The standard molar enthalpies of formation of $Pb_2CrO_5(s)$ and $Pb_5CrO_8(s)$ by acid solution calorimetry

Sulata Kumari Sahu [a], Rajesh Ganesan [a], T.G. Srinivasan [b], T. Gnanasekaran [a,*]

[a] Liquid Metals and Structural Chemistry Division, Chemistry Group, Indira Gandhi Centre for Atomic Research, Kalpakkam 603 102, India
[b] Fuel Chemistry Division, Chemistry Group, Indira Gandhi Centre for Atomic Research, Kalpakkam 603 102, India

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ABSTRACT

The standard molar enthalpies of formation, $\Delta_f H_m^\circ$ (298.15 K) of $Pb_2CrO_5(s)$ and $Pb_5CrO_8(s)$ were determined using an isoperibol calorimeter. The enthalpies of solution of pure compounds, *viz.*, $Pb_2CrO_5(s)$, and $Pb_5CrO_8(s)$ as well as mixtures *viz.*, {$PbCrO_4(s) + PbO(s)$} and {$PbCrO_4(s) + 4PbO(s)$} in HNO_3 (aq., 8 mol · dm^{-3}) at $T = 298.15$ K were measured. Using these values, $\Delta_f H_m^\circ$ (298.15 K) of $Pb_2CrO_5(s)$ and $Pb_5CrO_8(s)$ were determined as $-(1171.5 \pm 1.7)$ kJ · mol^{-1} and $-(1850.6 \pm 8.7)$ kJ · mol^{-1}, respectively.

1. Introduction

A study of the interaction of liquid lead with components of steel in the presence of trace amount of oxygen is needed in the context of lead-cooled nuclear reactors and accelerator driven sub-critical systems (ADSS) [1]. Corrosion in the (lead + steel) systems is mitigated by the formation of an adherent oxide layer on the structural steels. A detailed knowledge of the composition and the thermochemical data of this oxide layer are needed to exploit this process. Understanding the thermochemistry of ternary compounds of the (Pb + Cr + O) and (Pb + Fe + O) systems is of considerable interest in this regard. Preparation and thermal stability of the compounds existing in (Pb + Cr + O) system have been reported in the literature [2–8]. Three stable compounds, *viz.*, $PbCrO_4(s)$, $Pb_2CrO_5(s)$ and $Pb_5CrO_8(s)$ exist in this system. The enthalpy of formation of $PbCrO_4(s)$ at $T = 298$ K, $\Delta_f H_{m298K}^\circ$, had been determined by Dellien *et al.* [9] by solution calorimetry with NaOH and Na_4EDTA as the solvents. No corresponding data for $Pb_2CrO_5(s)$ and $Pb_5CrO_8(s)$ are available in the literature. Recently, the partial phase diagram of (Pb + Cr + O) system was established at the author's laboratory by long term equilibration studies [7] and also the standard molar Gibbs free energy of formation of $Pb_5CrO_8(s)$, $Pb_2CrO_5(s)$, and $PbCrO_4(s)$ were determined [8] by measuring equilibrium oxygen pressures over appropriate ternary phase fields either by manometry or by solid oxide electrolyte based emf cells. In the present work, the enthalpies of formation of $Pb_2CrO_5(s)$ and $Pb_5CrO_8(s)$ at $T = 298$ K have been determined using acid solution calorimetry.

2. Experimental

2.1. Chemicals

High purity PbO (mass fraction purity >0.999 on metal basis, M/s Aldrich Chem. Co., USA) and Cr_2O_3 (mass fraction purity >0.99999 on metal basis, M/s Johnson Matthey Materials Technology, UK) powders were used for preparation of ternary compounds. Thermo gravimetric analyses showed that PbO(s) absorbs carbon dioxide (∼0.1 wt%) and $Cr_2O_3(s)$ absorbs moisture (∼1.8 wt%) on prolonged exposure to ambient air. Hence, PbO(s) and $Cr_2O_3(s)$ were calcined for 3 h under flowing argon gas at temperatures of (673 and 973) K, respectively, stored in desiccators and handled with very short exposure to ambient air. Doubled distilled AR grade HNO_3 and HCl which were diluted with the distilled water to the required concentrations were used as the calorimetric solvents.

2.2. Compound preparation

$Pb_5CrO_8(s)$, $Pb_2CrO_5(s)$ and $PbCrO_4(s)$ were prepared by solid state reaction between powders of PbO(s) and $Cr_2O_3(s)$ taken in the required stoichiometric ratios. The conditions used for preparation of these ternary compounds are described in our earlier publication [7]. The compounds were characterised by X-ray diffraction using a Siemens D500 X-ray powder diffractometer with Cu Kα radiation and graphite monochromator. The XRD patterns obtained for $Pb_5CrO_8(s)$, $Pb_2CrO_5(s)$ and $PbCrO_4(s)$ matched

with the patterns reported in JCPDS files for these compounds, *viz.*, 49-0970, 29-0768, and 73-2059, respectively.

2.3. Calorimetric technique

The schematic diagram of the experimental set up is shown in figure 1. The main constituent of the isoperibol calorimeter is the vessel in which the reaction of interest takes place. It was made from a double walled glass Dewar of 0.4 dm^3 capacity with an evacuated inter space. The top of the vessel was fitted with an annular Perspex flange having an O-ring groove. It also had a mating top-cover flange with leak tight fittings for introducing a stirrer, a sample bulb, a heater enclosure and a thermistor. The Dewar with all the fittings was kept immersed into a water bath that maintained the temperature within ±0.002 K so as to minimise the exchange of heat with surroundings. The sample was taken inside a small glass tube provided with a thin walled bulb at the bottom. The glass tube had a glass push rod which was sealed to the inner wall of the sample tube using an O-ring. This arrangement enabled isolation of the sample from surroundings. A stirrer, made up of PTFE, enabled uniform stirring of the calorimetric fluid in the Dewar. The stirrer was driven by a motor so that the frictional heat generated by the stirring was constant both during the experiment as well as during the calibration. The calorimeter was calibrated by electrical as well as by chemical methods. A PTFE coated resistance wire with very low temperature coefficient of resistance (KARMA) was used as a calibration heater such that the change of resistance would be negligible during the calibration. The resistance of the heater was (4.261 ± 0.005) Ω. The heater was

enclosed in a glass bulb to avoid any possible interaction with the solvent. Silicone oil, which is inert and has a low heat capacity and low vapour pressure, was added to the bulb to immerse the heater. This design enabled conduction of heat from the heater to the calorimetric fluid. The electrical calibration was performed by applying a constant current using a stable power source, for a known period of time. The current and duration of its passage for the electrical calibration was decided by the time taken for the sample to dissolve completely under the experimental conditions and the weight of the sample taken for each experiment. The current was measured across a precision resistor (1.000 Ω) of suitable current rating, connected in series. The temperature was measured using a thermistor (M/s PARR Instruments Company, USA) connected to a data acquisition system, interfaced to a personal computer and was recorded as a function of time. Chemical calibration was carried out using KCl (SRM 1655, M/s N.B.S., USA) and double distilled water was used as the solvent. The sample for calibration was weighed accurately and taken inside the sample tube. 0.300 dm^3 of double distilled water 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 is in equilibrium with the surrounding water bath, a steady temperature signal was obtained. After a steady signal had been obtained from the control unit, the bulb was broken, the sample was allowed to dissolve in the solvent and the calorimeter signal was recorded. The system was calibrated electrically *in situ* before and after each of this calibration experiment. The temperature change ΔT during
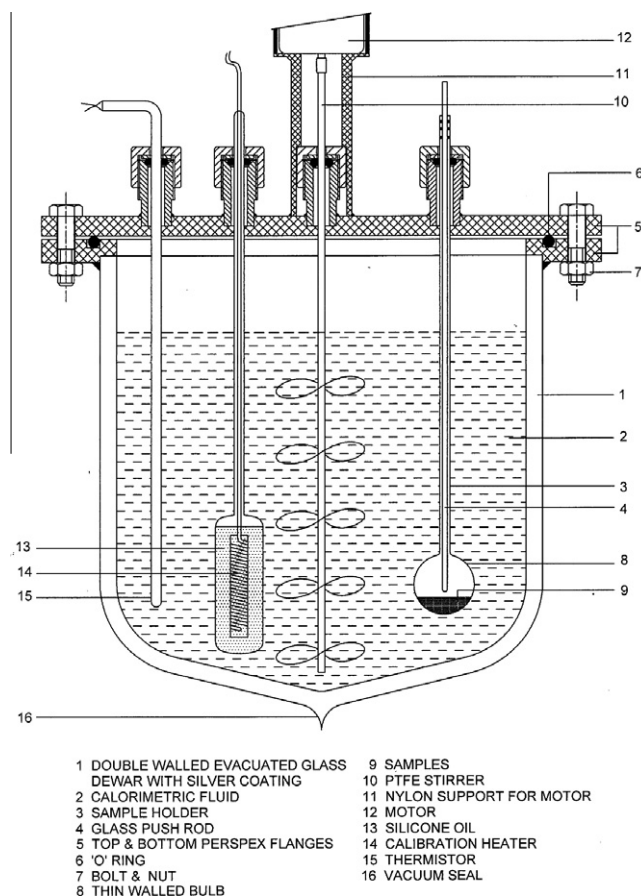

FIGURE 1. Schematics of acid solution calorimeter.

1 DOUBLE WALLED EVACUATED GLASS DEWAR WITH SILVER COATING
2 CALORIMETRIC FLUID
3 SAMPLE HOLDER
4 GLASS PUSH ROD
5 TOP & BOTTOM PERSPEX FLANGES
6 'O' RING
7 BOLT & NUT
8 THIN WALLED BULB
9 SAMPLES
10 PTFE STIRRER
11 NYLON SUPPORT FOR MOTOR
12 MOTOR
13 SILICONE OIL
14 CALIBRATION HEATER
15 THERMISTOR
16 VACUUM SEAL

TABLE 1
The enthalpy of solution $\Delta_{sol}H_m^\circ$ of KCl(s) in 0.300 dm^3 of water at T = 298.15 K (molar mass of KCl: 74.56).

Run	Mass of KCl/g	Experimental enthalpy change, ΔH/J	Molar enthalpy of solution, $\Delta_{sol}H_m$/(kJ · mol^{-1})	Molar enthalpy of solution at infinite dilution, $\Delta_{sol}H_m^\infty$/(kJ · mol^{-1})
1	0.2790	65.32	17.46	17.24
2	0.2401	55.99	17.39	17.16
3	0.2782	64.61	17.32	17.08
4	0.2820	65.73	17.38	17.14
5	0.2710	63.18	17.38	17.15
				Average: (17.15 ± 0.06)[a]

[a] Uncertainty is the standard deviation from the mean.

TABLE 2
The standard molar enthalpies of solution of Pb$_2$CrO$_5$(s) and mixture of {PbO(s) + PbCrO$_4$(s)} in 0.300 dm^3 of HNO$_3$ (aq., 8 mol · dm^{-3}) at T = 298.15 K.

Sample	Mass of sample/g	Experimental enthalpy change, ΔH/J	Molar enthalpy of solution, $\Delta_{sol}H_m$/(kJ · mol^{-1})
Pb$_2$CrO$_5$(s)	0.2947	−36.18	−67.08
(M: 546.371 g · mol^{-1})	0.3050	−36.91	−66.12
	0.2648	−31.90	−65.82
	0.2041	−24.45	−65.45
	0.2228	−27.05	−66.33
	Average $\Delta_{sol}H_m$ = −(66.16 ± 0.61)[a]		
PbO(s) + PbCrO$_4$(s)	0.3192	−53.30	−91.23
(M: 546.371 g · mol^{-1})	0.2861	−48.45	−92.53
	0.3066	−52.24	−93.09
	0.3132	−52.67	−91.88
	0.3635	−62.02	−93.22
	0.3424	−58.59	−93.49
	Average $\Delta_{sol}H_m$ = −(92.57 ± 0.87)[a]		

[a] Uncertainty is the standard deviation from the mean.