Title
The standard molar enthalpies of formation of Pb2Fe2O5(s) and PbFe5O8.5(s) by acid solution calorimetry

Permalink
https://escholarship.org/uc/item/77j8z99w

Journal
The Journal of Chemical Thermodynamics, 56

Author
Sahu, Sulata Kumari

Publication Date
2013

Peer reviewed
The standard molar enthalpies of formation of Pb$_2$Fe$_2$O$_5$(s) and PbFe$_5$O$_{8.5}$(s) by acid solution calorimetry

Sulata Kumari Sahu, Rajesh Ganesan, T. Gnanasekaran

Liquid Metals and Structural Chemistry Division, Chemistry Group, Indira Gandhi Centre for Atomic Research, Kalpakkam 603 102, India

Abstract

The standard molar enthalpies of formation, $\Delta H^0_m$ (298.15 K) of Pb$_2$Fe$_2$O$_5$(s) and PbFe$_5$O$_{8.5}$(s) have been determined using acid solution calorimetry. The enthalpies of solution of the compounds Pb$_2$Fe$_2$O$_5$(s) and PbFe$_5$O$_{8.5}$(s), as well as those of mixtures of Fe$_2$O$_3$(s) and Pb$_3$O$_4$(s) in HCl (aq, 6 mol dm$^{-3}$) at 298.15 K were measured. Using these values, the standard enthalpies of formation ($\Delta f H^0_m$) of Pb$_2$Fe$_2$O$_5$(s) and PbFe$_5$O$_{8.5}$(s) were determined as (1324.2 ± 11.1) kJ mol$^{-1}$ and (2347.8 ± 10.7) kJ mol$^{-1}$, respectively.

1. Introduction

Lead and lead-bismuth eutectic alloy are considered as suitable candidate coolants for the Accelerator Driven Sub-critical Systems (ADS) due to their desirable physical and chemical properties [1]. However, these coolants are highly corrosive towards the structural materials and this poses a critical challenge for their use. One of the approaches to reduce the corrosion is controlling the oxygen concentration thereby forming a protective oxide film on the surface of the structural steels. Such technique was first developed and deployed in Russia [2–4] and is being studied extensively worldwide [5,6]. The oxide film effectively separates the base material from LBE and the direct dissolution of the steel becomes negligible as the diffusion coefficients of the alloying components of steel in the oxide are very low [7,8]. Thermochemical data on Pb–M–O and Bi–M–O (M = alloying components in steel) systems are needed to understand the formation and stability of the oxide film over the surface in the lead and LBE coolant circuit. Phase diagram of Pb–Fe–O system has been established recently and this system has three ternary compounds namely Pb$_2$Fe$_2$O$_5$(s), PbFe$_5$O$_{8.5}$(s) and PbFe$_{12}$O$_{19}$(s) [9]. This paper presents the enthalpy of formation of Pb$_2$Fe$_2$O$_5$(s) and PbFe$_5$O$_{8.5}$(s) determined using acid solution calorimetry.

2. Experimental

2.1. Chemicals

Fe$_2$O$_3$(s) powder (mass fraction purity > 0.9999 on metal basis, M/s Alfa Aesar, UK), Pb$_3$O$_4$(s) (mass fraction purity > 0.99 on metal basis, M/s Aldrich Chem. Co, USA) and PbO(s) powder (mass fraction purity > 0.99 on metal basis, M/s Aldrich Chem. Co., USA) were the starting reagents used. Thermogravimetry experiments coupled with evolved gas analysis showed that PbO(s) and Fe$_2$O$_3$(s) contained 1.37 wt% and 0.17 wt% of moisture, respectively. It was also found that PbO(s) contained 2 wt% lead carbonate impurity. The PbO(s) powder was therefore heated in argon atmosphere at 773 K for 2 h while the Fe$_2$O$_3$(s) powder was calcined in air at 523 K for 2 h to remove the moisture before using them in experiments. Fe(NO$_3$)$_3$.9H$_2$O(s) (mass fraction purity > 0.9999 on metal basis, M/s Aldrich Chem. Co., USA) was also used for preparing finely divided Fe$_2$O$_3$(s).

2.2. Compound preparation

The compounds, Pb$_2$Fe$_2$O$_5$(s) and PbFe$_5$O$_{8.5}$(s) were prepared by solid state reaction and solution route, respectively. Pb$_2$Fe$_2$O$_5$(s) was prepared by the solid-state reaction of mixtures of appropriate molar ratios of lead and iron oxide powders. The mixtures were taken in the form of compacted pellets, heated in alumina crucibles in ambient air at 998 K for 50 h with one intermediate grinding and finally quenched in ice cold water. The compound ‘PbFe$_5$O$_{8.5}$(s)’ is non-stoichiometric with its stoichiometry ranging from PbO–2Fe$_2$O$_3$ to PbO–2.5Fe$_2$O$_3$. However for the present work, the
compound with exact composition of PbFe$_2$O$_8$(s) was prepared by co-precipitation method and used. For this preparation, stoichiometric amounts of PbO and high purity iron powder (mass fraction purity > 0.999 on metal basis, M/s Alfa Aesar, UK) were first dissolved in minimum amount of nitric acid and the resultant nitrate solution was added to an excess amount of ammonium hydroxide solution. The precipitate formed was then filtered, dried, pelletized and heated in air at 1048 K for 24 h. The products obtained by all these methods of preparation were characterized by X-ray diffraction using Siemens D500 X-ray powder diffractometer with Cu K$_\alpha$ radiation and graphite monochromator. The XRD patterns obtained for Pb$_2$Fe$_2$O$_5$(s) and PbFe$_5$O$_8$(s) matched with the patterns reported in JCPDS files for these compounds, viz., 33-0756 and 49-0753, respectively.

Commercially available Fe$_2$O$_3$(s) powders are usually sintered at high temperature and hence require prolonged time for their dissolution in the calorimetric solvent, namely HCl (aq, 6 mol dm$^{-3}$). To enhance the dissolution rate, fine Fe$_2$O$_3$(s) powder was prepared. This was achieved by dissolving high purity ferric nitrate in distilled water followed by precipitation as Fe(OH)$_3$ by the addition of ammonium hydroxide solution. The precipitate was filtered, dried and heated at 623 K for 4 h in air and the product was analysed by XRD.

2.3. Calorimetric technique

The enthalpy of formation of Pb$_2$Fe$_2$O$_5$(s) and PbFe$_5$O$_8$(s) were determined employing acid solution calorimetry and the details of the experimental set up are described in our earlier publication [10]. The temperature of the water bath was maintained within ±0.002 K and the accuracy of measurement of temperature using a thermometer inside the calorimeter was within ±0.001 K.

The performance of the calorimeter was tested with KCl (SRM 1655, M/s.N.B.S., USA) dissolution in 0.300 dm$^3$ double distilled water. The molar enthalpy of solution of KCl in distilled water at infinite dilution derived in this study was: $\Delta_{m}H^\circ = 298.15 K$ for KCl = 17.15 ± 0.06 kJ mol$^{-1}$. This value agreed well with the value of 17.21 ± 0.01 kJ mol$^{-1}$ reported by Venugopal et al. [11] and N.B.S. value of 17.241 ± 0.018 kJ mol$^{-1}$ [12]. The calorimeter performance was also tested with tris(hydroxyl methyl) amino-methane (TRIS). The enthalpy of solution was measured by dissolving known amount of TRIS (0.997 mass fraction purity) from MERK, UK, in 100 cm$^3$ of 0.1 mol dm$^{-3}$ HCl (aq) and the results are given in table 1. The value of the molar enthalpy of solution of TRIS measured in the present work is −29.99 ± 0.30 kJ mol$^{-1}$ which is in agreement with the NIST value of −29.770 ± 0.032 kJ mol$^{-1}$ [13]. The results obtained for KCl and TRIS dissolution which is exothermic and endothermic, respectively, established the suitability of the experimental set up for calorimetric measurements. Measurements were also carried out to quantify the thermal energy released during the breaking of the bulb by a blank run. However, the heat energy released during the process was found to be within the detection limit of temperature of the calorimeter (±0.001 K). It is to be pointed out that, the glass bulb was designed with ultra thin walled bulb which breaks completely into pieces with a little touch of the push rod, allowing the solutes to mix with the calorimetric solvent. In such case, the thermal energy associated with the breakage of the bulb containing the sample is expected to be negligible, which is evident from the calibration runs of KCl and TRIS in the respective solvents.

Calorimetric measurements involving samples of the lead ferrites, Fe$_2$O$_3$(s) and PbO$_2$(s) were carried out in HCl (aq, 6 mol dm$^{-3}$). The sample for the experiment was weighed accurately, placed inside the sample tube along with a glass push rod and isolated the sample from ambient using an O-ring. These operations were carried out inside an argon atmosphere glove box. 0.300 dm$^3$ of HCl (aq, 6 mol dm$^{-3}$) was transferred into calorimetric vessel and equilibrated at the bath temperature. The calorimeter was fitted with its flange and all the components were allowed to equilibrate at the bath temperature with the stirrer rotating at a constant speed. When the temperature of the calorimeter was in equilibrium with the surrounding water bath, a steady temperature signal was obtained. Under these conditions, the bulb containing the sample was broken and allowed to dissolve in the solvent, and the calorimeter signal was recorded. The maximum time taken for dissolution of samples during these experiments was 7 min. The system was calibrated electrically in situ before and after each of this dissolution experiment. The temperature change $\Delta T$ during electrical calibration as well as during sample dissolution was corrected for heat exchange between calorimeter and surroundings by the method suggested by Kubaschewski and Alcock [14] and was used for the evaluation of the enthalpy change of the reaction. Experiments were repeated for obtaining the reproducibility.

| Table 1 | The enthalpy of solution $\Delta_{m}H^\circ$ of TRIS(s) in 0.100 dm$^3$ of 0.1 M HCl at T = 298.15 K (Molar mass of TRIS: 121.1). |
| Run | Mass of TRIS / g (g) | Experimental enthalpy change, $\Delta H$ (J) | Molar enthalpy of solution, $\Delta_{m}H^\circ$ (kJ mol$^{-1}$) |
| 1 | 0.2046 | −50.45 | −29.86 |
| 2 | 0.2980 | −74.18 | −30.14 |
| 3 | 0.4013 | −97.84 | −29.53 |
| 4 | 0.4182 | −104.62 | −30.30 |
| 5 | 0.4014 | −99.79 | −30.11 |
| Average: | | | −(29.99 ± 0.30)$^a$ |

$^a$ Uncertainty is the standard deviation from the mean.
TABLE 3
Reaction scheme for the standard molar enthalpy of formation of Pb2Fe2O5(s), ΔHf°m at 298.15 K; ΔH denotes enthalpy of reaction ΔHf°m
(Pb2Fe2O5, cr) = ΔH(1) + ΔH(2) + ΔH(3).

<table>
<thead>
<tr>
<th>S. no.</th>
<th>Reaction</th>
<th>ΔHf°m (kJ mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>(2/3) PbO(s) + FeO(s) = Pb2Fe2O5(s) + (1/3)O2</td>
<td>ΔH(1) = −(216.1 ± 8.5)</td>
</tr>
<tr>
<td>2</td>
<td>(2/3) PbO(s) + 2O2(g) = Pb2O3(s)</td>
<td>ΔH(2) = (2/3) × (−718.8 ± 6.3) = −479.2 ± 4.2</td>
</tr>
<tr>
<td>3</td>
<td>2Fe(s) + 3/2O2(g) = Fe2O3(s)</td>
<td>ΔH(3) = (−823.4 ± 3.3)</td>
</tr>
<tr>
<td>4</td>
<td>2Pb(s) + 2Fe(s) + (5/2)O2 (g) = Pb2Fe2O5(s)</td>
<td>ΔH(4) = −(1324.2 ± 11.1)</td>
</tr>
</tbody>
</table>

TABLE 4
Reaction scheme for the standard molar enthalpy of formation of PbFe5O8.5(s), ΔHf°m at 298.15 K; ΔH denotes enthalpy of reaction ΔHf°m
(PbFe5O8.5, cr) = ΔH(8) − ΔH(5) − ΔH(6) − ΔH(7).

<table>
<thead>
<tr>
<th>S. no.</th>
<th>Reaction</th>
<th>ΔHf°m (kJ mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>(1/3)PbO(s) + (5/2)FeO(s) = PbFe5O8.5(s) + (1/6)O2(g)</td>
<td>ΔH(5) = (49.7 ± 8.0)</td>
</tr>
<tr>
<td>2</td>
<td>(1/3)PbO(s) + 2O2(g) = PbO2(s)</td>
<td>ΔH(6) = (1/3) × (−718.8 ± 6.3) = −239.6 ± 2.1</td>
</tr>
<tr>
<td>3</td>
<td>(5/2)Fe2O3(s) + (3/2)O2(g) = PbFe5O8.5(s)</td>
<td>ΔH(7) = (5/2) × (−823.4 ± 3.3) = −2058.5 ± 8.3</td>
</tr>
<tr>
<td>4</td>
<td>Pb(s) + 5Fe(s) + 4.25O2(g) = PbFe5O8.5(s)</td>
<td>ΔH(8) = (2347.8 ± 10.7)</td>
</tr>
</tbody>
</table>

3. Results and discussion

In the compounds Pb2Fe2O5 and PbFe5O8.5, valences of Pb and Fe are +2 and +3, respectively. Based on the studies on dissolution of Fe2O3 under the calorimetric condition within a reasonable time period, 6 M HCl was chosen as calorimetric solvent among the various mineral acids with varying concentrations tested. It also dissolved the ternary compounds, viz., Pb2Fe2O5 and PbFe5O8.5. However, in the case of PbO, it precipitated as PbCl2. On the other hand, Pb2O3 was found to dissolve completely in 6 M HCl. This could be probably due to the formation of a soluble complex in conc. HCl facilitated by Pb2O3. Hence, Pb2O3 was chosen for determining enthalpy of solution instead of PbO.

The results of the measurements of enthalpy of solution for the compounds Pb2Fe2O5(s) and PbFe5O8.5(s) and for the starting materials PbO(s) and Fe2O3(s) are given in table 2. The thermochemical reaction schemes used to derive the standard molar enthalpies of formation of PbO(s) and PbFe5O8.5(s) are given in tables 3 and 4, respectively. As mentioned in table 2, the enthalpy correction for the evolution of O2 gas was calculated and found to be negligible. However, due to the lack of facility and provision for carrying out controlled dissolution of oxygen in present calorimeter, we could not carry out the measurement of the enthalpy of dissolution of O2 in 6 M HCl.

The molar enthalpies of solution of Pb2Fe2O5(s) and PbFe5O8.5(s) and the starting materials PbO(s) and Fe2O3(s), deduced from the experiments are −270.7 ± 6.3 kJ mol⁻¹, −181.0 ± 1.4 kJ mol⁻¹, −294.0 ± 7.3 kJ mol⁻¹ and −53.1 ± 3.0 kJ mol⁻¹, respectively. The enthalpy ΔH (1), of the reaction: (2/3) PbO(s) + FeO(s) → Pb2-Fe2O5(s) + 0.33O2, was obtained in table 3 by using the Hess’s law, by subtracting the enthalpy of dissolution of Pb2Fe2O5(s) from that of (2/3) PbO(s) + FeO(s) and is −216.1 ± 8.5 kJ mol⁻¹. Similarly, enthalpy change ΔH (5) of the reaction: (1/3) PbO(s) + (5/2) Fe2O3(s) → PbFe5O8.5(s) + 0.16O2, given in table 4, was obtained by subtracting the enthalpy of dissolution of PbFe5O8.5(s) from that of (1/3) PbO(s) + (5/2) Fe2O3(s) and is −49.7 ± 8.0 kJ mol⁻¹. In all these measurements, the concentration ranges are narrow and hence extrapolation at infinite dilution could not be made. As the concentrations are very dilute, in the order of mmol l⁻¹, it is assumed that the enthalpy of solution is constant down to infinite dilution. By using the literature data on standard molar enthalpies of formation of PbO(s) and Fe2O3(s) [16], the standard molar enthalpies of formation of Pb2Fe2O5(s) and PbFe5O8.5(s) from the constituent elements, were obtained as −(1324.2 ± 11.1) kJ mol⁻¹ and −(2347.8 ± 10.7) kJ mol⁻¹, respectively.

4. Conclusions

The standard enthalpy of formation of Pb2Fe2O5(s) and PbFe5O8.5(s), at 298.15 K were determined by acid solution calorimetry and are found to be −(1324.2 ± 11.1) kJ mol⁻¹ and −(2347.8 ± 10.7) kJ mol⁻¹, respectively. These thermochemical data are reported for the first time.

Acknowledgements

The authors acknowledge Dr. G. Panneerselvam, Dr. K.V.G. Kutty and his team for their help in recording XRD pattern of the samples. One of the authors (SKS) acknowledges Department of Atomic Energy, India, for providing the financial support.

References


JCT 11-529