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# The Melting Point, Latent Heat of Solidification, and Enthalpy for Both Solid and Liquid $\alpha$-$Al_2O_3$ in the Range 550–2400 K[1]

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In this paper the authors describe the use of a high-temperature drop calorimeter with autoadiabatic control for the measurment of the enthalpy of $\alpha$-$Al_2O_3$ in the temperature range 550 to 2400 K for both solid and liquid phases. Equations representing the enthalpy of both solid and liquid states are obtained from the data with the use of a computer. In addition to the melting point, $T_m = 2328 \pm 7$ K, the latent heat of solidification, $L = 1137.90\ J \cdot g^{-1}$, has also been determined. The results of the present work are compared with those reported in the literature.

**KEY WORDS:** alumina; calorimetry; enthalpy; melting point; latent heat; solidification.

## 1. INTRODUCTION

The enthalpy and heat capacity of $\alpha$-$Al_2O_3$, the standard material for calorimetry, were measured below 1200 K by several investigators [1–5], but it has rarely been measured in the range 1200 to 2000 K. Moreover, the enthalpy and thermodynamic regularity of $\alpha$-$Al_2O_3$ were rarely studied in the range 2000 K to its melting point and especially in the liquid state.

The measurements in the present work have been performed with the use of the drop calorimeter described in Ref. 6. Over a wide temperature range, 550–2400 K, the enthalpy of $\alpha$-$Al_2O_3$ in both solid and liquid states was measured accurately. The results are in good agreement with those reported in the literature [1–5, 7, 9], which demonstrates the reliability of

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the method and apparatus. It is apparent that the calorimetric method is useful not only for measuring the enthalpy and heat capacity but also for measuring the melting point and latent heat.

## 2. METHOD AND APPARATUS

### 2.1. General Principle

In the classic drop calorimetry method, the sample container is used to eliminate the heat loss created by both convection and radiation during the travel of the sample from the furnace into the calorimeter. The experiments have to be performed twice, once with the empty container alone and another time with the sample and container together; then the enthalpy of sample can be obtained by subtracting the former from the latter. In the present experiments, however, the sample is heated to a certain temperature and then dropped into the calorimeter under vacuum ($10^{-3}$–$10^{-4}$ Torr); this makes the heat loss by convection negligibly small. A correction for the heat loss by radiation can be made based on the material and geometry of the sample. The sample container is unnecessary for a solid block sample and the enthalpy can be determined directly by only a single drop after correcting for the heat loss due to radiation, thus the enthalpy of the sample can be expressed as

$$\Delta H = \frac{A\,\Delta t + \delta Q}{m} \tag{1}$$

where $A$ and $\Delta t$ are the heat capacity and temperature increment of adiabatic calorimeter, respectively, $m$ is the mass of the sample, and $\delta Q$ is the heat loss by radiation and can be determined by the Stefan-Boltzmann radiation equation:

$$\delta Q = \varepsilon F C_0 \tau \left[ \left( \frac{T}{100} \right)^4 - \left( \frac{T_0}{100} \right)^4 \right] \tag{2}$$

where $\varepsilon$ is the thermal emissivity, $F$ is the surface area of sample, $C_0$ is the Stefan-Boltzmann constant, $\tau$ is the travel time of the sample from the furnace to the calorimeter, $T$ is the temperature of the sample, and $T_0$ is the temperature of the environment.

For powder and liquid samples, containers for the sample are necessary; in that case, the quantity $\delta Q$, in Eq. (1), could be canceled.

When the enthalpy of the sample is measured in the temperature range including the solid and liquid states and melting point, an equation for enthalpy, $\Delta H = f(T)$, can be obtained using the least-squares method by means of a computer.

The true specific heat of the sample as a function of temperature can be determined by differentiating the enthalpy relation, Eq. (1):

$$C_p = \frac{d\Delta H}{dT} = \frac{df(T)}{dT} \tag{3}$$

At the melting point, there is a rapid change in the enthalpy due to the released latent heat during solidification. The latent heat can be determined by subtraction of the liquid and solid enthalpy equations at the melting point $T_m$:

$$\begin{aligned} L &= \Delta H_{273}^{T_m}(\text{liquid}) - \Delta H_{273}^{T_m}(\text{solid}) \\ &= f(T_m)(\text{liquid}) - f(T_m)(\text{solid}) \end{aligned} \tag{4}$$

## 2.2. Apparatus

The calorimetric apparatus with the detailed features of vacuum, high temperature (200–2500°C), autorecord, and autoadiabatic control was described earlier [6]. It consists of the following main parts (Figs. 1):

(i) the vacuum furnace with a tungsten tube heater for heating the sample to high temperatures;

(ii) the autoadiabatic copper block for measuring the heat content released from the sample;

(iii) the autoadiabatic control system to prevent heat loss from the calorimeter to the environment; and

(iv) the system for measuring and recording the temperature variation of the calorimeter, which includes a bridge consisting of a platinum resistance thermometer and three other known resistances.

The signal corresponding to resistance is converted into potential, which is measured with a digital potentiometer and is recorded with a printer.

## 2.3. Samples

Two kinds of samples were used. Sample 1 was a solid cylinder for measuring enthalpy in the solid state, with a purity of 99.6%, entirely of the α phase, and density $\rho = 3.96\ \mathrm{g \cdot cm^{-3}}$. The temperature range of measurements was 550 to 2360 K, i.e., up to near the melting point. Sample

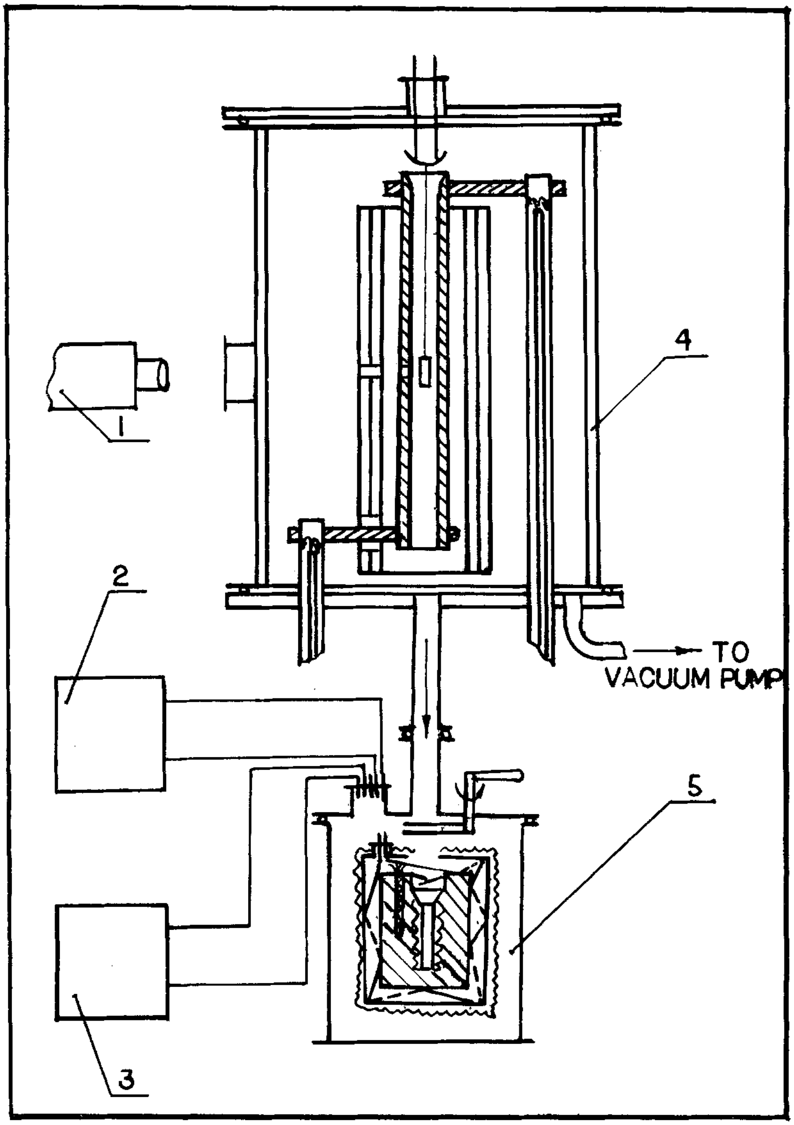

**Fig. 1.** Schematic diagram of the high-temperature calorimetric apparatus. (1) Micropyrometer; (2) autoadiabatic control system; (3) system for automeasuring and recording temperature; (4) vacuum furnace with tungsten tube heater; (5) copper block calorimeter.

2 was in powder form and was used for measurements of the enthalpy of the liquid state with a purity of 99.99%, entirely of the α phase. The temperature range of measurements was 2290 to 2380 K, i.e., including solid, molten, and liquid states.

## 3. RESULTS

### 3.1. The Enthalpy of Solid α-$Al_2O_3$ and the Empirical Equation

A total of 33 experimental data has been obtained for samples 1 and 2. The following equation for enthalpy (in $J \cdot g^{-1}$) of solid α-$Al_2O_3$ was obtained over the range 554 to 2328 K using the least-squares method by means of a computer:

$$\begin{aligned}\Delta H_{273}^{T}(\text{solid})\\ &= f(T) = A_0 + A_1 T + A_2 T^2 + A_3 T^3\\ &= -282.175 + 0.855153T + 2.46033 \times 10^{-4} T^2 - 4.11844 \times 10^{-8} T^3 \qquad (5)\end{aligned}$$

All the experimental data and computed results on enthalpy according to Eq. (5) and their relative deviations are listed in Table I. It may be seen that the computed results are in good agreement with the experimental results.

### 3.2. The Enthalpy of Liquid α-$Al_2O_3$ and the Empirical Equation

A total of seven experimental data has been obtained for sample 2 in the liquid state. Enthalpy (in $J \cdot g^{-1}$) for liquid $Al_2O_3$ can be expressed by the following quadratic equation within the temperature range 2328 to 2381 K:

$$\begin{aligned}\Delta H_{273}^{T}(\text{liquid}) &= f(T) = f(T) = B_0 + B_1 T + B_2 T^2\\ &= -6351.51 + 6.49671T - 9.43528 \times 10^{-4} T^2\end{aligned} \qquad (6)$$

### 3.3. The Melting Point of α-$Al_2O_3$

From the analysis of the results given in Table I, the melting point of α-$Al_2O_3$ was determined to be

$$T_m = 2328 \pm 7 \text{ K}$$

The temperture of the sample was measured with a micropyrometer made by the Continent Company of West Germany. Corrections have been

**Table I.** The Enthalpy of Solid and Liquid $\alpha$-$Al_2O_3$ Obtained from Measurements and Calculations

| Temp. (K) | $\Delta H^T_{273}$(exp.) ($J \cdot g^{-1}$) | $\Delta H^T_{273}$(calc.) ($J \cdot g^{-1}$) | Dev. (%) |
|---|---|---|---|
| | Solid phase | | |
| 554.00 | 258.28 | 260.09 | −0.69 |
| 564.00 | 268.79 | 271.00 | −0.82 |
| 564.00 | 267.41 | 271.00 | −1.33 |
| 573.00 | 284.48 | 280.86 | 1.29 |
| 584.00 | 299.33 | 292.94 | 2.18 |
| 595.00 | 299.21 | 305.07 | −1.92 |
| 684.00 | 414.27 | 404.68 | 2.37 |
| 797.00 | 533.81 | 534.81 | −0.19 |
| 798.00 | 534.98 | 535.98 | −0.19 |
| 884.00 | 640.29 | 637.59 | 0.42 |
| 962.00 | 741.30 | 731.51 | 1.34 |
| 976.00 | 742.72 | 748.53 | −0.78 |
| 1092.00 | 874.44 | 891.41 | −1.90 |
| 1190.00 | 1008.70 | 1014.46 | −0.57 |
| 1194.00 | 1024.14 | 1019.53 | 0.45 |
| 1224.00 | 1052.01 | 1057.61 | −0.53 |
| 1356.00 | 1220.59 | 1227.12 | −0.53 |
| 1382.00 | 1252.26 | 1260.84 | −0.68 |
| 1409.00 | 1300.88 | 1295.98 | 0.38 |
| 1600.00 | 1462.13 | 1547.22 | 0.96 |
| 1608.00 | 1585.48 | 1557.84 | 1.77 |
| 1788.00 | 1813.93 | 1797.98 | 0.89 |
| 1788.00 | 1788.83 | 1797.98 | −0.51 |
| 1831.00 | 1876.57 | 1855.64 | 1.13 |
| 1832.00 | 1829.96 | 1856.98 | −1.46 |
| 2018.00 | 2092.80 | 2107.00 | −0.67 |
| 2086.00 | 2182.97 | 2198.43 | −0.70 |
| 2218.00 | 2366.11 | 2375.54 | −0.40 |
| 2261.00 | 2448.20 | 2433.05 | 0.62 |
| 2296.00[a] | 2455.36 | 2479.77 | −0.98 |
| 2319.00[a] | 2508.33 | 2510.42 | −0.08 |
| 2324.00[a] | 2527.57 | 2517.08 | 0.42 |
| 2329.00[a] | 2543.56 | 2523.73 | 0.79 |
| | Liquid phase | | |
| 2327.00[a] | 3661.46 | 3657.19 | 0.12 |
| 2339.00[a] | 3663.72 | 3682.32 | −0.51 |
| 2342.00[a] | 3699.37 | 3688.56 | 0.29 |
| 2343.00[a] | 3716.44 | 3690.64 | 0.70 |
| 2348.00[a] | 3680.59 | 3700.99 | −0.55 |
| 2371.00[a] | 3779.16 | 3748.01 | −0.24 |
| 2381.00[a] | 3775.10 | 3768.14 | 0.18 |

[a] For sample 2; others for sample 1.

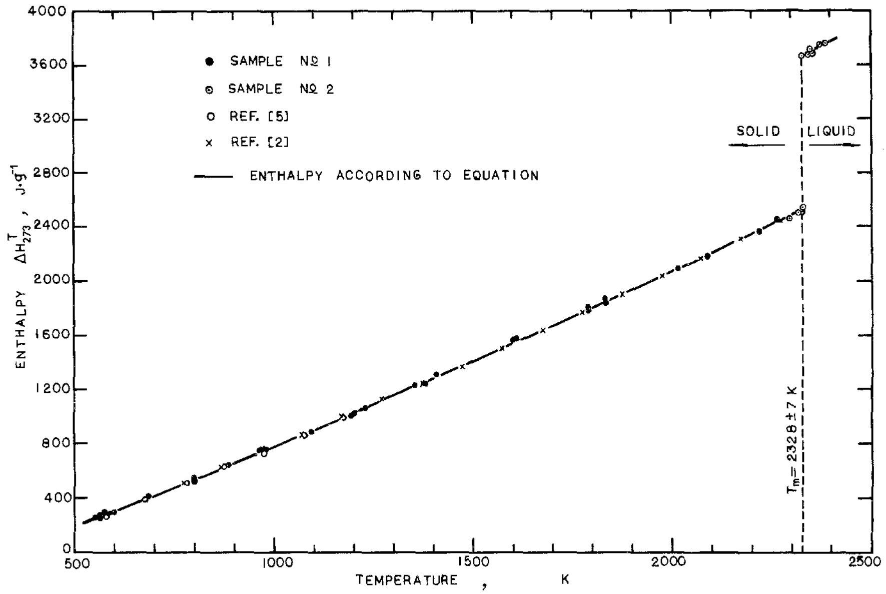

Fig. 2. The enthalpy of α-$Al_2O_3$.

made for emissativity, window absorption, and pyrometer calibration change. The resultant accuracy is estimated to be ±7 K.

### 3.4. The Latent Heat of Solidification

Once the enthalpy equations of both the solid and the liquid state and the melting point of α-$Al_2O_3$ are determined, the latent heat of solidification can be obtained by subtracting Eq. (5) from Eq. (6) at the melting point:

$$
\begin{aligned}
L &= \Delta H_{273}^{T_m}(\text{liquid}) - \Delta H_{273}^{T_m}(\text{solid}) \\
&= [A_0 + A_1 T_m + A_2 T_m^2 + A_3 T_m^3] - [B_0 + B_1 T_m + B_2 T_m^2] \\
&= 1137.90\ \mathrm{J \cdot g^{-1}}
\end{aligned}
$$

The enthalpy of both solid and liquid α-$Al_2O_3$, the melting point, and the latent heat of solidification are shown in Fig. 2.

## 4. DISCUSSION

The enthalpy of α-$Al_2O_3$ below 1173 K has been reported by several investigators; however, above 2000 K, especially near the melting point and

**Table II.** The Enthalpy of $\alpha$-$Al_2O_3$ of the Present Work Compared with That of SRM-720

| Temp. (K) | $\Delta H_{273}^{T}$ (this work) ($J \cdot g^{-1}$) | $\Delta H_{273}^{T}$(SRM-720) ($J \cdot g^{-1}$) | Dev. (%) |
|---|---|---|---|
| | Solid phase | | |
| 550 | 255.73 | 259.44 | −1.43 |
| 600 | 310.59 | 313.95 | −1.07 |
| 650 | 366.31 | 369.75 | −0.93 |
| 700 | 422.86 | 426.60 | −0.88 |
| 750 | 480.21 | 483.37 | −0.65 |
| 800 | 538.32 | 542.93 | −0.85 |
| 850 | 597.17 | 602.17 | −0.83 |
| 900 | 656.73 | 662.04 | −0.80 |
| 950 | 716.95 | 722.47 | −0.76 |
| 1000 | 777.83 | 783.40 | −0.71 |
| 1050 | 839.31 | 844.82 | −0.65 |
| 1100 | 901.38 | 906.67 | −0.58 |
| 1150 | 963.99 | 968.95 | −0.51 |
| 1200 | 1027.13 | 1031.72 | −0.44 |
| 1250 | 1090.75 | 1094.78 | −0.37 |
| 1300 | 1154.84 | 1158.23 | −0.29 |
| 1350 | 1219.35 | 1221.98 | −0.22 |
| 1400 | 1284.25 | 1286.13 | −0.15 |
| 1450 | 1349.53 | 1350.56 | −0.08 |
| 1500 | 1415.13 | 1415.29 | −0.01 |
| 1550 | 1481.04 | 1480.32 | 0.05 |
| 1600 | 1547.22 | 1545.54 | 0.11 |
| 1650 | 1613.65 | 1611.05 | 0.16 |
| 1700 | 1680.28 | 1676.86 | 0.20 |
| 1750 | 1747.10 | 1742.77 | 0.25 |
| 1800 | 1814.06 | 1808.97 | 0.28 |
| 1850 | 1881.14 | 1875.27 | 0.31 |
| 1900 | 1948.31 | 1941.87 | 0.33 |
| 1950 | 2015.54 | 2008.50 | 0.35 |
| 2000 | 2082.79 | 2075.45 | 0.35 |
| 2050 | 2150.03 | 2142.43 | 0.35 |
| 2100 | 2217.24 | 2209.61 | 0.35 |
| 2150 | 2284.39 | 2276.89 | 0.33 |
| 2200 | 2351.43 | 2344.37 | 0.30 |
| 2250 | 2418.35 | 2411.95 | 0.27 |
| 2300 | 2485.10 | | |
| 2328 | 2522.40 | | |
| | Liquid phase | | |
| 2328 | 3659.30 | | |
| 2340 | 3684.41 | | |
| 2350 | 3705.13 | | |
| 2360 | 3725.65 | | |
| 2370 | 3745.99 | | |
| 2380 | 2766.14 | | |

**Table III.** The Melting Point and Latent Heat of Solidification for $\alpha$-$Al_2O_3$ of This Work Compared with Those of Other Investigators

| Item | Ref. 7 | Ref. 8 | This work | Dev. (%) |
|---|---|---|---|---|
| Melting point (K) | $2315 \pm 4$ | $2327 \pm 6$ | $2328 \pm 7$ | $<0.6$ |
| Latent heat ($J \cdot g^{-1}$) | 1161.26 | | 1137.90 | $<2.1$ |

in the liquid state, only a limited amount of reported information exists. Our results, on enthalpy, are compared with those reported by the National Bureau of Standards [5] and by the Academy of the USSR [2, 3], which are considered to be reliable. Our results are also compared with those for the standard reference material SRM-720 of the NBS and are listed in Table II. From Table II, it can be seen that our results are in good agreement with those for SRM-720; the average deviation is about 0.43%.

The melting point of $\alpha$-$Al_2O_3$ is considered as a reference temperature above the melting point of platinum by the International Calorimetry Conference, which coordinated the cooperation of nine laboratories in seven countries in the measurement of the melting point of $\alpha$-$Al_2O_3$; the results have ben reported in Ref. 8.

The latent heat of solidification for $\alpha$-$Al_2O_3$ has been reported in Ref. 7.

A comparison of the melting point and latent heat of solidification for $\alpha$-$Al_2O_3$ in the present work with those of other investigators is shown in Table III.

## REFERENCES

1. Y. S. Touloukian, *Thermophysical Properties of Matter, Vol. 5* (Plenum, New York, 1970), pp. 24–25.
2. V. Ya. Chekhovskoi, *Eng. Fiz. Zh.* **5**:62 (1962) (Russian).
3. V. Ya. Chekhovskoi, *Teplofiz. Vysok. Temp.* **2**:296 (1964) (Russian).
4. M. Hoch and H. L. Johnston, *J. Phys. Chem.* **65**:1184 (1961).
5. D. A. Ditmars and T. B. Douglas, *J. Res . Natl. Bur. Stand.* **75A**:401 (1971).
6. P. H. Zhang, Z. H. Li, R. Z. Chang, and X. N. Zhou, *J. Eng. Thermophys.* **3**:413 (1982) (Chinese).
7. P. B. Kantor and L. S. Lazareva, *Ukr. Fiz. Zh.* **7**:205 (1963) (Russian).
8. S. J. Schneider, *Pure Appl. Chem.* **31**:116 (1970).
9. S. S. Chang, in *Proceeding of the Seventh Symposium on Thermophysical Properties*, A. Cezairliyan, ed. (Am. Soc. Mech. Eng., New York, 1977), p. 83.