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Standard molar Gibbs free energy of formation of Pb$_5$CrO$_8$(s), Pb$_2$CrO$_5$(s), and PbCrO$_4$(s)

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**A R T I C L E   I N F O**

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**A B S T R A C T**

Standard molar Gibbs free energy of formation of ternary oxides Pb$_5$CrO$_8$(s), Pb$_2$CrO$_5$(s), and PbCrO$_4$(s) were determined by measuring equilibrium oxygen partial pressures over relevant phase fields using manometry and solid oxide electrolyte based emf methods and are given by:

\[
\Delta G^\circ_{\text{Pb}_5\text{CrO}_8}(s) = -1473.6 \pm 0.1 \text{kJ} \cdot \text{mol}^{-1}
\]

\[
\Delta G^\circ_{\text{Pb}_2\text{CrO}_5}(s) = -1491.3 \pm 0.1 \text{kJ} \cdot \text{mol}^{-1}
\]

\[
\Delta G^\circ_{\text{PbCrO}_4}(s) = -1358.0 \pm 0.1 \text{kJ} \cdot \text{mol}^{-1}
\]

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1. Introduction

Lead and Lead–Bismuth eutectic alloy are considered as suitable candidates for the Accelerator Driven Sub-critical Systems (ADS) as spallation target and coolant due to their favorable nuclear, thermal, and physical properties [1]. However, they are highly corrosive towards the structural steels. One of the approaches to minimize this corrosion is to control the dissolved oxygen content in these liquid metals so as to form a protective oxide film on the steel surface [2–6]. Formation of a protective oxide film on the surface of the steel reduces direct dissolution of the steel components owing to the low diffusion coefficients of the alloying components through the oxide film [7]. To understand the composition of the protective oxide film and its stability, a detailed knowledge on the phase diagrams of (Pb + Cr + O) system at 973 K has been established by the present authors [8]. In the present work, standard molar Gibbs free energies of formation of PbCrO$_4$(s), Pb$_2$CrO$_5$(s), and Pb$_5$CrO$_8$(s) have been determined by measuring equilibrium oxygen pressures over appropriate phase fields by manometry and solid oxide electrolyte based emf cells and the results obtained are reported.

2. Literature survey

Preparation and thermal stability of the compounds existing in (Pb + Cr + O) system have been reported in the literature [8–13]. Three stable ternary compounds, viz., Pb$_5$CrO$_8$(s), Pb$_2$CrO$_5$(s), and PbCrO$_4$(s) are known in this system and are reported to be stable in the temperature range of (478 to 1030) K, (873 to 1197) K, and (948 to 1108) K, respectively. A detailed account of this is described elsewhere [8]. Through experiments involving thermal analysis in ambient of known oxygen partial pressures, Gadalla and Abadir [13] determined the standard Gibbs free energy of the two reactions:

\[
\text{a)} \ 2 \text{CrO}_3(l) + 2 \text{PbO}_2(s) = 2 \text{PbCrO}_4(s) + \text{O}_2(g) \quad (478 \text{ to } 508) \text{K}
\]

\[
\text{b)} \ (8/3) \text{PbCrO}_4(s) = (4/3) \text{Pb}_2\text{CrO}_5(s) + (2/3) \text{Cr}_2\text{O}_3(s) + \text{O}_2(g) \quad (1030 \text{ to } 1055) \text{K}
\]

The data obtained were reported as $\Delta G^\circ_{\text{react}} /[\text{kJ} \cdot \text{mol}^{-1}] = 108.43 + 0.2134(T/\text{K})$ and $304.60 + 0.2888(T/\text{K})$, respectively for the above reactions. It is to be pointed out that these measurements were made only in a limited temperature range (~25 to 30) K under four controlled ambient oxygen pressures. The enthalpy of formation of PbCrO$_4$(s) at 298 K ($\Delta H^\circ_{\text{f,298}}$) had been determined by Dellien et al. [14] by solution calorimeter with NaOH and Na$_4$EDTA as the calorimetric solvent. $\Delta H^\circ_{\text{f,298}}$ of PbCrO$_4$(s) was found to be $-927.02 \text{kJ} \cdot \text{mol}^{-1}$. The uncertainty in this data was calculated to be $\pm 1.39 \text{kJ} \cdot \text{mol}^{-1}$ by taking into account the uncertainty in the standard enthalpies of formation of PbO(s) and CrO$_3$(s) in the literature [15,16].

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3. Experimental

3.1. Materials

Pb₅CrO₈(s), Pb₂CrO₅(s), and PbCrO₄(s) were prepared by solid state reaction between powders of Pb₃O₄(s) (mass fraction purity > 0.99 on metal basis, M/s Aldrich Chem. Co. USA) and Cr₂O₃(s) (mass fraction purity > 0.99999 on metal basis, M/s Johnson Matthey Materials Technology, UK) taken in the required stoichiometric ratios. These compounds were also prepared using PbO(s) (mass fraction purity > 0.999 on metal basis, M/s Aldrich Chem. Co., USA) and Cr₂O₃(s) (mass fraction purity > 0.99999 on metal basis, M/s Johnson Matthey Materials Technology, UK) as starting materials. The conditions used for preparation of these ternary compounds are described in our earlier publication [8]. 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 Pb₅CrO₈(s), Pb₂CrO₅(s), and PbCrO₄(s) matched with the patterns reported in JCPDS files for these compounds, viz., 49-0970, 29-0768, and 73-2059, respectively.

3.2. Equilibrations for confirmation of coexistence of phases

In the present work, oxygen pressures were measured in the three phase fields, namely, Pb₅CrO₈(s)–PbO(s)–Cr₂O₃(s), Pb₅CrO₈(s)–Pb₂CrO₅(s)–Cr₂O₃(s), and Pb₂CrO₅(s)–PbCrO₄(s)–Cr₂O₃(s) in the temperature range of (837 to 1008) K, (859 to 1021) K and (863 to 1093) K, respectively. The existence of these phase fields at 973 K was established in our earlier work [8]. To confirm the existence of the phase fields over a large temperature range, additional long term equilibration experiments were conducted. For equilibrations in the PbO(s)–Cr₂O₃(s)–Pb₅CrO₈(s) phase field, an overall sample composition of Pb₀.2₄Cr₀.1₉O₀.₅₇ was chosen with two sets of starting materials, namely Pb(s) + Cr₂O₃(s) + Pb₅CrO₈(s) and PbO(s) + Cr₂O₃(s) + Pb₅CrO₈(s). For equilibration in Pb₂CrO₅(s)–Pb₅CrO₈(s)–Cr₂O₃(s) phase field, an overall composition Pb₀.₁₉Cr₀.₆₀O₀.₆₁ was chosen with PbO(s) + Cr₂O₃(s) + Pb₂CrO₅(s) and Pb₂CrO₅(s) + Pb₅CrO₈(s) + Cr₂O₃(s) as starting materials. The equilibration at 723 K was carried out for 400 h. The duration of equilibration was 240 h at (823 and 1023) K. Similarly for equilibrations in Pb₂CrO₅(s)–Pb₅CrO₈(s)–Cr₂O₃(s) phase field, a sample of the overall composition Pb₀.₁₆Cr₀.₁₉O₀.₆₅ was prepared from 5:1:1 molar ratio of Pb₂CrO₅(s), Pb₅CrO₈(s), and Cr₂O₃(s) and used. The duration of equilibration was 400 h at 723 K. The duration of equilibration at (823, 1023, and 1093) K was 240 h.

3.3. Emf measurements

The following two galvanic cells were constructed and studied:

\[
\text{(I) } \begin{align*}
\text{Pt, } \text{PbO(s), } & \text{Cr₂O₃(s), } \text{YSZ}, \text{O}_2; \text{Pt}(+) \\
\text{Pt, } \text{Pb₂CrO₅(s), } & \text{Cr₂O₃(s), } \text{YSZ}, \text{O}_2; \text{Pt}(+)
\end{align*}
\]

\[
\text{(II) } \begin{align*}
\text{Pt, } \text{PbO(s), } & \text{Cr₂O₃(s), } \text{YSZ}, \text{O}_2; \text{Pt}(+) \\
\text{Pt, } \text{Pb₂CrO₅(s), } & \text{Cr₂O₃(s), } \text{YSZ}, \text{O}_2; \text{Pt}(+)
\end{align*}
\]

The schematics of the experimental assembly of the galvanic cells are shown in figure 1. One end closed yttria stabilised zirconia (YSZ) solid electrolyte tube having a flat bottom (13 mm OD, 9 mm ID and 300 mm long) and supplied by M/s Nikkato Corporation, Japan was used for constructing the galvanic cells. For both cell-I and II, same electrolyte tube was used. The reference electrode for the cell was prepared by applying platinum paste (M/s Eltecks Corporation, India) over the inner bottom surface of the electrolyte tube and heating it at 1373 K for 2 h in air. This resulted in a uniform and porous platinum film over the electrolyte surface. A Pt wire, co-fired with the platinum paste served as the electrical lead. A similar porous platinum electrode was formed on the external surface of the electrolyte tube. The performance of the emf cell was first tested by measuring the null emf by maintaining the identical oxygen pressures on both sides of the electrolyte.

FIGURE 1. Schematics of the solid oxide based galvanic cells used.
(air–air and oxygen–oxygen). Latter the Pt-electrode present at the external surface of the electrolyte tube was removed, thoroughly cleaned and used for measurements with sample electrodes. Two sample electrodes with different compositions but falling within the phase field of PbO(s)–Cr2O3(s)–Pb2CrO4(s) were used for measurements with cell-I. In a similar manner, two sets of emf measurements were carried out in the Pb2CrO4(s)–PbCr2O4(s)–Cr2O3(s) phase field with two sample electrodes of different overall composition. Dense pellets of the electrodes were obtained by mixing of the appropriate quantities of the constituent phases and pelleting followed by sintering at 973 K after placing the samples in alumina crucibles kept in vacuum sealed quartz ampoules for about 40 h. For use in the emf cell, the sample electrode was placed over a platinum disc placed inside an alumina crucible of appropriate dimension. The alumina crucible was in turn placed in a small quartz crucible. The alumina and quartz crucibles had a small hole at their bottom so that the electrical lead from the platinum disc can be easily brought out through them. The zirconia solid electrolyte tube was placed over the sample electrode and was fastened to a stainless steel coupling using a high temperature epoxy seal. This sample and electrolyte assembly was surrounded by a one end closed quartz tube which was also attached to the stainless steel coupling using a O-ring seal. The quartz crucible in which sample electrode and the electrolyte tube were placed had holes in its circumference. Through these holes a pair of kanthal wires connected to springs could be attached and tightly hung from the hooks provided in the inner surface of the stainless steel coupling. This arrangement ensured good contact between the electrolyte and sample electrode. The stainless steel coupling had provisions for placing a K-type thermocouple very close to electrode–electrolyte assembly so that the cell temperature can be measured accurately and also for flowing high purity argon and synthetic air (purity 99.999%, M/s Inox Air Products Ltd., India) through the sample and reference compartments, respectively. High purity argon was obtained by passing commercial argon through a purification assembly. The purification train consisted of columns of regenerated LINDE 4A molecular sieves and active Cu impregnated MgSiO3 pellets (popularly known as BASF catalyst) maintained at ambient temperature followed by three columns containing metallic copper turnings held at 773 K, titanium sponge held at 1173 K and calcium metal shots held at 773 K. The gas exiting from the outlet of the emf cell was again passed over another column containing calcium metal shots maintained at 773 K before letting it out to ambient air. The cell assembly was placed in the constant temperature zone of a furnace. Additionally a 100 mm long and hollow cylindrical stainless steel block was placed in the constant temperature zone of the furnace to further enhance the uniformity of the temperature in the zone. Using this arrangement the cell temperature could be controlled within ±0.2 K using a PID temperature controller. The stainless steel block was grounded to avoid any a.c. pickup in the emf signal. The cell temperature was measured using the K-type thermocouple which was calibrated prior to actual experiments against a standard calibrated thermocouple supplied by National Physical Laboratory, India. The cell emf was measured using a high impedance electrometer (input impedance > 10^14 Ω, M/s Keithley, USA, model-6514) and the temperature was measured using a multimeter (M/s Agilent Technologies, Malaysia, model: 34970A Data acquisition/switch unit). An IBM PC using GPIB interface acquired the data. The readings were recorded when the cell emf was stable within ±0.05 mV for at least 6 h. Attainment of equilibrium was tested by passing a small amount of current through the cell or by shorting the two electrical leads and testing for restoration of the pre-test emf. After completion of the emf measurements (which involved several heating and cooling cycles), the constituents of the sample electrodes were analysed by XRD.

3.4. Manometric measurements

The schematics of the leak tight assembly used for measuring the equilibrium oxygen pressures over the Pb2CrO4(s)–PbCr2O4(s)–Cr2O3(s) phase field is shown in figure 2. Stainless steel flanges having knife edges with copper gaskets were used for the joints in the assembly and a bellows sealed valve was used for its isolation from the vacuum system. The assembly consisted of a one end closed quartz tube of 30 mm outer diameter which held the sample and was attached to a knife edged flange using a high temperature epoxy seal. To minimize the free volume in the assembly, the free space was filled with evacuated and sealed quartz ampoules and the available volume was ~110 cc. The whole experimental assembly was evacuated to 0.0001 kPa, degassed and isolated for 5 days from vacuum system to check the leak tightness of the system. The pressure in the assembly was continuously measured using a capacitance manometer (M/s MKS Baratron®, USA, model: 627B) capable of measuring the pressure up to 266 kPa with a resolution of 0.0001 kPa in the pressure range measured. This manometer was attached to the experimental assembly through a stainless steel flange. The increase in pressure due to residual leak and degassing was found to be ~0.008 kPa in five days (~0.002 kPa/day).

Six runs of the pressure measurements were made with samples of different overall composition but falling within the phase field of investigation. For runs 1 to 3, a sample mixture with an overall composition of Pb0.10Cr0.28O0.62 was prepared in the form of porous pellets from 5:1:1 molar ratio of PbCrO4(s), Pb2CrO4(s), and Cr2O3(s), respectively and used. For runs 4 to 6, another sample of overall composition of Pb0.15Cr0.28O0.62 prepared from a 0.3:0.3:1 mole ratio of PbCrO4(s), Pb2CrO4(s), and Cr2O3(s) was used. The porous pellets were obtained by mixing the constituent phases followed by compacting them into pellets of 12.5 mm diameter and approximately 4 mm thickness under a pressure of 10 MPa. The resulting porous pellets were placed inside a recrystallised alumina crucible, which in turn was kept inside the one end closed quartz tube of the experimental assembly. The quartz tube was placed in the constant temperature zone of a nichrome wire wound furnace. Additionally a hollow cylindrical stainless steel block of 100 mm long was placed in the constant temperature zone of the furnace to further enhance the uniformity of the temperature in the zone.

The assembly with the equilibrium phase mixture inside was first evacuated down to 0.0001 kPa, heated to 523 K and held at that temperature under vacuum for 150 h for degassing of the system and the pellets. The equilibrium phase mixture was then heated to a desired temperature and the temperature was controlled to be within ±0.2 K. A K-type thermocouple was used to control the temperature of the furnace and S-type thermocouple positioned close to the phase mixture inside the quartz tube was used to measure the temperature of the sample.

The pressure and temperature data were acquired for every minute using the data acquisition system (M/s Agilent Technologies, Malaysia, model: 34970A Data acquisition/switch unit) through an IBM PC using RS-232 interface. At each experimental temperature, attainment of equilibrium was tested by disturbing the equilibrium by increasing the pressure using an external oxygen source (99.99%, M/s Inox Air Products Ltd., India) or by reducing the pressure through partial evacuation. After each disturbance, the pressure was found to return to the original equilibrium pressure confirming the equilibration conditions. To eliminate the systematic errors introduced into the measured values by the steady air leak (albeit low and equal to ~0.002 kPa/day), the experimental assembly with the sample inside was intermittently cooled to room temperature and the gas plenum was evacuated down to 0.0001 kPa before beginning the measurements at a new
experimental temperature. After completion of these pressure measurements involving several heating and cooling cycles, the phase composition of the sample was analysed by XRD.

4. Results and discussion

4.1. Equilibriations study

The XRD pattern of the samples obtained after their equilibriations at different temperatures in conjunction with our results in reference [8] confirmed the existence of these phase fields namely: (a) PbO(s)–Cr₂O₃(s)–Pb₅CrO₈(s) and Pb₅CrO₈(s)–Pb₂CrO₅(s)–Cr₂O₃(s) phase field in the temperature range of (723 to 1023) K and (b) that of Pb₂CrO₅(s)–PbCrO₄(s)–Cr₂O₃(s) phase field in the temperature range of (723 to 1093) K. The confirmation of the coexistence of the phases in the mentioned temperature range revealed that the phases Pb₂CrO₅ and Pb₅CrO₈ are stable down to 723 K as against the ranges of stability reported in the literature. Also the results obtained from the XRD after completion of the emf and pressure measurements (which involved several heating and cooling cycles), confirmed the presence of starting constituents at the end of the emf/pressure measurements. It is to be pointed out that the present experiment have shown PbCrO₄(s) is stable at least up to 1093 K, although its maximum temperature of stability was reported in the literature as 1030 K.

4.2. EMF measurements

Emf values measured as a function of temperature from cell-I are given in table 1. The variation of emf with temperature is shown in figure 3 and is given by the following least squares fitted expression:

$$E_I \pm 0.0006/V = 0.5426 - 2.439 \times 10^{-4} (T/K)$$

$$T = (837 \text{ to } 1008) \text{ K} \quad (1)$$

<table>
<thead>
<tr>
<th>TABLE 1</th>
<th>Variation of emf of cell-1 with temperature.</th>
</tr>
</thead>
<tbody>
<tr>
<td>T/K</td>
<td>E/mV</td>
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<tr>
<td>Run 1</td>
<td></td>
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<tr>
<td>871.6</td>
<td>330.2</td>
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<tr>
<td>970.8</td>
<td>306.1</td>
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<td>335.9</td>
</tr>
<tr>
<td>959.1</td>
<td>307.6</td>
</tr>
</tbody>
</table>

Run 1: measurements with samples of overall composition Pb₀.₂₇Cr₁.₆₀O₅.₇₇.  
Run 2: measurements with samples of overall composition Pb₀.₃₅Cr₁.₀₆O₅.₅₅.
The error given is the standard deviation of the least squares fitted line.

The chemical equilibrium at the sample electrode is represented as below:

$$5 \text{PbO}(s) + 1/2 \text{Cr}_2\text{O}_3(s) + 3/4 \text{O}_2(g) = \text{Pb}_3\text{CrO}_5(s).$$

$$\Delta G_m^{\text{Pb}_3\text{CrO}_5} = 5 \Delta G_m^{\text{PbO}(s)} + 1/2 \Delta G_m^{\text{Cr}_2\text{O}_3(s)} + 3/4 \Delta G_m^{\text{O}_2}.$$  

(2)

$$\Delta G_m^{\text{Pb}_3\text{CrO}_5(s)} = -3FE + 3/4RT \ln(\text{pO}_2^{\text{ref}}/\text{pO}_2).$$

By substituting the emf data given by equation (1) and by using the values of $\Delta G_m^{\text{PbO}(s)}$ and $\Delta G_m^{\text{Cr}_2\text{O}_3(s)}$ reported in references [17,18], the standard molar Gibbs free energy of formation of $\text{Pb}_3\text{CrO}_5(s)$ was derived and is given below:

$$\Delta G_m^{\text{Pb}_3\text{CrO}_5(s)}/(k\cdot \text{mol}^{-1}) = -1809.3 + 0.6845(T/K) \quad T = (837 to 1008) \text{K}.$$

(7)

Gadalla and Abadir [13] had reported the equilibrium partial pressures of oxygen over $\text{Pb}_3\text{CrO}_5(s)$-eutectic melt at four temperatures between (1063 and 1078) K from thermo-gravimetric measurements under four different oxygen partial pressures. By assuming the activity of $\text{Cr}_2\text{O}_3$ in this melt to be unity, the oxygen pressures reported by Gadalla and Abadir are compared with the oxygen pressures deduced from the present emf data of cell-I and are shown in figure 4. The results show that the oxygen partial pressures reported by Gadalla and Abadir [13] are several orders high. This could be due to non-equilibrium conditions in their measurements or due to non-validity of the assumption of $a_{\text{Cr}_2\text{O}_3} = 1$ made for this comparison.

Emf values obtained as a function of temperature from cell-II are given in table 2 and are shown in figure 3. They can be represented by the following least squares fitted expression:

$$E = (RT / 4F) \ln(p_{O_2}^{ref} / p_{O_2}),$$

$$4FE = \Delta G_m^{\text{Pb}_3\text{CrO}_5} - \Delta G_m^{\text{Pb}_3\text{CrO}_5}.$$  

(3)

$$\Delta G_m^{\text{Pb}_3\text{CrO}_5} = \Delta G_m^{\text{Pb}_3\text{CrO}_5} - 4FE.$$  

(4)

$$\Delta G_m^{\text{Pb}_3\text{CrO}_5} = -1809.3 + 0.6845(T/K) \quad T = (837 to 1008) \text{K}.$$

(5)
Δ\(G_m^{\Delta}\text{Pb}_2\text{CrO}_5(s)\) = \(-1.88E + 0.45RT \ln 0.21\)
+ 0.4 Δ\(G_m^{\Delta}\text{Pb}_2\text{CrO}_8(s)\) + 0.3 Δ\(G_m^{\Delta}\text{Cr}_2\text{O}_3(s)\).  \(\text{(10)}\)

By incorporating the values of emf from equation \((8)\) and using values of Δ\(G_m^{\Delta}\text{Pb}_2\text{CrO}_5(s)\) from expression \((7)\) and the data on Δ\(G_m^{\Delta}\text{Pb}_2\text{CrO}_5(s)\) from reference \([18]\), Δ\(G_m^{\Delta}\text{Pb}_2\text{CrO}_5(s)\) could be obtained as

Δ\(G_m^{\Delta}\text{Pb}_2\text{CrO}_5(s)\) ± 0.30/(kJ·mol\(^{-1}\)) = −1161.3 + 0.4059\(T/K\).
\(\text{T = (859 to 1021) K.} \quad \text{(11)}\)

4.3. Manometric measurements

The test of the vacuum assembly used for pressure measurement was carried out by studying the well-established \{\text{PbO(s) + Pb}_3\text{O}_4(s)\} system. The equilibrium oxygen pressures were measured between \((777 \text{ and } 865) K\). The data obtained are given in table 3 and are also shown in figure 5. Figure also compares the current data with those of Reinders and Hamburger \([19]\), Otto \([20]\), Kharif et al. \([21]\), and Ganesan et al. \([22]\). It is seen that the present data are in very good agreement with those reported in literature. The Gibbs free energy of formation of \text{Pb}_2\text{O}_4(s)\), deduced from the present measurement is given below:

Δ\(G_m^{\Delta}\text{Pb}_2\text{O}_4(s)\) ± 0.30/(kJ) = −738.04 + 0.39233\(T/K\).
\(\text{T = (777 − 865) K.} \quad \text{(12)}\)

These results show the reliability of the pressure measurement assembly for the measurement of equilibrium oxygen pressures in the pressure range of studies.

<table>
<thead>
<tr>
<th>Run 1</th>
<th>Time required to attain equilibrium (h)</th>
<th>Total time of dwell (h)</th>
<th>(P_{O_2}/\text{kPa})</th>
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Runs 1 to 3: Experiments with composition \text{Pb}_{0.16}\text{Cr}_{0.19}\text{O}_{0.65}.
Run 4 to 6: Experiments with composition \text{Pb}_{0.10}\text{Cr}_{0.28}\text{O}_{0.62}.
After each run, the system was evacuated.
The oxygen pressures of the following equilibrium were measured as a function of temperature by the manometric method:

$$\frac{1}{2} \text{Pb}_2\text{Cr}_3\text{O}_8(s) + \frac{1}{4} \text{Cr}_2\text{O}_3(s) + \frac{3}{8} \text{O}_2(g) = \text{PbCrO}_4(s).$$  \hspace{1cm} (13)$$

The measured oxygen partial pressures at different experimental temperatures are given in Table 4 and are also shown in Figure 6. They can be represented by the following least squares fitted expression:

$$\log p_{O_2}/(\text{kPa}) = 0.0130 + 3.8621 - 7060/T \text{ K}^{-1}$$

$$T = (863 \text{ to } 1093) \text{ K}. \hspace{1cm} (14)$$

The error given is the standard deviation of the least squares fitted straight line.

Consideration of the total duration of the measurements of different experimental runs shown in Table 4 and the measured rate of residual leak and degassing (~0.002 kPa/day) discussed in Section 3.4 indicates that the maximum error that could have arisen due to steady air leak would be 0.02 kPa. This is much lower than the uncertainties in pressure deduced (±1 kPa) from experimental data given by Gadalla and Abadir [13] reported equilibrium oxygen pressures over PbCrO$_4(s)$–Pb$_2$CrO$_5(s)$–Cr$_2$O$_3(s)$ phase field based on their thermo-gravimetric measurements at four temperatures between (1030 and 1055) K. These values are compared with the present results in Figure 6. The figure clearly shows that the temperature dependence of the oxygen partial pressures reported by Gadalla and Abadir are very high compared to that observed in this work.

The $\Delta G^\circ(T)$ for the reaction (13) can be represented as

$$\Delta G^\circ(T) = \Delta G^\circ_m\text{PbCrO}_4(s) - \frac{1}{2} \Delta G^\circ_m\text{Pb}_2\text{Cr}_5\text{O}_8(s)$$

$$- \frac{1}{4} \Delta G^\circ_m\text{Cr}_2\text{O}_3(s) = (3/8)RT\ln p_{O_2}. \hspace{1cm} (15)$$

Using the data on $\Delta G^\circ_m\text{PbCrO}_4(s)$ from equation (11), $\Delta G^\circ_m\text{Cr}_2\text{O}_3(s)$ from reference [18], $\Delta G^\circ_m\text{PbCrO}_4(s)$ was computed from oxygen pressure data given by equation (14) and is given by

$$\Delta G^\circ_m\text{PbCrO}_4(s) = 0.17/(\text{kJ} \cdot \text{mol}^{-1})$$

$$= -909.8 + 0.3111(T/K) \hspace{1cm} T = (863 \text{ to } 1093) \text{ K}. \hspace{1cm} (16)$$

The mean enthalpy of formation of this compound within the temperature range of the present measurement is $-909.8 \pm 0.17 \text{ kJ} \cdot \text{mol}^{-1}$ and is in reasonable agreement with $\Delta H^\circ_{f,298}$ value reported by Dellien et al. [14] as $-927.02 \pm 1.39 \text{ kJ} \cdot \text{mol}^{-1}$.

5. Conclusion

Gibbs free energy of formation of Pb$_2$CrO$_5(s)$, Pb$_2$CrO$_5(s)$, and PbCrO$_4(s)$ have been determined over a wide temperature range by measuring the equilibrium oxygen partial pressures in appropriate ternary phase fields employing a manometric technique and emf method using a solid oxide electrolyte based cell. These thermochemical data are reported for the first time.

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References