ELSEVIER

Thermochimica Acta 253 (1995) 33–39

thermochimica
acta

Investigation of the thermodynamic properties of γ-Al_2O_3 ☆

Chen Qiyuan [a,*], Zeng Wenming [a], Chen Xinmin [a], Gu Songqing [b],
Yang Guanqun [b], Zhou Huifang [b], Yin Zhonglin [b]

[a] *Department of Chemistry, Central-South University of Technology, Changsha, Hunan 410083, People's Republic of China*

[b] *Zhengzhou Research Institute of Light Metals, Zhengzhou, Henan, People's Republic of China*

Received 5 July 1994; accepted 7 July 1994

Abstract

The heat capacities of γ-Al_2O_3 were measured from 50 to 700°C using an HT1000 calorimeter. The heat of transformation γ-Al_2O_3 to α-Al_2O_3 was directly measured using an HT1500 calorimeter. Combination of these results with the values from the literature led to $\Delta_f H_m^\ominus = -(1657.2 \pm 1.5)$ kJ mol^{-1}, $S_m^\ominus = (52.30 \pm 2.00)$ J mol^{-1} K^{-1} and $\Delta_f G_m^\ominus = -(1564.2 \pm 2.0)$ kJ mol^{-1}.

Keywords: Alumina; DTA; TG; Thermodynamics

1. Introduction

γ-Al_2O_3 is an important intermediate during the calcining of aluminium hydroxide in the final technological stage of the industrial production of aluminium oxide. At the temperatures above 1200°C, γ-Al_2O_3 is transformed to α-Al_2O_3 [1]. γ-Al_2O_3 is also an important chemical product as the carrier of catalyst and adsorbent [2]. Therefore, it is necessary to investigate the thermodynamic properties of γ-Al_2O_3,

---

[*] Corresponding author.

☆ Presented at the International and III Sino–Japanese Symposium on Thermal Measurements, Xi'an, 4–6 June 1994.

SSDI 0040-6031(94)01969-X

which are useful for the understanding of the mechanism of transformation of γ-Al_2O_3 to α-Al_2O_3 and for the further application of γ-Al_2O_3. To date, the measurement of the heat capacities of γ-Al_2O_3 has not been reported [3]. The standard enthalpy of formation of γ-Al_2O_3 has only been determined on the basis of the heat of transformation from γ-Al_2O_3 to α-Al_2O_3 measured indirectly by Yokokawa and Kleppa [4] at 705°C by solution calorimetry. In the present work, the heat capacities of γ-Al_2O_3 have been measured between 50 and 705°C by the drop method with an HT1000 high temperature calorimeter and the heat of transformation of γ-Al_2O_3 has been measured directly in an HT1500 very high temperature calorimeter. Combining the data with the standard enthalpy of formation of α-Al_2O_3, the standard enthalpy of formation of γ-Al_2O_3 has been calculated. The standard free energy of formation of γ-Al_2O_3 has also been computed, based on the recommended value of the standard entropy of γ-Al_2O_3 [5].

2. Experimental

2.1. Samples

The samples of γ-Al_2O_3 for determination were prepared from pure synthetic diaspore powder. Diaspore powder was calcined at 550°C for 10 h and then cooled to room temperature. A TG–DTA analysis made with a TSA100 thermal analyser (Rigaku, Japan) and an XRD analysis carried out with a D500 X-ray diffraction analyser (Siemens, Germany) showed that the samples were pure γ-Al_2O_3. The results of elemental spectral analysis are shown in Table 1. The particle size of samples ranged from 0.5 to 20 μm, with average of 6.59 μm.

Table 1
Results of the spectral analysis of γ-Al_2O_3 in %

Cu	0.0012	Mg	0.0011	Bi	<0.001	Si	<0.001
Ca	0.012	Ga	0.0026	Ni	<0.001	Ti	<0.001
Sn	<0.001	Sb	<0.001	Mn	<0.001	Fe	0.010

2.2. Determination of the heat capacities of γ-Al_2O_3

A Calvet–Tian high temperature microcalorimeter HT1000 (Setaram, France), was used for the determination of the heat capacities of γ-Al_2O_3. Before experiments, the sensitivity and temperature scales of the calorimeter were calibrated carefully. An enthalpy determination for standad material α-Al_2O_3 was made using the "drop" method in this calorimeter. The results are shown in Table 2. Putting the mean values into the equation [6]

$$\Delta H = a(T - T_0) + b(T^2 - T_0^2) + c[(1/T) - (1/T_0)] \qquad (1)$$

gives the parameters as $a = 108.02$, $b = 10.37 \times 10^{-3}$ and $c = 30.71 \times 10^5$. The results of calculations with Eq. (1) are shown in the sixth column of Table 2 and it can be seen that they are very close to the values from Ditmars et al. [7] (see the seventh column of Table 2). The concord between the experimental results from two runs at the same temperature and the good agreement between our results and the values from Ditmars et al. [7] show the good reproducibility and accuracy of this calormetric determination.

γ-Al_2O_3 powder was pressed into pellets and was kept in a desiccator prior to determinations. A small amount of corundum powder was put on the bottom of both the sample cell and the reference cell. The calorimeter was heated to the temperature required for determination and kept constant. After the baseline reached a stable state, a sample of known mass of γ-Al_2O_3 was dropped into the sample cell. The calorimetric signals were collected and processed by an IBM PC-XT286 computer. The results of 16 runs are listed in Table 3.

Putting the average values of ΔH into Eq. (1) gives the following expression for the enthalpy of γ-Al_2O_3

Table 2
Experimental results of the enthalpy of α-Al_2O_3 [a] using the "drop" method with an HT1000 calorimeter

Mass/mg	T_0/K	T/K	ΔH_{exp}/ (J mol^{-1})	ΔH_{exp}(mean value)/ (J mol^{-1})	ΔH_{calc}/ (J mol^{-1})	ΔH/ (J mol^{-1}) [7]
277.870	288.75	321.45	2646.09	2648.36 ± 2.27	2657.26	2630.62
163.304	288.75	321.45	2650.63			
187.818	289.45	374.15	7313.10	7310.89 ± 2.21	7330.32	7234.18
138.690	289.45	374.15	7308.68			
120.682	291.85	477.95	17478.93	17481.81 ± 2.64	17490.96	17318.31
123.036	291.85	477.95	17484.21			
110.312	291.35	582.15	28784.22	28780.86 ± 3.36	28781.03	28633.03
150.426	291.35	582.15	28777.50			
178.173	293.65	685.55	40330.36	40334.15 ± 3.79	40334.10	40255.13
139.233	293.65	685.55	40337.94			
166.342	294.15	788.55	52420.17	52415.74 ± 4.43	52410.25	52388.41
82.347	294.15	788.55	52411.31			
85.984	293.65	890.45	64785.13	64789.80 ± 4.67	64785.31	64755.18
93.633	293.65	890.45	64794.47			
49.930	293.15	992.85	77544.58	77539.08 ± 5.50	77529.91	77467.34
76.142	293.15	992.85	77533.58			

[a] Molar mass is 101.9613 g mol^{-1}.

Table 3
Heat capacities of γ-Al_2O_3[a] determined usins an HT1000 calorimeter

Mass/mg	T_0/K	T/K	ΔH/ ($J\ mol^{-1}$)	ΔH(mean value)/ ($J\ mol^{-1}$)	$C_{p,m}$/ ($J\ mol^{-1}\ K^{-1}$)
330.186	288.75	321.45	2774.43	2771.85 ± 2.58	88.81
264.222	288.75	321.45	2769.27		
280.298	289.45	374.15	7663.68	7666.40 ± 2.72	98.41
218.770	289.45	374.15	7669.12		
218.154	291.85	477.95	18339.07	18335.90 ± 3.17	109.78
262.980	291.85	477.95	18332.73		
161.190	291.35	582.15	30192.69	30197.60 ± 4.91	116.64
201.941	291.35	582.15	30202.51		
263.003	293.65	685.55	42338.67	42333.04 ± 5.63	121.44
279.697	293.65	685.55	42327.41		
169.004	294.15	788.55	54993.80	54999.64 ± 5.84	125.21
73.250	294.15	788.55	55005.48		
40.177	293.65	890.45	67972.61	67966.42 ± 6.13	128.38
76.473	293.65	890.45	67960.35		
42.165	293.15	992.85	81291.29	81297.64 ± 6.35	131.21
31.927	293.15	992.85	81303.99		

[a] Molar mass is 101.9613 g mol^{-1}.

$$\Delta H = 115.25(T - T_0) + 9.765 \times 10^{-3}(T^2 - T_0^2) + 33.81 \times 10^{-5}[(1/T) - (1/T_0)] \qquad (2)$$

Therefore, the relationship between the heat capacity of γ-Al_2O_3 and temperature could be expressed as

$$C_p = 115.25 + 19.53 \times 10^{-3}T - 33.81 \times 10^{5}T^{-2} \qquad (3)$$

in the range 298.15–1000 K.

The heat capacities calculated using Eq. (3) are shown in the sixth column of Table 3. The heat capacity of γ-Al_2O_3 is 4.98% larger than that of α-Al_2O_3 at 101.0°C, 4.45% larger at 412.4°C and 5.92% larger at 719.7°C. Chase et al. [5] estimated according to the results of Marchidan et al. [8] that the heat capacities of γ-Al_2O_3 between 730 and 940°C are 4.7% larger than those of α-Al_2O_3. Their estimated values are very close to our results, but the deviations become appreciable at higher temperatures.

2.3. Determination of the enthalpy of transformation from γ-Al_2O_3 to α-Al_2O_3

An HT1500 very high temperature calorimeter (Setaram, France) was used to determine the enthalpy of transformation from γ-Al_2O_3 to α-Al_2O_3. Before determi-

Table 4
Results of the determinations of the melting enthaplies of Au, Ag, NaCl and Al

Substance	θ_{fus}/°C	ΔH_{exp}/ (kJ mol^{-1})	ΔH(mean value)/ (kJ mol^{-1})	ΔH/ (kJ mol^{-1}) [9]
Au	1064.47	12.61	12.59 ± 0.078	12.55
	1064.32	12.50		
	1064.31	12.65		
Ag	962.08	11.36	11.26 ± 0.083	11.30
	961.98	11.20		
	962.25	11.24		
NaCl	801.25	28.28	28.28 ± 0.065	28.16
	801.28	28.21		
	801.75	28.34		
Al	661.17	10.72	10.68 ± 0.047	10.7
	660.74	10.63		
	660.74	10.70		

Table 5
Measured heats of transformation from γ-Al_2O_3 to α-Al_2O_3

T/K [a]	Mass/mg	ΔH_{trs}/(kJ mol^{-1})	ΔH_{trs}(mean value)/(kJ mol^{-1})
1469.8	760.218	−27.25	-26.78 ± 0.41
1468.5	762.751	−26.57	
1471.1	763.194	−26.52	

[a] Average value of the start temperature and the end temperature of peak.

nation, the sensitivity and temperature scale were calibrated carefully. The accuracy of the calorimeter was checked by determining the melting enthaplies of metallic gold, silver, aluminium and sodium hydroxide; comparison of these results (see Table 4) with the values in the literature [9] confirmed the reliability of our calorimeter.

The sample cell of calorimeter HT1500 was filled with corundum powder. Then the γ-Al_2O_3 sample was put onto the corundum powder. The reference cell was also filled with corundum powder. After the baseline of the heat flow curve reached a stable state, sample and reference cells were heated simultaneously at a rate of 5°C min^{-1}. The signals were collected and processed by a personal computer. An XRD analysis on the material produced indicated that all the γ-Al_2O_3 sample had been transformed to α-Al_2O_3. The results of three determination runs are listed in Table 5; these are in good agreement with each other.

3. Discussion

Combining the heat capacity values of α-Al_2O_3 [10] and γ-Al_2O_3 obtained above gives an expression for the relationship between temperature and ΔC_p for the reaction

$$\gamma\text{-Al}_2\text{O}_3(\text{cr}) = \alpha\text{-Al}_2\text{O}_3(\text{cr}) \tag{4}$$

as

$$\Delta C_p = 0.13 - 7.19 \times 10^{-3}T - 3.15 \times 10^{5}T^{-2} \tag{5}$$

Using Eq. (5), the heat of transformation obtained above was calibrated to room temperature. Then, by combining this value with the standard enthalpy of formation of α-Al_2O_3, we obtained the standard enthalpy of γ-Al_2O_3 at 25°C as $-(1657.1 \pm 1.5)$ kJ mol^{-1}.

Yokokawa and Kleppa [4] indirectly measured the heat of transformation from γ-Al_2O_3 to α-Al_2O_3 at 978 K as -22.18 kJ mol^{-1}. Calibrating to room temperature with Eq. (5) gives the value -18.41 kJ mol^{-1}. Therefore, the standard enthalpy of formation of γ-Al_2O_3 from Yokokawa and Kleppa's value is -1657.3 kJ mol^{-1}, which is only 0.23 kJ mol^{-1} higher than our result (see Table 6). Therefore the average of the values from Yokokawa and Kleppa [4] and ourselves ($-(1657.2 \pm 1.5)$ kJ mol^{-1}) is recommended as the standard enthalpy of formation of γ-Al_2O_3.

Because of the lack of experimental data for the low temperature heat capacity of γ-Al_2O_3, there are no experimental data for the standard entropy of γ-Al_2O_3 to be found in the literature. Chase et al. [5] suggested the value (52.30 ± 2.00) J mol^{-1} K^{-1} as the standard entropy of γ-Al_2O_3 at 25°C, based on the statistical mechanical analysis of the construction of γ-Al_2O_3.

Combining the standard enthalpy of formation obtained above and the standard entropy suggested by Chase et al. [5] with the standard entropies of Al(cr) and O_2(g) [11], we obtain $-(1564.2 \pm 2.0)$ kJ mol^{-1} for the standard free energy of formation of γ-Al_2O_3.

Table 6
Standard enthalpy of formation of γ-Al_2O_3

Method	T/K	$(\Delta_{trs}H^{\ominus}_{T} - \Delta_{trs}H^{\ominus}_{298.15})$/ (kJ mol^{-1})	$\Delta_{trs}H^{\ominus}_{298.15}$/ (kJ mol^{-1})	$\Delta_f H^{\ominus}_{298.15}(\gamma\text{-Al}_2\text{O}_3)$/ (kJ mol^{-1})
Indirect calorimetry	978	-3.77	-18.41	-1657.3
Direct calorimetry	1469.8	-8.14	-18.64	-1657.1

Acknowledgement

This project was supported by the National Fund for Doctoral Program of China.

References

[1] T. Sato, Thermochim. Acta, 88 (1985) 69.

[2] B.C. Lippens and J.J. Steggerda, Physical and Chemical Aspects of Adsorbents and Catalysts, Academic Press, New York, 1970, p. 171.

[3] J.A. Apps and J.M. Neil, ACS Symp. Ser. 416, Washington DC, 1990, p. 415.
[4] T. Yokokawa and O.J. Kleppa, J. Phys. Chem., 68 (1964) 3246.
[5] M.W. Chase, Jr., J.L. Curnutt, R.A. McDonald and A.N. Syverud, J. Phys. Chem. Ref. Data, 7 (1978) 838.
[6] J.P. McCullough and D.W. Scott, Experimental Thermodynamics, Vol. I, Calorimetry of Non-Reacting Systems, Butterworths, London, 1968, p. 327.
[7] P.A. Ditmars, S. Ishihara, S.S. Chang and G. Bernstein, J. Res, Natl. Bur. Stand., 87 (1982) 159.
[8] D.I. Marchidan, L. Pandele and A. Nicolescu, Rev. Roum. Chim., 17 (1972) 1493.
[9] W.J. Borer and H.H. Gunthard, Helv. Chim. Acta, 53 (1970) 1043.
[10] W. Zeng, Dissertation, Central-South University of Technology, China, 1993.
[11] J.D. Cox, D.D. Wagman and V.A. Medevedev, CODATA Key Values for Thermodynamics, Hemisphere Publishing Corporation, New York, 1989.