O-94

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Sodium zirconium oxide: molar enthalpy of formation at 298.15 K and molar heat capacity from 5 to 1168 K

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The molar heat capacity of Na_2ZrO_3 was measured from 5 to 305 K by adiabatic calorimetry and from 438 to 1168 K by differential scanning calorimetry. The molar enthalpy of formation was determined by hydrofluoric-acid solution calorimetry. The molar enthalpy of formation at 298.15 K is $-(1686.3 \pm 2.0)$ kJ·mol^{-1}. The values at 298.15 K of $C^\circ_{p,m}$, $\{S^\circ_m(T) - S^\circ_m(0)\}$, and $-\{G^\circ_m(T) - H^\circ_m(0)\}/T$ are 125.88, 125.50, and 54.88 J·K^{-1}·mol^{-1}, respectively. These functions are also calculated from 5 to 1170 K.

1. Introduction

Part of the mission of the U.S. Bureau of Mines is to provide values of thermodynamic properties for minerals and related inorganic compounds. As part of this effort, the molar heat capacity of sodium zirconium oxide (Na_2ZrO_3) was measured from 5 to 305 K by adiabatic calorimetry and from 438 to 1168 K by differential scanning calorimetry (d.s.c.), and the molar enthalpy of formation was determined by hydrofluoric-acid solution calorimetry. No reports of measurements of this type on this compound were found in the literature.

2. Experimental

SAMPLE PREPARATION

Na_2ZrO_3 was synthesized in the solid state by following the method used by Grizik and Plyushchev.[1] Stoichiometric amounts of powdered Na_2CO_3 and ZrO_2, sufficient to yield 1 mol of Na_2ZrO_3, were thoroughly blended and ground in a mortar. The mixture was lightly compacted into a large platinum dish and slowly heated over a period of several days to 1393 K. The sample was then held at 1393 K for a total of 70 h. This heating period was interrupted several times so that the sample could be ground and to determine the completeness of reaction by monitoring the mass loss. X-ray powder-diffraction analysis showed the sample to be Na_2ZrO_3 with a trace of monoclinic ZrO_2. Conversion of the trace ZrO_2 to Na_2ZrO_3 was accomplished by reacting the sample with $NaNO_3$ at 1173 for 4 h.

Excess Na_2O not volatilized during heating was removed from the Na_2ZrO_3 by repeated washing with dimethyl sulfoxide. To ensure that the Na_2ZrO_3 was anhydrous, the sample was dried at 383 K and then heated to 973 K for 4 h.

All lines of the X-ray powder-diffraction pattern were indexed using Lang's[2] results which showed the Na_2ZrO_3 to be single-phase crystalline with a pseudo-orthorhombic structure. The diffraction pattern also closely agrees with the X-ray powder-photograph results of Grizik and Plyushchev[1] and the patterns given on Powder-Diffraction File[3] cards 8–242 and 21–1179. Emission spectrographic analysis indicated total metallic impurities to be less than 0.05 mass per cent. Gravimetric analysis showed the composition to be 33.42 mass per cent of Na_2O and 66.62 mass per cent of ZrO_2, which compare to the theoretical values of 33.47 and 66.53, mass per cent, respectively.

CALORIMETRIC TECHNIQUE

Heat capacities from 5 *to* 300 K. The heat capacity of Na_2ZrO_3 was measured with an adiabatic calorimeter. This apparatus and its operation and performance have been described previously by Beyer *et al.*[4] A sample of 60.5959 g was loaded into a 90 cm^3 gold-plated copper calorimeter. Before the calorimeter was sealed, it was evacuated and backfilled with 1.97×10^{-4} mol of He. The uncertainties of the heat-capacity values are ± 2 per cent from 5 to 15 K, ± 1 per cent from 15 to 50 K, ± 0.2 per cent from 50 to 200 K, and ± 0.1 per cent from 200 to 300 K.

Heat capacities from 438 *to* 1168 K. A d.s.c. (Model TA2000C) manufactured by Mettler Instrument Corporation† was used. This d.s.c. is a heat-flow type with a nominal temperature range of 298 to 1473 K and has a sensitivity of approximately 1.0 $\mu V \cdot mW^{-1}$. A 0.09263 g sample was weighed into a platinum crucible, and the d.s.c. was operated with an argon atmosphere. Both the full and empty crucible along with an Al_2O_3 reference sample, were scanned in the d.s.c. The d.s.c. was operated at a scan rate of 10 $K \cdot min^{-1}$ in 50 K steps from 413 to 1013 K. A scan rate of 2 $K \cdot min^{-1}$ in 10 K steps was used in the region 1125 to 1173 K. Measurements were not made above 1173 K because of the onset of decomposition, as indicated by a sample mass loss. In the non-isothermal transition region the d.s.c. was operated at a scan rate of 10 $K \cdot min^{-1}$ from 1013 to 1123 K. The results were analyzed according to the "enthalpy method", as described by Mraw and Naas.[5] The accuracy of the heat-capacity values was determined by measuring the heat capacity of MgO and comparing with accepted values from Pankratz.[6] The uncertainties are ± 3 per cent from 298 to 700 K and ± 1 per cent from 700 to 1473 K.

Enthalpy of solution at 346.85 K. An isoperibol calorimeter described by Bennington *et al.*,[7] by King,[8] and by Torgeson and Sahama[9] was used. The acid used was a 948.7 g mixture of 20.0 mass per cent of HF, 5.0 mass per cent of HCl, and 75.0 mass per cent of H_2O. The acids were reagent-grade and were not treated except for dilution to proper strength. The masses of reacting substances were chosen to be

† Reference to specific products does not imply endorsement by the Bureau of Mines.

stoichiometric with 0.3 g of ZrO_2. The samples were placed in paraffin-sealed Teflon-tape capsules. The samples, at 298.15 K, were dropped at the appropriate time into the calorimeter, which was operated at 346.85 K. Separate measurements were made to provide corrections for the heat capacities of the Teflon capsules and paraffin sealant. Electrical calibrations of the calorimeter were made following each enthalpy-of-solution measurement.

3. Results

The experimental heat capacities are listed in chronological order in tables 1 and 2. The experimental heat capacities were smoothed using a curve-fitting routine described by Justice.[10] Below 5 K, a $C_{p,m}/T$ against T^2 plot was used to extrapolate $C_{p,m}$ values to $T \rightarrow 0$. The low- and high-temperature heat capacities were also joined by the curve-fitting routine. Calculated values for $C^\circ_{p,m}$, $\{S^\circ_m(T)-S^\circ_m(0)\}$, $-\{G^\circ_m(T)-H^\circ_m(0)\}/T$, and $\{H^\circ_m(T)-H^\circ_m(0)\}$ are listed in table 3.

TABLE 1. Experimental molar heat capacities of Na_2ZrO_3 by adiabatic calorimetry

T/K	$C^\circ_{p,m}$/J·K^{-1}·mol^{-1}	T/K	$C^\circ_{p,m}$/J·K^{-1}·mol^{-1}	T/K	$C^\circ_{p,m}$/J·K^{-1}·mol^{-1}	T/K	$C^\circ_{p,m}$/J·K^{-1}·mol^{-1}
Series I		145.43	78.138	295.30	125.230	17.76	0.775
46.00	12.743	154.61	82.641	304.76	127.073	19.55	1.006
48.85	14.539	163.80	87.253	Series II		21.45	1.323
52.87	17.047	173.04	91.356	4.98	0.024	23.21	1.777
57.17	20.141	182.31	94.985	5.63	0.030	24.90	2.266
61.85	23.732	191.59	98.485	6.15	0.052	26.78	2.901
66.97	26.864	200.89	101.816	6.75	0.081	28.78	3.636
72.56	31.001	210.19	104.944	7.41	0.111	30.95	4.489
78.64	35.435	219.50	107.907	8.17	0.135	33.31	5.493
85.34	40.339	228.87	110.539	9.02	0.157	35.86	6.694
92.73	45.543	238.27	113.033	9.96	0.178	38.64	8.191
100.81	51.184	247.66	115.324	10.99	0.206	41.66	9.972
109.45	56.906	257.07	117.627	12.13	0.238	44.94	12.056
118.33	62.600	266.51	119.780	13.36	0.295	48.51	14.279
127.28	68.003	276.19	121.892	14.71	0.392		
136.32	73.288	285.86	123.572	16.18	0.525		

TABLE 2. Experimental molar heat capacities of Na_2ZrO_3 by d.s.c.

T/K	$C^\circ_{p,m}$/J·K^{-1}·mol^{-1}	T/K	$C^\circ_{p,m}$/J·K^{-1}·mol^{-1}	T/K	$C^\circ_{p,m}$/J·K^{-1}·mol^{-1}	T/K	$C^\circ_{p,m}$/J·K^{-1}·mol^{-1}
438	148.52	788	164.11	1073	171.51	1129	165.16
488	149.58	838	163.82	1081	207.16	1145	171.87
538	156.05	888	164.04	1089	197.96	1148	165.87
588	158.62	938	164.27	1097	179.10	1158	163.75
638	160.54	988	164.66	1105	166.87	1168	164.06
688	161.08	1057	171.64	1113	168.04		
738	160.54	1065	170.98	1121	159.52		

TABLE 3. Molar thermodynamic functions of Na_2ZrO_3 (p° = 101325 Pa)

T / K	$C^\circ_{p,m}$ / J·K^{-1}·mol^{-1}	$S^\circ_m(T)-S^\circ_m(0)$ / J·K^{-1}·mol^{-1}	$-\{G^\circ_m(T)-H^\circ_m(0)\}/T$ / J·K^{-1}·mol^{-1}	$H^\circ_m(T)-H^\circ_m(0)$ / kJ·mol^{-1}
5	0.016	0.003	0.001	0.000
10	0.185	0.069	0.015	0.001
15	0.422	0.173	0.049	0.002
20	1.082	0.376	0.103	0.005
25	2.282	0.735	0.190	0.014
30	4.070	1.301	0.325	0.029
35	6.344	2.094	0.519	0.055
40	9.006	3.111	0.777	0.093
45	11.996	4.341	1.103	0.146
50	15.264	5.772	1.496	0.214
60	22.163	9.167	2.483	0.401
70	29.236	13.108	3.713	0.658
80	36.459	17.483	5.157	0.986
90	43.612	22.192	6.786	1.387
100	50.580	27.149	8.572	1.858
110	57.277	32.287	10.494	2.397
120	63.646	37.546	12.528	3.002
130	69.652	42.880	14.657	3.669
140	75.280	48.250	16.865	4.394
150	80.527	53.625	19.137	5.173
160	85.402	58.980	21.460	6.003
170	89.921	64.295	23.823	6.880
180	94.104	69.554	26.218	7.801
190	97.977	74.747	28.636	8.761
200	101.564	79.865	31.070	9.759
210	104.888	84.902	33.514	10.792
220	107.974	89.854	35.962	11.856
230	110.842	94.717	38.411	12.950
240	113.510	99.492	40.857	14.072
250	115.996	104.176	43.297	15.220
260	118.314	108.772	45.727	16.392
270	120.479	113.278	48.146	17.586
273.15	121.131	114.679	48.905	17.966
280	122.504	117.696	50.551	18.801
290	124.407	122.029	52.941	20.035
298.15	125.881	125.497	54.877	21.055
300	126.208	126.277	55.315	21.289
325	131.174	136.579	61.173	24.507
350	135.574	146.464	66.914	27.843
375	139.462	155.953	72.536	31.281
400	142.886	165.066	78.036	34.812
425	145.892	173.820	83.415	38.422
450	148.525	182.235	88.673	42.103
475	150.822	190.329	93.811	45.846
500	152.820	198.117	98.833	49.642
550	156.054	212.841	108.537	57.368
600	158.461	226.528	117.806	65.233
650	160.238	239.286	126.665	73.203
700	161.542	251.211	135.140	81.249
750	162.499	262.390	143.255	89.352
800	163.207	272.902	151.033	97.495
850	163.739	282.813	158.496	105.669
900	164.146	292.184	165.665	113.867

TABLE 3—*continued*

T / K	$C^\circ_{p,m}$ / J·K^{-1}·mol^{-1}	$S^\circ_m(T)-S^\circ_m(0)$ / J·K^{-1}·mol^{-1}	$-\{G^\circ_m(T)-H^\circ_m(0)\}/T$ / J·K^{-1}·mol^{-1}	$H^\circ_m(T)-H^\circ_m(0)$ / kJ·mol^{-1}
950	164.464	301.067	172.560	122.083
1000	164.716	309.510	179.198	130.312
1025[a]	164.822	313.579	182.426	134.432
1110[a]	164.933	327.616	193.006	149.417
1125	164.903	329.829	194.816	151.890
1150	164.822	333.453	197.790	156.012
1170	164.732	336.294	200.134	159.308

[a] Non-isothermal transition from 1025 to 1110 K.

The experimental enthalpies of solution are listed in table 4. The experimental enthalpies in table 4 include the necessary heat-capacity corrections to change from 346.85 K, the final temperature of the reaction, to 298.15 K. Enthalpies of solution for reactions 1 to 3 were measured consecutively in the same charge of acid. Enthalpies of solution for reactions 4 and 5 were measured consecutively in a different charge of acid. These reactions and their mean enthalpies are listed in table 5.

TABLE 4. Molar enthalpies of solution $\Delta_{sln}H_m$ at 298.15 K

Reactant:	1. ZrO_2	2. H_2O	3. NaCl	4. $HCl\cdot 12.731H_2O$	5. Na_2ZrO_3
			$\Delta_{sln}H_m$/(kJ·mol^{-1})		
	−158.14	3.025	1.540	43.363	−359.03
	−159.01	3.025	1.540	43.250	−359.29
	−158.84	3.021	1.527	43.396	−359.49
	−158.37	3.021	1.536	43.396	−359.49
	−158.61	3.017	1.544	43.380	−359.28
	−157.03	3.017	1.531	43.325	−359.20
	−157.09				−359.03
Mean values:[a]	−158.16 ± 0.61	3.021 ± 0.003	1.536 ± 0.006	43.352 ± 0.056	−359.26 ± 0.19

[a] Uncertainties are twice the standard deviation of the mean.

TABLE 5. Reaction scheme for the overall calorimetric reaction:
$\Delta_6H_m = \Delta_1H_m + \Delta_2H_m + \Delta_3H_m - \Delta_4H_m - \Delta_5H_m$

Reaction	Δ_iH_m/(kJ·mol^{-1})
1. $ZrO_2(cr) + 4HF(sln) = ZrF_4(sln) + 2H_2O(sln)$	−158.16 ± 0.61
2. $26.462H_2O(l) = 26.462H_2O(sln)$	79.942 ± 0.079
3. $2NaCl(cr) + 2HF(sln) = 2NaF(sln) + 2Cl^-(sln) + 2H^+(sln)$	3.072 ± 0.012
4. $2(HCl\cdot 12.731H_2O)(sln) = 2H^+(sln) + 2Cl^-(sln) + 25.462H_2O(sln)$	86.704 ± 0.112
5. $Na_2ZrO_3(cr) + 6HF(sln) = 2NaF(sln) + ZrF_4(sln) + 3H_2O(sln)$	−359.26 ± 0.19
6. $ZrO_2(cr) + 2NaCl(cr) + 26.462H_2O(l) = Na_2ZrO_3(cr) + 2(HCl\cdot 12.731H_2O)(sln)$	197.41 ± 0.65

TABLE 6. Reaction scheme for the standard molar enthalpy of formation of Na_2ZrO_3(cr) at 298.15 K: $\Delta_6 H_m = \Delta_1 H_m + \Delta_2 H_m - \Delta_3 H_m + \Delta_4 H_m + \Delta_5 H_m$

Reaction	$\Delta_i H_m$/(kJ·mol^{-1})
1. $2Na(cr) + Cl_2(g) = 2NaCl(cr)$	-822.24 ± 0.67 [a]
2. $H_2(g) + \frac{1}{2}O_2(g) = H_2O(l)$	-285.83 ± 0.42 [b]
3. $H_2(g) + Cl_2(g) + 25.462H_2O(l) = 2HCl \cdot 12.731H_2O(sln)$	-324.85 ± 0.42 [c]
4. $Zr(c) + O_2(g) = ZrO_2(c)$	-1100.5 ± 1.7 [d]
5. $ZrO_2(cr) + 2NaCl(cr) + 26.462H_2O(l) = Na_2ZrO_3(cr) + 2HCl \cdot 12.731H_2O(sln)$	197.41 ± 0.65 [e]
6. $Zr(cr) + \frac{3}{2}O_2(g) + 2Na(cr) = Na_2ZrO_3(cr)$	-1686.3 ± 2.0

[a] Wagman *et al.*[11] [b] Wagman *et al.*[12] [c] Wagman *et al.*[13] [d] Wagman *et al.*[14] [e] This work.

TABLE 7. Thermodynamic quantities for the reaction: $2Na(cr \text{ or } l) + Zr(cr) + \frac{3}{2}O_2(g) = Na_2ZrO_3(cr)$ (p° = 101325 Pa)

T/K	$\Delta_r H_m^\circ$/kJ·mol^{-1}	$\Delta_r G_m^\circ$/kJ·mol^{-1}	$\log_{10} K^\circ$	T/K	$\Delta_r H_m^\circ$/kJ·mol^{-1}	$\Delta_r G_m^\circ$/kJ·mol^{-1}	$\log_{10} K^\circ$
298.15	−1686.30	−1589.71	278.51	900	−1681.05	−1391.75	80.77
300	−1686.29	−1589.10	276.68	1000	−1678.81	−1359.73	71.02
371 [a]	−1686.09	−1566.12	220.50	1025 [b]	−1678.28	−1351.76	68.89
371	−1691.30	−1566.13	220.50	1110 [b]	−1675.57	−1324.80	62.34
400	−1691.15	−1556.34	203.24	1125	−1675.29	−1320.06	61.29
500	−1689.90	−1522.76	159.08	1136 [c]	−1675.08	−1316.59	60.54
600	−1687.98	−1489.50	129.67	1136	−1679.06	−1316.59	60.54
700	−1685.73	−1456.61	108.69	1150	−1678.69	−1312.09	59.60
800	−1683.39	−1424.04	92.98	1170	−1678.21	−1305.71	58.29

[a] Melting temperature of Na.
[b] Transition temperatures of Na_2ZrO_3.
[c] Transition temperature of Zr(α) = Zr(β).

The molar enthalpy of formation of Na_2ZrO_3 was determined by combining the molar enthalpy of solution for reaction 6 in table 5 with the molar enthalpies of formation of each of the reactants. These reactions and the references used are listed in table 6. The standard molar enthalpy of formation: $\Delta_f H_m^\circ\{Na_2ZrO_3, cr, 298.15 K\}$, was calculated to be $-(1686.3 \pm 2.0)$ kJ·mol^{-1}. For the reaction:

$$Na_2O(cr) + ZrO_2(cr) = Na_2ZrO_3(cr), \quad (1)$$

the $\Delta H_m^\circ\{Na_2ZrO_3, cr, 298.15 K\}$ was calculated to be $-(171.0 \pm 1.1)$ kJ·mol^{-1}.

4. Discussion

No reports of low- or high-temperature heat-capacity measurements on Na_2ZrO_3 were found in the literature. The only reference to the molar enthalpy of formation found was an estimate given by Kohli,[15] who reported a value of -1700.08 kJ·mol^{-1}. A non-isothermal transition was found over the range 1025 to

1110 K. The molar enthalpy of transition $\{H_m^\circ(1110\ K) - H_m^\circ(1025\ K)\}$ was calculated to be 14.99 $kJ \cdot mol^{-1}$. For the reaction

$$2Na(cr, l) + Zr(cr) + \tfrac{3}{2}O_2(g) = Na_2ZrO_3(cr), \quad (2)$$

the values for $\Delta_r H_m^\circ$, $\Delta_r G_m^\circ$, and $\log_{10} K^\circ$ are given in table 7.

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