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Thermodynamic properties of $KAlO_2$

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The heat capacity of $KAlO_2$ has been measured from 5 to 303 K by adiabatic calorimetry. High-temperature enthalpies were determined up to 1197.8 K by copper-block drop calorimetry. A reversible transition was found at 810 K with an enthalpy of transition of 1295 J mol^{-1}. The values at 298.15 K of C_p°, $\{S^\circ(T)-S^\circ(0)\}$, and $-\{G^\circ(T)-H^\circ(0)\}/T$ are calculated as 76.12, 85.55, and 40.76 J K^{-1} mol^{-1}, respectively. These thermodynamic functions are also calculated from 5 to 1400 K.

1. Introduction

As part of a goal to advance mineral technology, to reduce energy use, and to abate pollution, the Bureau of Mines generates thermodynamic quantities on various minerals and metals. This study on potassium aluminate, $KAlO_2$, was undertaken to further this aim. Although of possible importance to the cement and ceramic industries, the current interest in potassium aluminate is its role in magnetohydrodynamic (MHD) power generation. Potassium, in the form of a seed material used to enhance the electrical conductivity of the high-temperature MHD generator plasma, reacts with alumina. Alumina is a major constituent of coal slag and a material of construction in MHD power generators. A better understanding of the potassium and alumina interaction will help with the problems of corrosion, seed material recycling, *etc.*

No similar experimental studies were found in the literature. Otsubo *et al.*(1) investigated d.t.a. and high-temperature X-ray diffraction and found a reversible transition at 808 K. Eliezer and Howard(2) reported a calculated phase diagram for (potassium oxide + aluminum oxide) for compositions from pure α-Al_2O_3 to pure $KAlO_2$.

2. Experimental

SAMPLE PREPARATION

Potassium aluminate was synthesized by reacting stoichiometric amounts of K_2O and Al_2O_3 in the form of K_2CO_3 and $Al(OH)_3$. The mixture was heated in platinum dishes in air at 1170 K for 4 h; 870 K for 64 h; 1185 K for 20.5 h; 1185 h for 5 h;

and 1185 K for 25 h. The mixture was cooled and thoroughly blended after each of the 1185 K heatings. All handling of the sample was done in an inert-atmosphere dry box. After the final heating, the mixture was transferred immediately while hot, to a quartz bowl in a vacuum desiccator. The $KAlO_2$ was then cooled under vacuum because it was very moisture sensitive. An additional heating for 2.5 h at 1075 K in a platinum capsule was done for the high-temperature enthalpy measurements.

X-ray powder diffraction analysis showed the sample as single-phase $KAlO_2$ with a unit cell parameter $a = (0.7700 \pm 0.0002)$ nm. Optical emission spectrographic analysis showed Na as the only impurity. The amount of Na was determined to be 0.05 mole per cent by atomic absorption. Chemical analysis showed Al_2O_3 as 52.09 mass per cent and K_2O as 47.87 mass per cent (Na impurity included) as compared with theoretical values of 51.98 and 48.02 mass per cent respectively.

CALORIMETRIC TECHNIQUE

From 5 *to* 303 K. The heat capacity of $KAlO_2$ was measured with an adiabatic calorimeter. A description of the apparatus and details of operation have been reported elsewhere by Stuve *et al.*(3) The calorimeter was made of gold-plated oxygen-free copper with an internal volume of approximately 90 cm^3. After the calorimeter was loaded with 89.17894 g of $KAlO_2$, it was evacuated and backfilled to a pressure of 6.7 kPa with helium at 300 K before it was sealed. For the calculations of molar quantities 98.078 g mol^{-1} was used based on the 1973 IUPAC Table of Atomic Weights.(4) The heat capacity of the empty calorimeter ranged from 0.025 J K^{-1} at 5 K to 38.83 J K^{-1} at 300 K. Temperatures were determined potentiometrically using a standard platinum resistance thermometer and a germanium resistance thermometer. Both thermometers were calibrated at the National Bureau of Standards according to IPTS–68 for the platinum thermometer and the National Bureau of Standards Provisional Scale 2 to 20 K (1965) for the germanium thermometer.

From 406 *to* 1198 K *enthalpy increments relative to* 298.15 K. A copper-block drop calorimeter as described by Douglas and King(5) was used. For the present work, the drop calorimeter was modified to incorporate a more sensitive potentiometric system capable of detecting a temperature change of ±0.05 mK. The calorimeter was calibrated electrically before and after measurements on a substance. The entire apparatus was also checked at these times by measuring the enthalpy of MgO. These measurements on MgO agreed with Victor and Douglas(6) to better than ±0.1 per cent. A sample of $KAlO_2$ of 6.7523 g was used. The sample container was a (platinum + 10 mass per cent of rhodium) capsule with a volume of approximately 6 cm^3 and a mass of approximately 10 g. The capsule was evacuated and backfilled with helium to a pressure of 101 kPa before it was sealed. The temperature of the capsule in the furnace was measured with a platinum-to-(platinum + 10 mass per cent rhodium) thermocouple, which was calibrated at the melting temperature of pure gold. Temperatures relate to the IPTS–68.

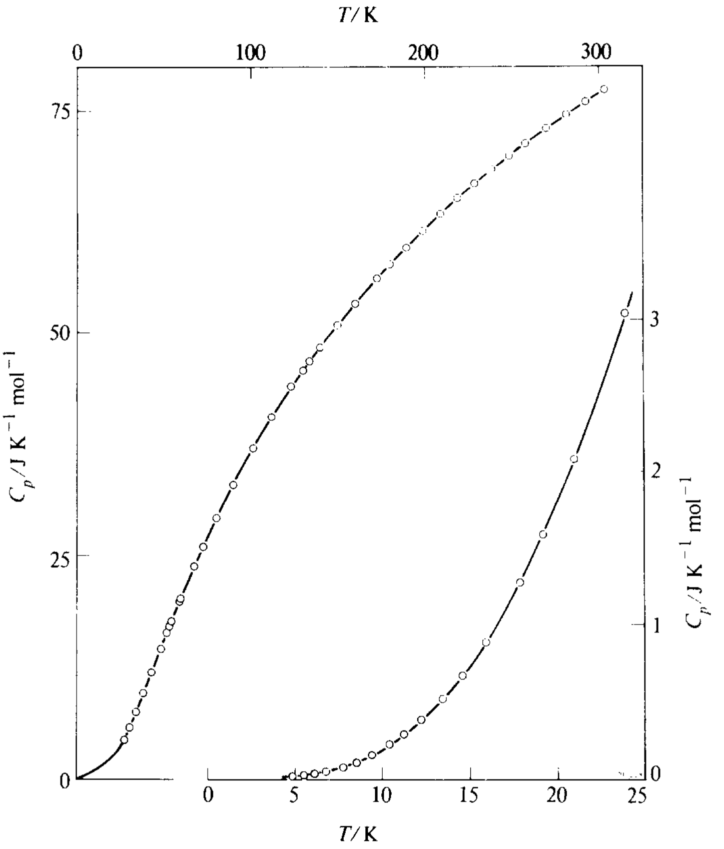

FIGURE 1. Low-temperature heat capacity of KAlO$_2$. ○, experimental values; ——, smoothed curve.

3. Results

LOW-TEMPERATURE

The experimental heat capacities from the low-temperature calorimeter are listed chronologically in table 1. These heat capacities are also shown in figure 1. As can be seen from figure 1, no transitions were observed over the measured temperature range of 4.87 to 303.07 K. The overall uncertainty of the heat-capacity measurements was estimated to be ± 1 per cent below 25 K, ± 0.5 per cent from 25 to 50 K, and ± 0.2 per cent from 50 to 310 K.

HIGH-TEMPERATURE

The enthalpy increments from the drop calorimeter are listed chronologically in table 2. These values are plotted as mean heat capacities, $\{H^\circ(T)-H^\circ(298.15\ \mathrm{K})\}/(T-298.15\ \mathrm{K})$, in figure 2. As can be seen from the diagram, a first-order reversible transition was found at 810 K. Pre-transition effects below

TABLE 1. Heat capacity of $KAlO_2$

$\frac{T}{K}$	$\frac{C_p^\circ}{J\ K^{-1}\ mol^{-1}}$	$\frac{T}{K}$	$\frac{C_p^\circ}{J\ K^{-1}\ mol^{-1}}$	$\frac{T}{K}$	$\frac{C_p^\circ}{J\ K^{-1}\ mol^{-1}}$	$\frac{T}{K}$	$\frac{C_p^\circ}{J\ K^{-1}\ mol^{-1}}$
Series I		149.53	50.29	6.78	0.038	30.23	5.653
51.58	16.209	159.70	52.72	7.76	0.067	33.94	7.385
58.64	19.606	179.60	57.11	8.53	0.096	38.07	9.410
67.35	23.527	188.91	59.04	9.41	0.146	42.81	11.799
72.36	25.669	198.49	60.92	10.40	0.222	43.08	14.460
80.16	28.840	208.69	62.84	11.22	0.289	53.11	16.958
89.75	32.505	218.40	64.60	12.21	0.385	54.18	17.485
101.19	36.547	228.14	66.23	13.42	0.519	59.35	19.933
111.76	39.961	238.10	67.82	14.58	0.674	172.23	55.52
122.99	43.313	248.31	69.37	15.91	0.895	257.71	70.75
133.57	46.246			17.87	1.293	269.61	72.47
		Series III		19.19	1.611	281.19	73.97
Series II		4.87	0.008	21.02	2.117	292.19	75.40
129.92	45.208	5.53	0.017	23.96	3.100	303.07	76.73
139.44	47.765	6.14	0.025	27.07	4.284		

TABLE 2. Enthalpy increments above 298.15 K obtained in the drop calorimeter

$\frac{T}{K}$	$\frac{H^\circ(T)-H^\circ(298.15\ K)}{J\ mol^{-1}}$	$\frac{\delta H\ ^a}{J\ mol^{-1}}$	$\frac{T}{K}$	$\frac{H^\circ(T)-H^\circ(298.15\ K)}{J\ mol^{-1}}$	$\frac{\delta H\ ^a}{J\ mol^{-1}}$
406.1	8850	+13	780.5	45470	+184 [b]
501.9	17485	+21	818.4	50405	−155 [b]
601.4	26970	−29	741.8	41240	+13
704.0	37330	+8	837.5	52440	−67
802.9	48180	+527 [b]	1051.1	74540	−29
902.0	59255	+142	1098.7	79535	−29
952.4	64450	+142	1149.4	84840	−67
1001.9	69555	+113	1197.8	90100	−54

[a] Deviation from smoothed curve.

[b] Transition region not used in curve fit.

TABLE 3. Thermodynamic functions of $KAlO_2$

$\frac{T}{K}$	$\frac{C_p^\circ}{J\ K^{-1}\ mol^{-1}}$	$\frac{S^\circ(T)-S^\circ(0)}{J\ K^{-1}\ mol^{-1}}$	$\frac{-\{G^\circ(T)-H^\circ(0)\}/T}{J\ K^{-1}\ mol^{-1}}$	$\frac{H^\circ(T)-H^\circ(0)}{J\ mol^{-1}}$
5	0.013	0.004	0.001	0.013
10	0.188	0.046	0.009	0.368
15	0.736	0.213	0.045	2.519
20	1.828	0.561	0.127	8.686
25	3.473	1.134	0.265	21.732
30	5.548	1.946	0.475	44.145
35	7.895	2.975	0.756	77.67

TABLE 3. Thermodynamic functions of $KAlO_2$

T/K	C_p°/J K^{-1} mol^{-1}	$S^\circ(T)-S^\circ(0)$/J K^{-1} mol^{-1}	$-\{G^\circ(T)-H^\circ(0)\}/T$/J K^{-1} mol^{-1}	$H^\circ(T)-H^\circ(0)$/J mol^{-1}
40	10.381	4.192	1.109	123.33
45	12.908	5.561	1.526	181.56
55	17.88	8.636	2.532	335.70
60	20.24	10.293	3.109	431.02
70	24.69	13.753	4.382	656.0
80	28.80	17.32	5.774	923.7
90	32.59	20.94	7.263	1230.9
100	36.11	24.56	8.813	1574.7
110	39.38	28.15	10.402	1952.3
120	42.42	31.71	12.032	2361.4
130	45.26	35.22	13.682	2799.9
140	47.93	38.67	15.34	3266.0
150	50.44	42.06	17.01	3758.0
160	52.82	45.40	18.69	4274.3
170	55.07	48.66	20.34	4813.9
180	57.21	51.87	22.01	5375
190	59.25	55.02	23.66	5958
200	61.20	58.11	25.31	6560
210	63.05	61.14	26.94	7181
220	64.83	64.12	28.57	7821
230	66.52	67.04	30.18	8478
240	68.13	69.90	31.77	9151
250	69.66	72.71	33.35	9840
260	71.12	75.48	34.93	10544
270	72.51	78.19	36.48	11262
273.15	72.93	79.03	36.94	11491
280	73.84	80.85	38.01	11994
290	75.11	83.46	39.54	12738
298.15	76.12	85.55	40.76	13355
300	76.34	86.03	41.04	13496
350	81.89	98.25	48.36	17462
400	86.21	109.47	55.30	21668
450	89.84	119.84	61.90	26071
500	92.99	129.47	68.18	30644
550	95.78	138.47	74.17	35364
600	98.27	146.91	79.88	40216
650	100.53	154.87	85.35	45187
700	102.55	162.39	90.58	50270
750	104.39	169.53	95.61	55440
800	106.03	176.32	100.45	60700
810[a]	106.34	177.64	101.39	61760
810[a]	101.69	179.24	101.39	63060
900	102.77	190.01	109.72	72260
1000	103.97	200.90	118.30	82600
1050	104.57	205.99	122.36	87810
1100	105.17	210.87	126.27	93060
1150	105.77	215.56	130.06	98330
1200	106.37	220.07	133.71	103633
1250	106.97	224.43	137.25	108967
1300	107.57	228.63	140.68	114330
1350	108.17	232.70	144.02	119724
1400	108.77	236.65	147.26	125147

[a] First order transition.

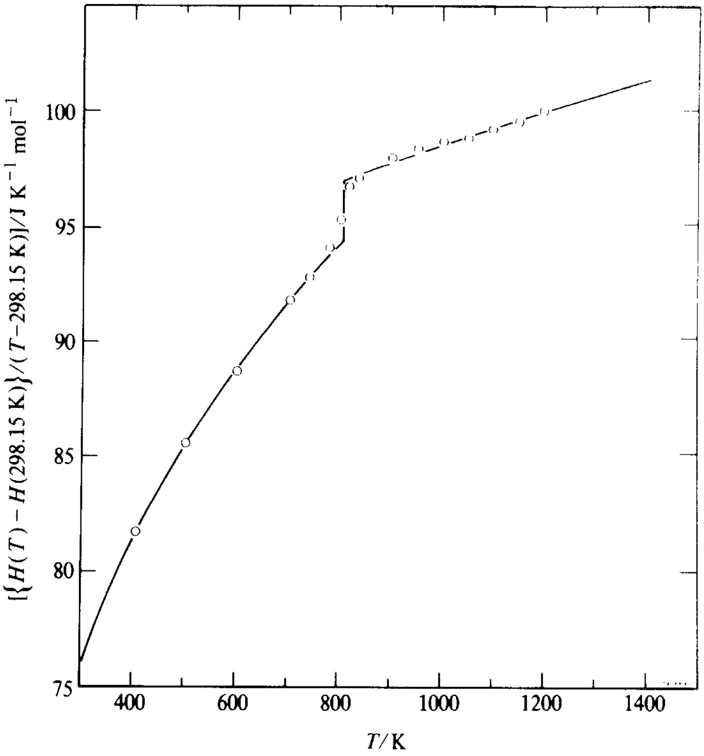

FIGURE 2. High-temperature mean heat capacity of $KAlO_2$. ○, experimental values; ——, smoothed curve.

810 K and sluggishness of conversion above 810 K were evidenced by the scatter in the results near 810 K. The absolute uncertainty of the enthalpy measurements was estimated to be ±0.3 per cent. The standard error of measurement was ±0.2 per cent.

THERMODYNAMIC FUNCTIONS

Both the experimental heat capacities and enthalpies were smoothed using a curve-fitting routine developed by Justice.(7) Below 5 K, a C_p/T against T^2 plot was used to extrapolate C_p values to $T = 0$. Entropy and enthalpy values below 5 K were calculated by graphical integration using Simpson's rule. Calculated values of the thermodynamic functions generated by the curve-fitting routine are listed in table 3 for values of C_p°, $\{S^\circ(T)-S^\circ(0)\}$, $-\{G^\circ(T)-H^\circ(0)\}/T$, and $\{H^\circ(T)-H^\circ(0)\}$ from 5 to 1400 K.

4. Discussion

In the high-temperature measurements, a reversible transition was observed at 810 K. This transition was also found by Otsubo *et al.*(1) Their X-ray analysis showed a discontinuous expansion over the range 673 to 873 K, and their d.t.a. showed a reversible transition at 808 K. They concluded that there was an anomalous expansion at this peak temperature of 0.3 per cent. If the transition is considered to be first order, then the enthalpy of transition is calculated to be $\Delta H_{tr} = 1295$ J mol^{-1}. Measurements were discontinued above 1198 K due to a capsule failure. There was a bulge in the bottom of the capsule after this last measurement, and the capsule had a mass loss of 0.04 per cent. This behavior is possibly due to decomposition of the $KAlO_2$. Chizhikov *et al.*(8) also observed similar behavior at higher temperatures in a study on the decomposition kinetics of potassium aluminate. However, the X-ray powder diffraction pattern of the sample after the enthalpy measurements was identical to the pattern before the measurements.

Enthalpy-of-formation measurements were also made on $KAlO_2$ in a hydrochloric-acid calorimeter. However, uncertainty in the final state of the solution, as evidenced by a slight cloudiness, caused us to reject the values obtained.

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