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THERMODYNAMIC FUNCTIONS OF BARIUM AND STRONTIUM ZIRCONATES FROM CALORIMETRIC MEASUREMENTS

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ABSTRACT

Enthalpy increment measurements have been carried out on $BaZrO_3$ and $SrZrO_3$ in the temperature range 1030–1700 K using a high-temperature differential calorimeter. From the measured enthalpy increment values, other thermodynamic functions, such as heat capacity, entropy and free energy functions, of these compounds have been calculated. The free energies of formation of $BaZrO_3$ and the equilibrium barium partial pressures for the formation reactions have been computed and compared with literature data. The equilibrium strontium pressures for the formation reactions of $SrZrO_3$ have also been computed.

INTRODUCTION

The alkaline earth elements barium and strontium are produced with yields of 6.6 and 9.1%, respectively, during the fission of ^{235}U, and 5 and 3.7%, respectively, during the fission of ^{239}Pu. The possible chemical forms in which they can exist in the mixed oxide fast reactor fuel are: (1) in solid solution with the oxide fuel; (2) as a separate oxide phase; and (3) in chemical combination with other fission products. The important compounds to be considered are molybdates and zirconates. In order to predict whether these compounds can exist under the prevailing conditions of temperature and oxygen potential at different locations in the fuel, thermodynamic data of these compounds are necessary. However, only limited data are available from the literature [1–4] for the thermodynamic functions of these compounds, especially at high temperatures. In this paper, we report the enthalpy increment measurements for barium and strontium zirconates in the temperature range 1030–1700 K. Using these measured enthalpy increment values, other thermodynamic functions have been computed.

EXPERIMENTAL

Materials

The zirconates of barium and strontium used in the present work were prepared by pelletising and heating an intimate mixture of the appropriate

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alkaline earth carbonate and zirconium dioxide in air at 1373 K for 40 h. The X-ray diffraction patterns of the products were in very good agreement with those reported in the literature [5]. Some of the measurements on barium zirconate were also carried out using a sample (99% purity) supplied by CERAC/PURE Inc., U.S.A. The results of the measurements on the sample prepared in our laboratory and the commercial sample were in very good agreement.

Calorimeter

A high-temperature differential calorimeter (model HT-1500 from M/s. Setaram, France) was employed for the enthalpy increment measurements. It is based on the measurement of heat flow between a reference and a working crucible using a calorimetric detector. The detector is made up of 18 thermocouples connected in series to form two rings, each having junctions of the same type and supporting one crucible. A detector made of either Pt/Pt–10%Rh or Pt–30%Rh/Pt–6%Rh thermocouples is used, depending on the temperature of the experiment. Another thermocouple, kept near the working crucible, measures the temperature of the experiment. The two crucibles are suspended inside an alumina muffle tube of a graphite resistance furnace by means of an alumina support tube. They are positioned inside the constant-temperature zone of the graphite furnace whose temperature is controlled by a PID type temperature programmer–controller. The control accuracy is better than $\pm 0.5°C$. The gas flow control system of the calorimeter enables the use of two different gases in the graphite resistor zone and inside the alumina muffle tube of the furnace. Hence, measurements can be carried out in any gaseous environment desired.

Method of measurement

For the enthalpy increment measurement at a given temperature, the sample which is initially at ambient temperature is dropped into the working crucible maintained at the experimental temperature. The resultant output of the detector is amplified and fed simultaneously to an integrator and a recorder. The recorder gives the trace of the heat flow (Q) against time (t) curve. The area under this curve can be calculated using the printed output of the integrator and is proportional to the heat transfer between the sample and the working crucible. The proportionality constant is evaluated using measurements on an NBS-supplied heat capacity standard, α-alumina.

Procedure

In a typical experiment, five pairs of sample and a standard, each weighing about 100 mg, were dropped alternately into the working crucible maintained at the experimental temperature. From the relative values of heat flow measured in the case of standard and sample, and the known enthalpy increment data of the standard, the enthalpy increment, $H_T^0 - H_{298}^0$, of the sample was calculated. After the completion of the measurements over a certain temperature range, the $H_T^0 - H_{298}^0$ values at various temperatures were fitted to a polynomial in temperature of the form

$$H_T^0 - H_{298}^0 = AT + BT^2 + CT^{-1} + D$$

using Shomate's method [6]. Literature values [1] for C_p at 298 K and S_{298}^0 were used in this regression analysis. From the above fit, other thermodynamic functions, namely, C_p, S_T^0 and free energy functions were calculated over the temperature range studied.

RESULTS

$BaZrO_3$

The measurements covered a temperature range of 1030–1687 K. The enthalpy increment values are given in column 2 of Table 1. These were fitted to the following expression

$$H_T^0 - H_{298}^0(\text{cal mol}^{-1}) = 28.1456T + 1.074 \times 10^{-3}T^2 + 3.979 \times 10^5 T^{-1} - 9821.7 \ (298\text{–}1687 \text{ K})$$

The measured values and the values from the fit are in agreement within ±2% as is clear by comparing columns 2 and 3 of Table 1. These data were

TABLE 1

Thermodynamic functions of $BaZrO_3$

Temp. (K)	Measured $H_T^0 - H_{298}^0$ values (cal mol^{-1})	$H_T^0 - H_{298}^0$ from fit (cal mol^{-1})	Temp. (K)	C_p (cal K^{-1} mol^{-1})	S_T^0 (cal K^{-1} mol^{-1})	$-(G_T^0 - H_{298}^0/T)$ (cal K^{-1} mol^{-1})
1030	21282	20694	1000	29.90	63.33	43.53
1076	22127	22071	1100	30.18	66.19	45.47
1123	23263	23495	1200	30.45	68.83	47.30
1167	24807	24828	1300	30.70	71.28	49.06
1213	25599	26227	1400	30.95	73.56	50.73
1258	27545	27602	1500	31.19	75.71	52.32
1344	30015	30242	1600	31.43	77.73	53.85
1386	31944	31539	1700	31.66	79.64	55.31
1427	32194	32809				
1605	38533	38368				
1647	40480	39690				
1687	40753	40953				

TABLE 2

Thermodynamic functions of $SrZrO_3$

Temp. (K)	Measured $H_T^0 - H_{298}^0$ (cal mol^{-1})	$H_T^0 - H_{298}^0$ from fit (cal mol^{-1})	Temp. (K)	C_p (cal K^{-1} mol^{-1})	S_T^0 (cal K^{-1} mol^{-1})	$-(G_T^0 - H_{298}^0/T)$ (cal K^{-1} mol^{-1})
1030	22877	22146	1000	32.32	63.20	42.02
1076	23572	23640	1100	32.63	66.29	44.09
1123	24996	25174	1200	32.92	69.14	46.06
1168	25974	26648	1300	33.19	71.79	47.94
1212	27786	28095	1400	33.45	74.26	49.73
1258	29035	29614	1500	33.70	76.58	51.44
1288	31136	30939	1600	33.94	78.76	53.08
1342	33180	32409	1700	34.18	80.82	54.66
1386	33756	33869				
1469	37047	36651				
1563	38998	39822				
1613	41661	41518				
1652	43318	42822				
1694	44307	44277				

then used to compute heat capacity, entropy and free energy function values of $BaZrO_3$ at various temperatures. These are listed in columns 5, 6 and 7 of Table 1.

$SrZrO_3$

The measurements on strontium zirconate were carried out over the temperature range 1030–1694 K. The measured values are represented by the expression

$$H_T^0 - H_{298}^0(\text{cal mol}^{-1}) = 30.8135T + 1.0570 \times 10^{-3}T^2 + 5.9822 \times 10^5 T^{-1} - 11286.33 \ (298\text{–}1694 \text{ K})$$

These enthalpy increment values and the values of other derived functions are given in Table 2.

DISCUSSION

Prior to this study, no experimental determination of the high-temperature heat capacity or enthalpy increment of $BaZrO_3$ has been reported. Only the estimated values of Odoj and Hilpert [7] are available in the literature. The present values for enthalpy increment, heat capacity and entropy of $BaZrO_3$ are in good agreement with the estimated values of Odoj and Hilpert [7] within ±2%. For $SrZrO_3$, the only values available in the literature are those given by Barin and Knacke [4] who quote the compilation of Kubaschewski [8]. The present enthalpy increment values are about 3% higher than those of the above authors. The C_p and entropy values derived from the present data are within 0.6 and 2 cal K^{-1} mol^{-1}, respectively, of those reported in ref. 7 over the range 298–1700 K. The C_p values from the present study for $BaZrO_3$ and $SrZrO_3$ agree well with the low-temperature results of King and Weller [1].

Derived results

Free energies of formation

Levitskii et al. [2] reported the free energies and enthalpies of the following formation reactions from their EMF cell measurements

$$Ba(l) + Zr(s) + 3/2O_2(g) \rightleftharpoons BaZrO_3(s) \tag{1}$$

$$BaO(s) + ZrO_2(s) \rightleftharpoons BaZrO_3(s) \tag{2}$$

Using the free energy functions of $BaZrO_3$ from the present study and those of Ba(l), BaO(s), Zr(s), $O_2(g)$ and $ZrO_2(s)$ from the literature [4,9,10], we have calculated the change in free energy functions, namely, $\Delta(G_T^0 - H_{298}^0/T)$ for the above reactions. Then, substituting the ΔH_{298}^0 values of Levitskii et al. [2], the ΔG_T^0 values have been calculated. These values are given in Table 3. As Levitskii et al. [2] stated that the ΔH_{298}^0 data are in agreement with those of L'vova and Feodosev [3], their data are used in this computation. The calculated ΔG_T^0 values for reaction (1) at 1200 and 1300 K were -340.04 and -333.01 kcal mol^{-1}, respectively, which are in very good agreement with those (-341.88 and -335.09 kcal mol^{-1}, respectively) reported by Levitskii et al. [2]. Similarly, the ΔG_T^0 value at 1000 K calculated for reaction (2) (-21.887 kcal mol^{-1}) agrees well with that reported by Levitskii et al. [2] (-22.01 kcal mol^{-1}).

Equilibrium barium pressures

O'Hare et al. [11] computed the equilibrium barium partial pressures at

TABLE 3

Free energies of formation, ΔG_T^0 (kcal mol^{-1}), of $BaZrO_3$

Reaction	Present study	Levitskii et al. [2]
$BaO(s)+ZrO_2(s) \rightleftharpoons BaZrO_3(s)$		
at 1000 K	−21.887	−22.01
$Ba(l)+Zr(s)+3/2O_2(g) \rightleftharpoons BaZrO_3(s)$		
at 1200 K	−340.04	−341.88
at 1300 K	−333.01	−335.09

TABLE 4

Equilibrium partial pressures of barium (atm) at 1000 K

Reaction	Oxygen potential (kcal mol^{-1})			
	-100	-110	-120	-130
$Ba(g) + Zr(s) + 3/2O_2(g) \rightleftharpoons BaZrO_3(s)$				
Present data	4.557×10^{-50}	8.62×10^{-47}	1.64×10^{-43}	3.10×10^{-40}
O'Hare et al. [11]	1.48×10^{-49}	2.81×10^{-46}	5.33×10^{-43}	1.01×10^{-39}
O'Hare et al. [11] [a]	5.38×10^{-50}	1.02×10^{-46}	1.94×10^{-43}	3.69×10^{-40}
$Ba(g) + ZrO_2(s) + \frac{1}{2}O_2(g) \rightleftharpoons BaZrO_3(s)$				
Present data	1.57×10^{-24}	2.78×10^{-23}	3.45×10^{-22}	4.27×10^{-21}
O'Hare et al. [11]	4.83×10^{-24}	5.85×10^{-23}	7.23×10^{-22}	8.95×10^{-21}
O'Hare et al. [11] [a]	3.96×10^{-24}	4.91×10^{-23}	6.08×10^{-22}	7.53×10^{-21}

[a] Recalculated by ΔH^0 and ΔS^0 variation with temperature.

1000 K and at an oxygen potential of -100 kcal mol^{-1} for the following reactions

$$Ba(g) + Zr(s) + 3/2O_2(g) \rightleftharpoons BaZrO_3(s) \tag{3}$$

$$Ba(g) + ZrO_2(s) + \tfrac{1}{2}O_2(g) \rightleftharpoons BaZrO_3(s) \tag{4}$$

In computing these barium pressures, O'Hare et al. [11] used the ΔH^0_{298} and ΔS^0_{298} values of Levitskii et al. [2], assuming that these do not vary with temperature. We have calculated the barium partial pressures using the change in free energy functions, $\Delta(G^0_T - H^0_{298}/T)$, computed from the present data and the ΔH^0_{298} values of Levitskii et al. [2]. For the calculation of $\Delta(G^0_T - H^0_{298}/T)$, the free energy function of $BaZrO_3$ from the present data and the free energy functions of Ba(g), Zr(s), O_2(g) and ZrO_2(s) from the literature [4,9,10] were used. The present values are marginally lower than those of O'Hare et al. [11] (as shown in Table 4). These differences can be attributed to the assumption of O'Hare et al. [11] that ΔH^0 and ΔS^0 values of the above reactions do not vary with temperature above 298 K. This fact is substantiated by barium pressures obtained by recalculating O'Hare's results after taking into account the variation of ΔH^0 and ΔS^0 with temperature. These are also given in Table 4. In this computation, the C_p values of $BaZrO_3$ from the present study and those of Zr(s), ZrO_2(s) and O_2(g) from the literature [12] were employed. For the C_p value of Ba(g), the ideal gas value was assumed.

Equilibrium strontium pressures

Using the free energy function data of $SrZrO_3$ from the present study and the free energy functions of Sr(g), Zr(s) and O_2(g) from the literature [9,10], the change in the free energy function, namely $\Delta(G^0_T - H^0_{298}/T)$, at 1000 K for the following reaction has been computed

$$Sr(g) + Zr(s) + 3/2O_2(g) \rightleftharpoons SrZrO_3(s) \tag{5}$$

The ΔH^0_{298} value for the above reaction was calculated using $\Delta H^0_{f,298}$ for

TABLE 5

Equilibrium partial pressures of strontium (atm) at 1000 K

Reaction	Oxygen potential (kcal mol^{-1})			
	−100	−110	−120	−130
$Sr(g)+Zr(s)+3/2O_2(g) \rightleftharpoons SrZrO_3(s)$	8.73×10^{-56}	1.66×10^{-52}	3.15×10^{-49}	6.00×10^{-46}
$Sr(g)+ZrO_2(s)+\frac{1}{2}O_2(g) \rightleftharpoons SrZrO_3(s)$	6.59×10^{-31}	8.16×10^{-30}	1.01×10^{-28}	1.25×10^{-27}

$SrZrO_3$ from L'vova et al. [3] and $\Delta H^0_{sub,298}$ for Sr(s) from the literature [13]. Substituting this into the function $\Delta(G^0_{1000} - H^0_{298}/1000)$, ΔG^0_{1000} was obtained, from which the equilibrium strontium pressures for the above reaction at various oxygen potentials have been computed. These are given in Table 5. The free energy change at 1000 K for the following reaction

$$Sr(g) + ZrO_2(s) + \tfrac{1}{2}O_2(g) \rightleftharpoons SrZrO_3(s) \qquad (6)$$

was calculated using ΔG^0_{1000} for reaction (5) and $\Delta G^0_{f,1000}$ for ZrO_2 [12]. Using these free energy data, the equilibrium strontium pressures for various oxygen potentials were evaluated. These values are also given in Table 5. There is no other report of the equilibrium strontium pressures for these reactions (5 and 6).

CONCLUSION

This work provides the only experimental data for the thermodynamic functions of $BaZrO_3$ in the temperature range 1030–1700 K. The present data agree with the estimated thermodynamic functions of Odoj and Hilpert [7]. The agreement of the results derived for the free energies of formation of $BaZrO_3$ and the equilibrium barium pressures with the values reported in the literature shows the reliability of the present data. This paper also reports the equilibrium strontium pressures at 1000 K for the formation reactions of $SrZrO_3$.

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