWR cladding failure due to halogen SCC.

For fission-product rubidium, the principal chemical reactions leading to halogen SCC of the zircaloy cladding are [3,5]

$$2RbI(s) + Zr(s) + 3/2O_2(g) = Rb_2ZrO_3(s) + 2I(g) \quad (4)$$

$$2RbBr(s) + Zr(s) + 3/2O_2(g) = Rb_2ZrO_3(s) + 2Br(g) \quad (5)$$

The temperature of the cladding is approximately 650 K in the fuel-clad gap. Using the available thermodynamic data at 650 K for RbI, RbBr, Zr, I, and Br from ref. 9 and for Rb_2ZrO_3 from the present work, the partial pressures of I and Br are calculated to be 10^{-5} and 10^{-7} MPa for reactions (4) and (5), 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 [11]. This is a very important conclusion since we now have a thermodynamic justification for halogen SCC of zircaloy.

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