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The standard molar enthalpy of formation of Cs₂ZrO₃

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The enthalpy of Cs_2ZrO_3 has been derived from its enthalpy of solution in $HF \cdot 100H_2O$, as measured calorimetrically, in combination with auxiliary values. For the standard molar enthalpy of formation of Cs_2ZrO_3 the value $\Delta_f H^{\circ}_m(298.15 \text{ K}) = -(1584.8 \pm 1.9) \text{ kJ} \cdot \text{mol}^{-1}$ has been found.

1. Introduction

The fission products cesium and zirconium are relatively abundant. In order to predict whether cesium zirconate Cs_2ZrO_3 can be formed as a stable compound under the conditions of oxygen potential and temperature in a fuel pin, its thermodynamic properties are required. However, not only are these completely lacking, but even its existence has been questioned.⁽¹⁾ This paper describes the preparation of this compound and the determination of its enthalpy of formation.

2. Experimental

The best way to prepare $C_{s_2}ZrO_3$ is, in our experience, the direct reaction of $C_{s_2}O$ and ZrO_2 at about 875 K. By varying the ratio n(Cs)/n(Zr) between 0.5 and 3.0 it was evident that Cs_2ZrO_3 is the only compound in (cesium + zirconium + oxygen). Because Cs_2O and Cs_2ZrO_3 are both very sensitive to moisture and CO_2 the reactions had to be performed in carefully purified argon gas, and since Cs_2O is somewhat volatile and aggressive to most materials, the reactions had to be done in a silver container closed with a screw cap.

The preparative procedure was as follows: equal amounts of substance of metallic Cs and ZrO_2 were mixed in an argon-filled glove box. This mixture was placed in a silver boat in a reaction tube, and oxidized outside the box with dry CO_2 -purified air at 400 K. The mixture was then transferred into the box and brought into the silver container which was heated outside the box at about 875 K for 6 h. The reaction product was homogenized, and again heated at 875 K for 6 h. The reaction was then complete, and the resulting product had a weak violet colour. The X-ray pattern of Cs_2ZrO_3 (after correction with α -SiO₂ as an internal standard) could be

Compound	$M/(g \cdot mol^{-1})$	10 ² w(Cs)		$10^2 w(\mathbf{Zr})$	
		Obs.	Cale.	Obs.	Cale.
Cs_2ZrO_3-1 Cs_2ZrO_3-2	405.028		65.63	22.41 ± 0.14 22.94 ± 0.03	22.52
CsF	151.904	87.45 ± 0.06	87.49		DL:0D
ZrO_2	123.219	—		71.29 ± 0.10	74.00
Zr	91.22			—	

TABLE 1. Analytical results; molar mass M and mass fraction w

indexed with an orthorhombic unit cell, isomorphic with Rb_2ZrO_3 .⁽²⁾ with a = 1.1297(3) nm, b = 0.7730(2) nm, and c = 0.5944(1) nm.

Two different samples were prepared for the calorimetric experiments. The chemical analyses of these samples are given in table 1. The cesium content was determined gravimetrically with kalignost; zirconium was determined as ZrO_2 , after precipitation with ammonia, by heating it in oxygen at 1400 K. Zirconium metal (Hf free) was obtained from Highways, ingot 4N. Cesium fluoride (Cerac C 1170) was dried in argon at 675 K. ZrO_2 was prepared by heating zirconyl nitrate in air at 675 K; the resulting product was poorly crystalline and could be dissolved readily in hydrofluoric acid.

The enthalpies of solution were measured in a calorimeter which has been described previously, together with the calorimetric procedure and calibration method.⁽³⁾ Corrections to the temperature rise in the calorimeter were based on a complete calculation of the pre- and post-period according to Newton's cooling law.

3. Results

Details of the measurements are given in table 2, where *m* denotes the mass of the sample dissolved, ε the energy equivalent of the calorimeter, $\Delta\theta$ the temperature change, $\Delta_{sol}H_m$ the molar enthalpy of solution; θ is an arbitrary temperature.

The reaction scheme to derive $\Delta_{\rm f} H^{\circ}_{\rm m}({\rm Cs}_2 {\rm ZrO}_3)$ is given in table 3. For the enthalpy of solution of ${\rm Cs}_2 {\rm ZrO}_3$ in HF \cdot 100H₂O two different series of experiments were available, tables 2(a) and 2(b). According to the Zr-analysis sample 1 was almost pure and no corrections for impurities have been made. Sample 2 contained some ZrO₂, mass fraction 0.0083, for which the enthalpy of solution of Cs₂ZrO₃ was corrected using the enthalpy of solution of ZrO₂ given in table 2(e). The weighted mean of both determinations gave $\Delta_{\rm sol}H^{\circ}_{\rm m} = -(452.93\pm0.82)$ kJ \cdot mol⁻¹.

The enthalpy of solution of Zr metal in $HF \cdot 100H_2O$, table 2(d), had to be corrected for the evaporation of water during dissolution. If we assume that the hydrogen evolved will be saturated for 75 per cent, and take $p(H_2O) = 3.157$ kPa for $HF \cdot 100H_2O$ at 298.15 K,⁽⁴⁾ the enthalpy of evaporation is +2.06 kJ·mol⁻¹ for Zr dissolved.

The enthalpy of solution of Cs_2ZrO_3 had to be combined with the enthalpies of solution of Zr and CsF, tables 2(c) and 2(d), and with auxiliary values for the enthalpies of formation of CsF(s), H₂O(l), and HF in HF · 100H₂O. The last value

m(solute)/g	$\epsilon heta / J$	$\Delta heta / heta$	$\Delta_{\rm sol} H_{\rm m}/(\rm kJ\cdot \rm mol^{-1})$
(a) Cs_2ZrO_3-1		_	
0.13367	75.673	1.9760	-453.08
0.13302	76.592	1.9505	- 454.88
0.13420	75.427	1.9901	-453.04
			average: -453.67 ± 1.22
(b) Cs_2ZrO_3-2			corrected for 0.0083 mass fraction of ZrO ₂ :
0.13197	76.659	1.9179	-451.00
0.13732	76.008	2.0165	-451.85
0 13039	76.296	1.9136	- 453.31
0.13719	76.707	2.0019	453.14
			average: -452.33 ± 1.10
(c) CsF			
0.09946	75.896	0.2523	-29.25
0.10087	74.705	0.2600	- 29.25
0.10355	74.758	0.2650	-29.06
0.09974	73,793	0.2557	-28.74
0.09290	73.721	0.2395	- 28.87
			average: -29.03 ± 0.20
(d) Zr			
0.03149	76.376	2.9302	- 648.29
0.03152	77.755	2.8844	-649.06
0.03189	77.206	2.9438	-650.12
0.03058	73.903	2.9504	650.42
			average: -649.47 ± 0.98
			correction for evaporation: + 2.06
			-651.53 ± 0.98
(c) ZrO_2			corrected for 0.037 mass fraction of H_2O :
0.09734	76.987	1.4403	-145.76
0.09096	76.635	1.3503	145.57
			average: -145.67 ± 0.10

TABLE 2. Enthalpy of solution of mass m of a specified solute in 150 cm³ of HF · 100H₂O at 298.15 K

TABLE 3. Reaction scheme for the enthalpy of formation of Cs₂ZrO₃(s); (sln) refers to HF · 100H₂O. $\Delta H_8 = -\Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4 - \Delta H_5 + \Delta H_6 + \Delta H_7$

Reaction	$\Delta H_m/(k\mathbf{J}\cdot\mathbf{mol}^{-1})$	
1. $Cs_2ZrO_3(s) + 6HF(sln) = (2CsF + ZrF_4 + 3H_2O)(sln)$	-452.93 ± 0.82	
2. $2CsF(s) + (sln) = 2CsF(sln)$	-58.06 ± 0.40	
3. $2Cs(s) + F_2(g) = 2CsF(s)$	-1114.58 ± 1.34	
4. $\operatorname{Zr}(s) + 4\operatorname{HF}(sln) = \operatorname{ZrF}_4(sln) + 2\operatorname{H}_2(g)$	-651.53 ± 0.98	
5. $H_2(g) + F_2(g) + (sln) = 2HF(sln)$	-643.96 ± 0.084	
6. $3\tilde{H}_2(g) + \frac{3}{2}O_2(g) = 3H_2O(1)$	-857.49 ± 0.126	
7. $3H_2O(1) + (sin) = 3H_2O(sin)$	≈0	
8. $2Cs(s) + Zr(s) + \frac{3}{2}O_2(g) = Cs_2ZrO_3(s)$	-1584.77 ± 1.90	

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was the partial value that had been used before.⁽⁵⁾ For CsF(s) we adopted the value previously derived,⁽⁵⁾ $\Delta_f H_m^{\varsigma}(298.15 \text{ K}) = -(557.29 \pm 0.67) \text{ kJ} \cdot \text{mol}^{-1}$. We then obtained for $\Delta_f H_m^{\varsigma}(\text{Cs}_2\text{ZrO}_3, \text{s}, 298.15 \text{ K})$ the value $-(1584.8 \pm 1.9) \text{ kJ} \cdot \text{mol}^{-1}$.

4. Discussion

The standard enthalpy of formation of $Cs_2ZrO_3(s)$, as derived here, cannot be compared with experimental values previously measured. The only values available were based on estimations. Kohli⁽¹⁾ estimated the value $-1748 \text{ kJ} \cdot \text{mol}^{-1}$, whereas Lindemer *et al.*⁽⁶⁾ estimated the value $-1510 \text{ kJ} \cdot \text{mol}^{-1}$. The latter value is in fair agreement with the value derived in this paper.

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