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THERMODYNAMIC PROPERTIES OF CALCIUM ZIRCONATE ($CaZrO_3$)

R.R. BROWN and K.O. BENNINGTON

Albany Research Center, Bureau of Mines, U.S. Department of the Interior, Albany, Oregon (U.S.A.)

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ABSTRACT

Characterized synthetic $CaZrO_3$ was used by the Bureau of Mines to determine the standard enthalpy of formation ($\Delta Hf^0_{298} = -424.58 \pm 0.47$ kcal mol^{-1}; -1776.43 ± 1.97 kJ mol^{-1}) and the standard enthalpy of formation from the oxides (ΔH^0_{298} (from oxides) = -9.75 ± 0.11 kcal mol^{-1}; -40.78 ± 0.46 kJ mol^{-1}) at 298.15 K. These data compare with the reaction calorimetric values determined by L'vova) ($\Delta Hf^0_{298} = -422.3$ kcal mol^{-1}; -1766.90 kJ mol^{-1}) listed in NBSTN 270-6 by Parker. This compound, $CaZrO_3$, easily prepared and characterized, is potentially useful for a calorimetric standard. The reaction scheme for hydrofluoric acid solution calorimetry does not require a reaction step adding a liquid to the solvent.

INTRODUCTION

The thermodynamic properties of some of the alkaline-earth zirconates are of interest in ceramic and high-temperature refractories. There are other applications for metallic activities in thermocathodes and interaction of substances capable of thermal emission. Several studies have been made on the properties of $CaZrO_3$; King and Weller [1] determined the low-temperature heat capacities, Gvelesiani et al. [2] determined the high-temperature enthalpy, and L'vova and Feodos'ev [3] determined the heat of formation by reaction calorimetry in a calorimetric bomb in which the reaction was initiated by the combustion of a known quantity of lamp black. L'vova et al. calculated the standard enthalpy of formation, $\Delta Hf^0_{298} = -418.7$ kcal mol^{-1}, from their data using other values from the literature, notably $\Delta Hf^0_{298} = -259.5$ kcal mol^{-1} for ZrO_2, for the constituent elements and oxides. A value of $\Delta Hf^0_{298} = -422.3$ kcal mol^{-1} is listed by Parker [4] which was calculated from L'vova data but using the more recent determination of $\Delta Hf^0_{298} = -263.04$ kcal mol^{-1} [5] for the enthalpy of formation of ZrO_2.

The compound $CaZrO_3$ is unusual for use in hydrofluoric (HF) acid solution calorimetry in that there is no step in the reaction scheme involving

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a liquid. It therefore offers an opportunity to trace the differences or make some correlations between the results of measurements made by combustion calorimetry, molten-salt solution calorimetry, and HF solution calorimetry. Such correlation of data would provide a means of isolating an experimental error characteristic of a given calorimetry technique or individual calorimetric reaction step. A difficulty with the HF method for Ca compounds is the precipitation of CaF_2. This does detract from the ideality of $CaZrO_3$ as a comparative compound; however, the error effects may be minimized by very careful control of the stoichiometry.

MATERIALS

Acids

The acids were reagent-grade products that were used without treatment except for dilution with distilled water to the proper strength.

Calcium oxide

Reagent-grade $CaCO_3$ of very high purity was calcined overnight at 970°C to provide the calcium oxide (CaO) for each determination. A preweighed $CaCO_3$ sample was loaded into a cylindrically shaped platinum foil container. After calcination, the slightly sintered sample, cooled over CaO in a desiccator, could be easily transferred and sealed in the Teflon tape drop container. Separate tests indicated vapor adsorption by the undisturbed sample to be undetectable within the time of exposure of a few seconds.

Zirconium oxide

The ZrO_2 used was a high-purity product, obtained specifically for low hafnium content. Spectrographic analysis showed trace amounts of magnesium, iron, silicon, titanium, and hafnium. No corrections were made for impurities. This product was aged for 12 h at 1100°C. X-ray analysis proved it to be monoclinic, the pattern matching Powder Diffraction File (PDF) [6] Card 13-307.

Calcium zirconate

Calcium zirconate ($CaZrO_3$) was prepared by reacting in the solid state a mixture of high-purity $CaCO_3$ and ZrO_2. The CaO and ZrO_2 contents of the reactants were first determined by ignition at 1000°C, the ignited weights reflecting the per cent CaO and ZrO_2 content of the reactants. Precisely

measured stoichiometric amounts of −200 mesh $CaCO_3$ and ZrO_2 were thoroughly blended and compacted in a large platinum dish. The mixture was heated slowly to 500°C, then to 930°C over a period of 36 h to ensure the decomposition of the $CaCO_3$ and initial reaction with the ZrO_2. Monitoring the weight loss of the sintered product indicated that the stoichiometric $CaO:ZrO_2$ ratio was maintained. The sintered product was ground to −200 mesh and reheated at 930°C for 118 h, followed by two additional heating periods at 1200°C for 18 and 16 h, respectively. After each heating period, the sintered product was ground to −200 mesh. X-ray diffraction analysis indicated the product to be polycrystalline single-phase $CaZrO_3$. The diffraction pattern matched the pattern given on PDF card 9-364. Emission spectrographic analysis of the $CaZrO_3$ indicated total metallic impurities of approximately 0.06%, with Al, Fe, and Si at $< 0.02\%$ and Mg and Mn at $< 0.002\%$.

EXPERIMENTAL DETERMINATIONS

Enthalpies of solution at 298.15 K

The enthalpies of solution of calcium zirconate were determined by hydrofluoric acid solution calorimetry. The apparatus used was described by Torgeson and Sahama [7] with later modifications described by King [8]. Some more recent alterations are described by Bennington et al. [9].

The aqueous solution medium was 948.7 g of a mixture containing 20.0 wt% HF and 5.0 wt% HCl. The quantities of the reacting substances were calculated stoichiometrically with 0.300 g of ZrO_2 substituted in reaction (1) (Table 1).

Weighed amounts of the substances to be dissolved were placed in a paraffin-sealed Teflon-tape capsule and dropped at the appropriate time from room temperature into the calorimeter, which was operated at 73.7°C. Each measured enthalpy change resulted from a process of converting a pure substance at 25°C to a solution product at 73.7°C. Combination of the enthalpy measurements in accordance with reaction schemes resulted in the evaluation of an enthalpy of reaction at 25°C (298.15 K) involving compounds in their standard states. Separate measurements provided corrections for the enthalpy effects caused by the Teflon capsules and paraffin sealant. Electrical calibrations of the calorimeter were made over the temperature range of the measurements following each determination.

Throughout this report uncertainties were assigned to measured and derived enthalpy values as follows: (i) when several individual enthalpy values were measured for a reaction, the precision uncertainty was taken as $2\sqrt{[\Sigma d_i^2/n(n-1)]}$, where Σd_i^2 is the sum of the squares of the deviation from the mean value and n is the number of determinations; (ii) when the

TABLE 1

Reaction scheme for $CaZrO_3$ [a]

Reaction	ΔH (kcal)	Uncertainty (kcal)
(1) $ZrO_2(c) + 4HF(sol) \rightarrow ZrF_4(sol) + 2H_2O(sol)$	−37.606	±0.047
(2) $CaO(c) + 2HF(sol) \rightarrow CaF_2(p) + H_2O(sol)$	−55.492	±0.062
(3) $CaZrO_3(c) + 6HF(sol) \rightarrow CaF_2(p) + ZrF_4(sol) + 3H_2O(sol)$	−83.352	±0.079
$\Delta H_4 = \Delta H_1 + \Delta H_2 - \Delta H_3$		
(4) $ZrO_2(c) + CaO(c) \rightarrow CaZrO_3(c)$		
$\Delta H_4 = -9.746 \pm 0.111$ kcal mol^{-1}		
ΔH^0_{298} (from oxides) $= \Delta H_4 = -9.75 \pm 0.11$ kcal mol^{-1}		

[a] For reactions (1) through (3) introduced reactants are at 25°C and reaction products are at 73.7°C.

Note: symbols c, sol, and p in parentheses denote substances that are crystalline, in solution, or crystalline precipitate, respectively, in all reactions.

enthalpies of two or more reactions were added, the uncertainty was taken as the square root of the sum of the squares of the uncertainties for the individual reactions. These procedures followed the recommendations of Rossini and Deming [10].

All energy units are expressed in terms of the defined calorie (1 cal = 4.1840 J). All weighings were corrected to vacuum, and molecular weights are in accordance with the 1981 table of atomic weights [11]. Final values are rounded to 0.01 kcal. All calibrations are traceable to the National Bureau of Standards (NBS), and sample temperatures are based on the International Practical Temperature Scale of 1968 (IPTS-68) [12].

The reaction scheme for the solution calorimetric investigation is presented in Table 1. The reactions are written in an abbreviated form,

TABLE 2

Experimental enthalpies of solution (kcal mol^{-1})

ZrO_2 reaction (1)	CaO reaction (2)	$CaZrO_3$ reaction (3)
−37.673	−55.552	−83.179
−37.622	−55.503	−83.436
−37.542	−55.570	−83.298
−37.544	−55.498	−83.394
−37.508	−55.538	−83.391
−37.634	−55.327	−83.414
−37.635	−55.457	
−37.693		
−37.606	−55.492	−83.352
±0.047	±0.062	±0.079

adequate to show that stoichiometry was maintained in such a way as to permit cancellation of appropriate reactants and products. Also included are the mean measured enthalpy values and their precision uncertainties, taken from Table 2.

The final solution after conducting reactions (1) and (2) sequentially in the original charge of acid was identical to the solution obtained after conducting reaction (3) in another charge of acid. The enthalpy of solution values were substituted into the reaction scheme and combined according to

$$\Delta H_4 = \Delta H_1 + \Delta H_2 - \Delta H_3$$

to obtain the enthalpy change for reaction (4), the overall calorimetric reaction, which also represents the standard enthalpy of formation from the oxides,

$$\Delta H^0_{298} = -9.746 \pm 0.111 \text{ kcal mol}^{-1}$$

Standard enthalpy of formation

The calculation of the standard enthalpy of formation for calcium zirconate requires additional data from the literature. All of the necessary data for the elements and oxides are from Pankratz [13], as shown in Table 3.

The standard enthalpy of formation for calcium zirconate was derived from these reactions and enthalpies according to the scheme

$$\Delta H_7 = \Delta H_4 + \Delta H_5 + \Delta H_6$$

from which it follows that

$$Zr(c) + 1.5\ O_2(g) + Ca(c) \rightarrow CaZrO_3(c) \qquad (7)$$

for which $\Delta Hf^0_{298} = -424.58 \pm 0.47$ kcal mol^{-1}.

TABLE 3

Enthalpy of formation of $CaZrO_3$

Reaction	ΔHf^0_{298} (kcal mol^{-1})	Uncertainty (kcal)
(5) $Zr(c) + O_2(g) \rightarrow ZrO_2(c)$	−263.04	±0.4
(6) $Ca(c) + 0.5\ O_2(g) \rightarrow CaO(c)$	−151.79	±0.21
$\Delta H_7 = \Delta H_4 + \Delta H_5 + \Delta H_6$		
(7) $Zr(c) + 1.5\ O_2(g) + Ca(c) \rightarrow CaZrO_3(c)$		
$\Delta H_7 = -424.576 \pm 0.465$ kcal mol^{-1}		
$\Delta Hf^0_{298} = \Delta H_7 = -424.58 \pm 0.47$ kcal mol^{-1}		

Low-temperature thermal properties

Low-temperature thermal property data were taken directly from the measurements made and published by King and Weller [1].

High-temperature thermal properties

High-temperature relative enthalpies were measured over the range 298.15–1500 K by Gvelesiani [2] and have been adopted directly.

Thermodynamic properties of calcium zirconate

The experimentally determined thermal data for $CaZrO_3$, the enthalpy of formation, the low-temperature heat capacity, and the high-temperature thermal data may be combined with the additional necessary data for the constituent elements and oxides for the calculation of the enthalpies, Gibbs energies of formation, and other relevant properties as a function of temper-

TABLE 4

Standard formation data, reaction $Ca(c,l) + Zr(c) + 1.5\ O_2(g) = CaZrO_3(c)$

T (K)	ΔHf^0 (kcal mol^{-1})	ΔGf^0 (kcal mol^{-1})	Log Kf
298.15	−424.580	−404.053	296.175
300.00	−424.577	−403.924	294.255
400.00	−424.325	−397.073	216.948
500.00	−423.941	−390.303	170.599
600.00	−423.542	−383.611	139.728
700.00	−423.175	−376.991	117.700
720.00 [a]	−423.109	−375.670	114.030
720.00	−423.329	−375.667	114.029
800.00	−423.043	−370.388	101.184
900.00	−422.759	−363.807	88.343
1000.00	−422.622	−357.284	78.083
1100.00	−422.573	−350.750	69.687
1112.00 [b]	−422.575	−349.975	68.782
1112.00	−424.615	−349.969	68.781
1136.00 [c]	−424.527	−348.359	67.018
1136.00	−425.478	−348.359	67.018
1200.00	−425.152	−344.026	62.655
1300.00	−424.648	−337.288	56.703
1400.00	−424.150	−330.584	51.606
1500.00	−423.656	−323.922	47.195

[a] $\alpha-\beta$ transition of Ca.
[b] Melting point of Ca.
[c] $\alpha-\beta$ transition of Zr.

TABLE 5

Formation data from the oxides, reaction $CaO(c) + ZrO_2(c) = CaZrO_3(c)$

T (K)	ΔHr^0 (kcal mol^{-1})	ΔGr^0 (kcal mol^{-1})	log Kf
298.15	−9.750	−10.579	7.754
300.00	−9.750	−10.585	7.711
400.00	−9.686	−10.872	5.940
500.00	−9.611	−11.176	4.885
600.00	−9.546	−11.496	4.187
700.00	−9.494	−11.826	3.692
800.00	−9.457	−12.161	3.322
900.00	−9.433	−12.500	3.035
1000.00	−9.419	−12.842	2.807
1100.00	−9.412	−13.184	2.619
1200.00	−9.410	−13.528	2.464
1300.00	−9.407	−13.871	2.332
1400.00	−9.399	−14.215	2.219
1478.00 [a]	−9.387	−14.483	2.141
1478.00	−11.317	−14.482	2.141
1500.00	−11.314	−14.528	2.117

[a] $\alpha-\beta$ transition of ZrO_2.

ature. The thermodynamic properties for the formation of $CaZrO_3$ from the elements and oxides are presented in Tables 4 and 5, respectively. $CaZrO_3$ is shown to be stable throughout the range of measurements.

DISCUSSION

The enthalpy of formation of $CaZrO_3$ was previously determined by L'vova and Fecdos'ev [3] and also Korneev et al. [14] by combustion calorimetry techniques. These values were the only experimentally determined values found in the literature. When the reaction calorimetry value of L'vova is combined with the more recent values from the literature for the constituent elements and oxides, a final value is obtained ($\Delta Hf^0_{298} = -422.3$ kcal mol^{-1}) which is in excellent agreement with the HF solution calorimetry value of $\Delta Hf^0_{298} = -424.6 \pm 0.47$ kcal mol^{-1} reported here. Because this compound, $CaZrO_3$, is easily synthesized and characterized, it potentially can be used in molten salt solution calorimetry to derive the enthalpy of formation and therefore provide a direct comparison and correlation of three calorimetric techniques.

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