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

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ABSTRACT

Standard molar Gibbs free energy of formation of ternary oxides $\text{Pb}_5\text{CrO}_8(\text{s})$, $\text{Pb}_2\text{CrO}_5(\text{s})$, and $\text{PbCrO}_4(\text{s})$ 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:

$$\Delta_f G_m^\circ \text{Pb}_5\text{CrO}_8(\text{s}) \pm 0.55 / (\text{kJ} \cdot \text{mol}^{-1}) = -1809.4 + 0.6845(T/\text{K}) \quad (837 \leq T/\text{K} \leq 1008),$$

$$\Delta_f G_m^\circ \text{Pb}_2\text{CrO}_5(\text{s}) \pm 0.30 / (\text{kJ} \cdot \text{mol}^{-1}) = -1161.3 + 0.4059(T/\text{K}) \quad (859 \leq T/\text{K} \leq 1021),$$

$$\Delta_f G_m^\circ \text{PbCrO}_4(\text{s}) \pm 0.17 / (\text{kJ} \cdot \text{mol}^{-1}) = -909.8 + 0.3111(T/\text{K}) \quad (863 \leq T/\text{K} \leq 1093),$$

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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 + M + O) and (Bi + M + O) (M = alloying components of steels) systems as well as the thermochemical data on ternary oxygen compounds formed in these systems are essential. Recently, a partial phase diagram 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 $\text{PbCrO}_4(\text{s})$, $\text{Pb}_2\text{CrO}_5(\text{s})$, and $\text{Pb}_5\text{CrO}_8(\text{s})$ have been determined by measuring equilibrium oxygen pressures over appropriate ternary 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., $\text{PbCrO}_4(\text{s})$, $\text{Pb}_2\text{CrO}_5(\text{s})$, and $\text{Pb}_5\text{CrO}_8(\text{s})$ 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 detail 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: (a) $2 \text{CrO}_3(\text{l}) + 2 \text{PbO}_2(\text{s}) = 2 \text{PbCrO}_4(\text{s}) + \text{O}_2(\text{g})$ (478 to 508) K and (b) $(8/3) \text{PbCrO}_4(\text{s}) = (4/3) \text{Pb}_2\text{CrO}_5(\text{s}) + (2/3) \text{Cr}_2\text{O}_3(\text{s}) + \text{O}_2(\text{g})$ (1030 to 1055) K. The data obtained were reported as $\Delta G^{\text{rxn}} / (\text{kJ} \cdot \text{mol}^{-1}) = 108.43 + 0.2134(T/\text{K})$ 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 $\text{PbCrO}_4(\text{s})$ at 298 K ($\Delta H_{f,298}^\circ$) had been determined by Dellien et al. [14] by solution calorimeter with NaOH and Na₄EDTA as the calorimetric solvent. $\Delta H_{f,298}^\circ$ of $\text{PbCrO}_4(\text{s})$ 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 the account of the uncertainties reported by Dellien et al [14] for their measurements and the uncertainties reported for standard enthalpies of formation of $\text{PbO}(\text{s})$ and $\text{CrO}_3(\text{s})$ in the literature [15,16].

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3. Experimental

3.1. Materials

$\text{Pb}_5\text{CrO}_8(\text{s})$, $\text{Pb}_2\text{CrO}_5(\text{s})$, and $\text{PbCrO}_4(\text{s})$ were prepared by solid state reaction between powders of $\text{Pb}_3\text{O}_4(\text{s})$ (mass fraction purity > 0.99 on metal basis, M/s Aldrich Chem. Co. USA) and $\text{Cr}_2\text{O}_3(\text{s})$ (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 $\text{PbO}(\text{s})$ (mass fraction purity > 0.999 on metal basis, M/s Aldrich Chem. Co., USA) and $\text{Cr}_2\text{O}_3(\text{s})$ (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 K_α radiation and graphite monochromator. The XRD patterns obtained for $\text{Pb}_5\text{CrO}_8(\text{s})$, $\text{Pb}_2\text{CrO}_5(\text{s})$, and $\text{PbCrO}_4(\text{s})$ matched with the patterns reported in JCPDS files for these compounds, viz., 49-0970, 29-0768, and 73-2059, respectively.

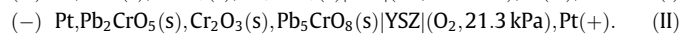
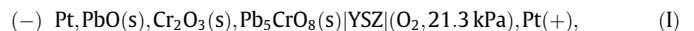
3.2. Equilibrations for confirmation of coexistence of phases

In the present work, oxygen pressures were measured in the three phase fields, namely, $\text{Pb}_5\text{CrO}_8(\text{s})$ – $\text{PbO}(\text{s})$ – $\text{Cr}_2\text{O}_3(\text{s})$, $\text{Pb}_5\text{CrO}_8(\text{s})$ – $\text{Pb}_2\text{CrO}_5(\text{s})$ – $\text{Cr}_2\text{O}_3(\text{s})$, and $\text{Pb}_2\text{CrO}_5(\text{s})$ – $\text{PbCrO}_4(\text{s})$ – $\text{Cr}_2\text{O}_3(\text{s})$ 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 $\text{PbO}(\text{s})$ – $\text{Cr}_2\text{O}_3(\text{s})$ – $\text{Pb}_5\text{CrO}_8(\text{s})$ phase field, an overall sample composition of $\text{Pb}_{0.24}\text{Cr}_{0.19}\text{O}_{0.57}$ was chosen

with two sets of starting materials, namely $\text{Pb}(\text{s}) + \text{Cr}_2\text{O}_3(\text{s}) + \text{Pb}_2\text{CrO}_5(\text{s})$ and $\text{PbO}(\text{s}) + \text{Cr}_2\text{O}_3(\text{s}) + \text{Pb}_5\text{CrO}_8(\text{s})$. For equilibration in $\text{Pb}_2\text{CrO}_5(\text{s})$ – $\text{Pb}_5\text{CrO}_8(\text{s})$ – $\text{Cr}_2\text{O}_3(\text{s})$ phase field, an overall composition $\text{Pb}_{0.19}\text{Cr}_{0.20}\text{O}_{0.61}$ was chosen with $\text{PbO}(\text{s}) + \text{Cr}_2\text{O}_3(\text{s}) + \text{PbCrO}_4(\text{s})$ and $\text{Pb}_2\text{CrO}_5(\text{s}) + \text{Pb}_5\text{CrO}_8(\text{s}) + \text{Cr}_2\text{O}_3(\text{s})$ 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 $\text{Pb}_2\text{CrO}_5(\text{s})$ – $\text{PbCrO}_4(\text{s})$ – $\text{Cr}_2\text{O}_3(\text{s})$ phase field, a sample of the overall composition $\text{Pb}_{0.16}\text{Cr}_{0.19}\text{O}_{0.65}$ was prepared from 5:1:1 molar ratio of $\text{PbCrO}_4(\text{s})$, $\text{Pb}_2\text{CrO}_5(\text{s})$, and $\text{Cr}_2\text{O}_3(\text{s})$ 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:



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 at the bottom 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

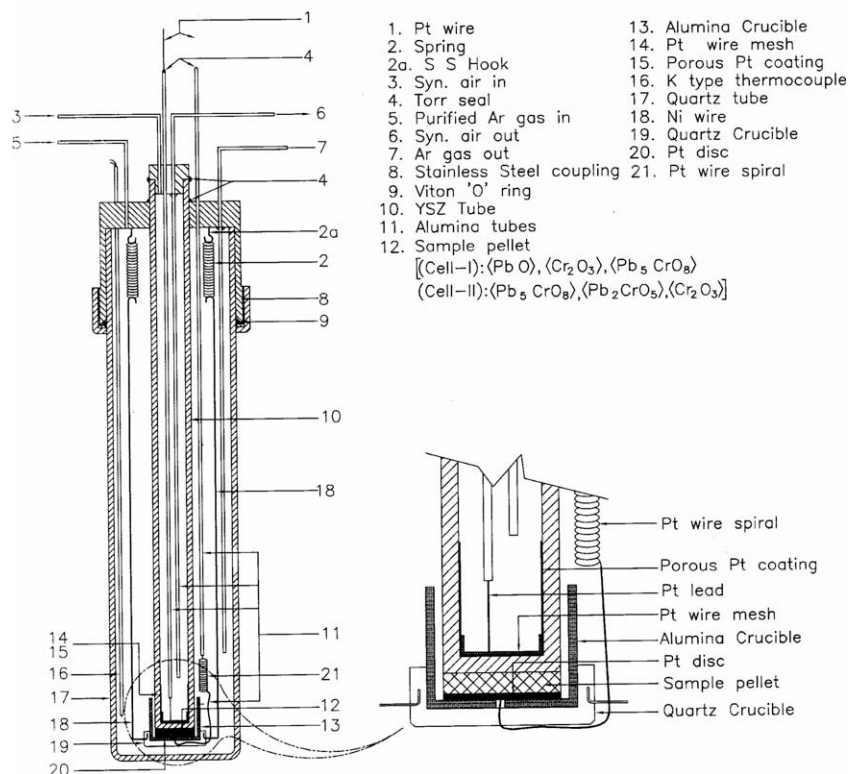


FIGURE 1. Schematics of the solid oxide based galvanic cells used.

(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 $\text{PbO(s)}\text{--Cr}_2\text{O}_3\text{(s)}\text{--Pb}_5\text{CrO}_8\text{(s)}$ were used for measurements with cell-I. In a similar manner, two sets of emf measurements were carried out in the $\text{Pb}_2\text{CrO}_5\text{(s)}\text{--Pb}_5\text{CrO}_8\text{(s)}\text{--Cr}_2\text{O}_3\text{(s)}$ 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 pelletising 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 MgSiO_3 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 $> 10^{14} \Omega$, 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 $\text{Pb}_2\text{CrO}_5\text{(s)}\text{--PbCrO}_4\text{(s)}\text{--Cr}_2\text{O}_3\text{(s)}$ 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 bellow 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 0.0013 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 $\text{Pb}_{0.16}\text{Cr}_{0.19}\text{O}_{0.65}$ was prepared in the form of porous pellets from 5:1:1 molar ratio of $\text{PbCrO}_4\text{(s)}$, $\text{Pb}_2\text{CrO}_5\text{(s)}$, and $\text{Cr}_2\text{O}_3\text{(s)}$, respectively and used. For runs 4 to 6, another sample of overall composition of $\text{Pb}_{0.10}\text{Cr}_{0.28}\text{O}_{0.62}$ prepared from a 0.3:0.3:1 mole ratio of $\text{PbCrO}_4\text{(s)}$, $\text{Pb}_2\text{CrO}_5\text{(s)}$, and $\text{Cr}_2\text{O}_3\text{(s)}$ 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 intermediately cooled to room temperature and the gas plenum was evacuated down to 0.0001 kPa before beginning the measurements at a new

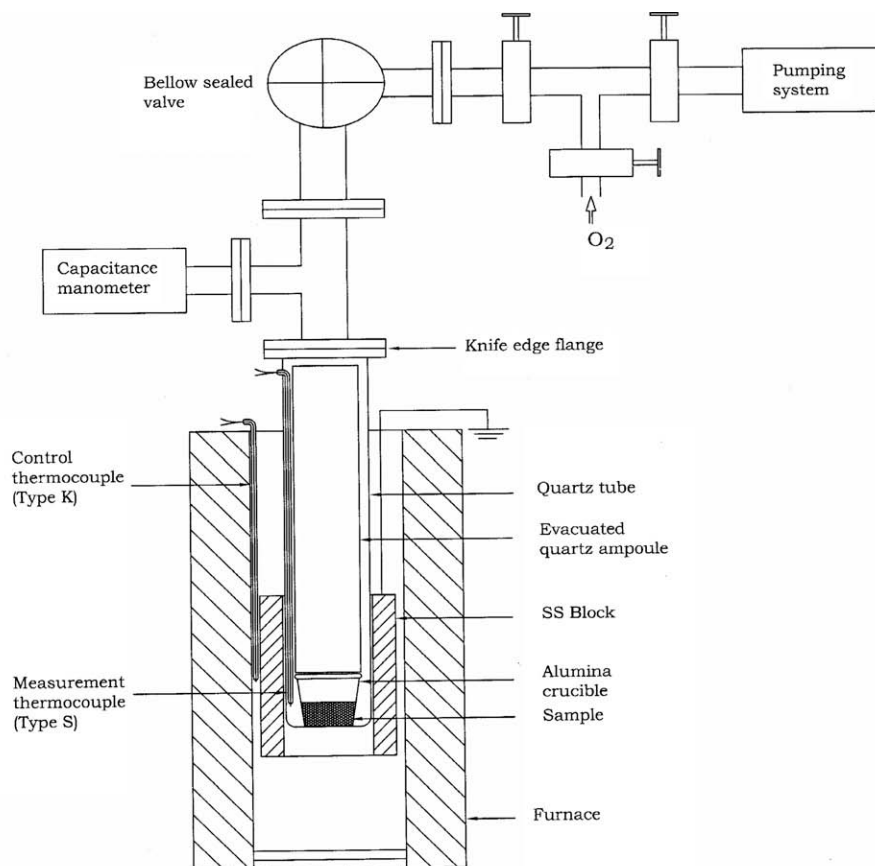


FIGURE 2. Experimental assembly used for equilibrium oxygen pressure measurements (free volume in the assembly ≈ 110 cc).

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. Equilibrations study

The XRD pattern of the samples obtained after their equilibration at different temperatures in conjunction with our results in reference [8] confirmed the existence of these phase fields namely: (a) $\text{PbO}(s)\text{-Cr}_2\text{O}_3(s)\text{-Pb}_5\text{CrO}_8(s)$ and $\text{Pb}_5\text{CrO}_8(s)\text{-Pb}_2\text{CrO}_5(s)\text{-Cr}_2\text{O}_3(s)$ phase field in the temperature range of (723 to 1023) K and (b) that of $\text{Pb}_2\text{CrO}_5(s)\text{-PbCrO}_4(s)\text{-Cr}_2\text{O}_3(s)$ 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 Pb_2CrO_5 and Pb_5CrO_8 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 $\text{PbCrO}_4(s)$ 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:

$$E_1 \pm 0.0006/V = 0.5426 - 2.439 \times 10^{-4} (T/K) \\ T = (837 \text{ to } 1008) \text{ K} \quad (1)$$

TABLE 1

Variation of emf of cell-I with temperature.

	T/K	E/mV
Run 1	871.6	330.2
	970.8	306.1
	994.8	300.2
	946.4	311.6
	852.2	335.0
	956.1	308.3
	884.7	327.0
	909.4	321.1
	837.2	339.1
	862.3	332.4
	1008.2	297.4
	983.4	303.0
	934.2	314.7
	921.3	318.1
	970.7	306.0
871.1	330.3	
945.8	312.0	
896.3	324.5	
Run 2	978.7	304.6
	949.5	309.6
	923.9	317.7
	842.8	335.9
	959.1	307.6

Run 1: measurements with samples of overall composition $\text{Pb}_{0.27}\text{Cr}_{0.16}\text{O}_{0.57}$.
Run 2: measurements with samples of overall composition $\text{Pb}_{0.35}\text{Cr}_{0.10}\text{O}_{0.55}$.

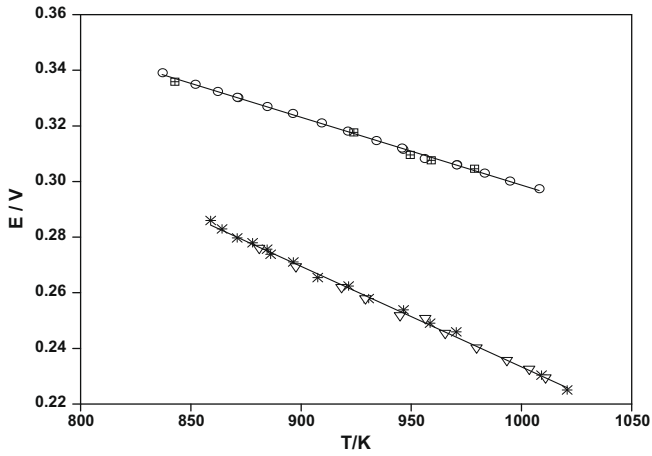
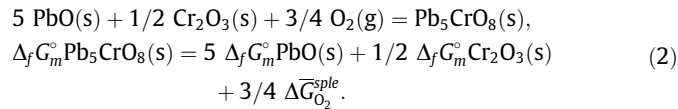


FIGURE 3. Variation of emf with temperature in cell I and cell II. ○ (Cell I run 1), ◻ (Cell I run 2), ◻ (Cell II run 1), ✱ (Cell II run 2). Cell I: PbO(s)–Cr₂O₃(s)–Pb₅CrO₈(s) phase field. Cell II: Pb₅CrO₈(s)–Pb₂CrO₅(s)–Cr₂O₃(s) phase field.

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

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



$\Delta G_{\text{O}_2}^{\text{sple}}$ is related to the cell emf as given below:

$$E = (RT/4F) \ln(p_{\text{O}_2}^{\text{ref}}/p_{\text{O}_2}^{\text{sple}}), \quad (3)$$

$$4FE = \Delta G_{\text{O}_2}^{\text{ref}} - \Delta G_{\text{O}_2}^{\text{sple}}, \quad (4)$$

$$\Delta G_{\text{O}_2}^{\text{sple}} = \Delta G_{\text{O}_2}^{\text{ref}} - 4FE. \quad (5)$$

The standard molar Gibbs free energy of formation of Pb₅CrO₈(s) can be obtained from the measured emf values as given below:

$$\Delta_f G_m^\circ \text{Pb}_5\text{CrO}_8\text{(s)} = -3FE + 3/4RT \ln 0.21 + 5\Delta_f G_m^\circ \text{PbO(s)} + 1/2 \Delta_f G_m^\circ \text{Cr}_2\text{O}_3\text{(s)}. \quad (6)$$

By substituting the emf data given by equation (1) and by using the values of $\Delta_f G_m^\circ \text{PbO(s)}$ and $\Delta_f G_m^\circ \text{Cr}_2\text{O}_3\text{(s)}$ reported in references [17,18], the standard molar Gibbs free energy of formation of Pb₅CrO₈(s) was derived and is given below:

$$\Delta_f G_m^\circ \text{Pb}_5\text{CrO}_8\text{(s)} \pm 0.55 / (\text{kJ} \cdot \text{mol}^{-1}) = -1809.3 + 0.6845(T/\text{K}) \quad T = (837 \text{ to } 1008) \text{ K}. \quad (7)$$

Gadalla and Abadir [13] had reported the equilibrium partial pressures of oxygen over Pb₅CrO₈(s)–PbO(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 Cr₂O₃ 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:

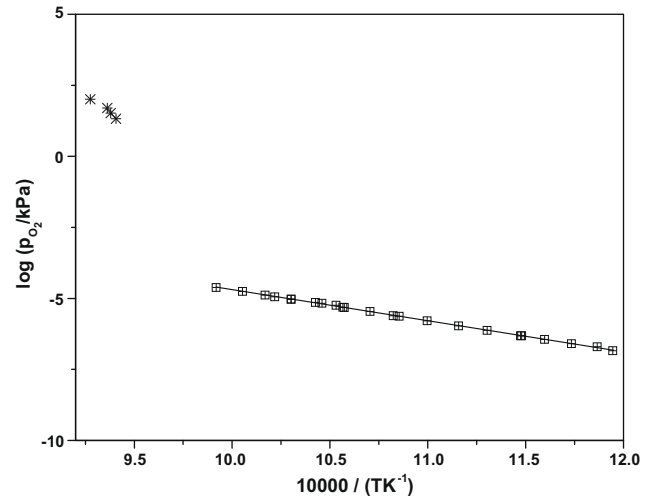


FIGURE 4. Comparison of oxygen pressures deduced from emf data over PbO(s)–Cr₂O₃(s)–Pb₅CrO₈(s) phase field of present work and oxygen pressures reported in reference [13] over PbO(s)–melt–Pb₅CrO₈(s). ◻ This work, ✱ Data reported by Gadalla and Abadir [13].

TABLE 2
Variation of emf of cell-II with temperature.

	T/K	E/mV
Run 1	970.4	245.9
	946.4	253.9
	921.5	262.4
	896.5	271.1
	884.5	275.7
	930.6	257.9
	958.5	249.1
	907.5	265.5
	878.0	278.0
	864.1	282.9
	871.0	279.7
	858.9	286.0
	886.3	273.9
	1020.7	225.0
1009.1	230.4	
Run 2	993.4	235.7
	897.6	269.4
	944.9	251.8
	1010.9	229.5
	881.0	276.1
	965.4	245.5
	929.3	257.9
	1003.6	232.6
	918.4	261.9
	979.6	240.3
	956.4	250.8

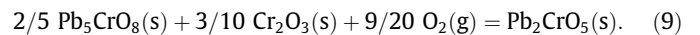
Run 1: measurements with samples of overall composition Pb_{0.24}Cr_{0.15}O_{0.61}.
Run 2: measurements with samples of overall composition Pb_{0.26}Cr_{0.15}O_{0.59}.

$$E_{\text{II}} \pm 0.0009/\text{V} = 0.5949 - 3.615 \times 10^{-4}(T/\text{K})$$

$$T = (859 \text{ to } 1021) \text{ K}. \quad (8)$$

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

The cell reaction can be represented as below:



The standard molar Gibbs free energy of formation of Pb₂CrO₅(s) can be related to the measured emf values by the following expression:

TABLE 3
Variation of oxygen partial pressures with temperature over {PbO(s) + Pb₃O₄(s)} system.

T/K	P _{O₂} /kPa
826.2	32.331
776.7	7.094
852.8	67.790
807.5	19.431
865.3	94.146

$$\Delta_f G_m^\circ \text{Pb}_2\text{CrO}_5(\text{s}) = -1.8FE + 0.45RT \ln 0.21 + 0.4\Delta_f G_m^\circ \text{Pb}_5\text{CrO}_8(\text{s}) + 0.3\Delta_f G_m^\circ \text{Cr}_2\text{O}_3(\text{s}). \quad (10)$$

By incorporating the values of emf from equation (8) and using values of $\Delta_f G_m^\circ \text{Pb}_5\text{CrO}_8(\text{s})$ from expression (7) and the data on $\Delta_f G_m^\circ \text{Cr}_2\text{O}_3(\text{s})$ from reference [18], $\Delta_f G_m^\circ \text{Pb}_5\text{CrO}_8(\text{s})$ could be obtained as

$$\Delta_f G_m^\circ \text{Pb}_2\text{CrO}_5(\text{s}) \pm 0.30/(\text{kJ} \cdot \text{mol}^{-1}) = -1161.3 + 0.4059(T/\text{K})$$

$$T = (859 \text{ to } 1021)\text{K}. \quad (11)$$

4.3. Manometric measurements

The test of the vacuum assembly used for pressure measurement was carried out by studying the well-established {PbO(s) + Pb₃O₄(s)} system. The equilibrium oxygen pressures were measured between (777 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

TABLE 4
Variation of oxygen partial pressure with temperature for the phase field PbCrO₄(s)–Pb₂CrO₅(s)–Cr₂O₃(s).

T/K	Time required to attain equilibrium (h)	Total time of dwell (h)	P _{O₂} /kPa
<i>Run 1</i>			
951.1	8	42	8.522
902.0	2	40	3.328
926.8	4	26	5.461
1001.5	4	8	20.545
978.6	8	17	14.373
993.3	8	22	17.908
944.4	7	31	7.816
<i>Run 2</i>			
967.1	7	20	11.456
911.7	6	26	4.235
<i>Run 3</i>			
880.1	14	20	2.121
892.7	6	16	2.801
869.1	5	18	1.721
863.2	6	29	1.441
959.9	7	29	10.137
<i>Run 4</i>			
1002.1	10	60	20.674
903.7	10	25	3.696
933.1	12	19	6.413
913.5	8	24	4.528
<i>Run 5</i>			
883.3	16	26	2.421
920.4	22	35	4.962
<i>Run 6</i>			
1034.2	12	120	31.841
1017.1	18	46	26.229
1046.8	6	70	40.858
1042.1	4	70	39.950
1093.2	6	50	81.086

Runs 1 to 3: Experiments with composition Pb_{0.16}Cr_{0.19}O_{0.65}.
Run 4 to 6: Experiments with composition Pb_{0.10}Cr_{0.28}O_{0.62}.
After each run, the system was evacuated.

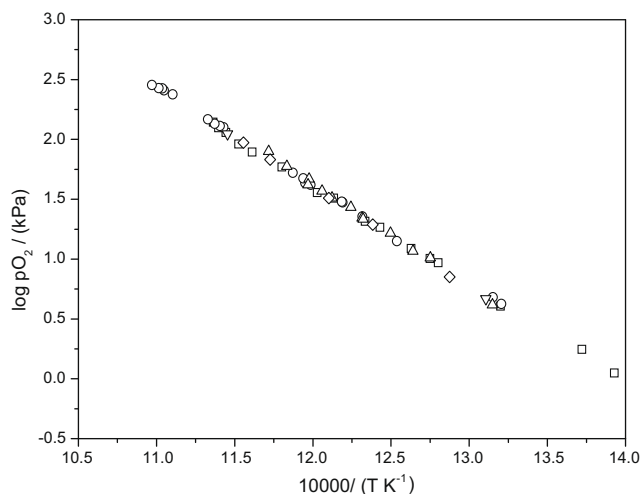


FIGURE 5. Variation of oxygen pressure in {PbO(s) + Pb₃O₄(s)} system with temperature. □ Reinders and Hamburger [19], ○ Otto [20], ▽ Kharif *et al.* [21], △ Ganesan *et al.* [22], ◇ Present work.

literature. The Gibbs free energy of formation of Pb₃O₄(s), deduced from the present measurement is given below:

$$\Delta_f G_m^\circ \text{Pb}_3\text{O}_4(\text{s}) \pm 0.30/\text{kJ} = -738.04 + 0.39233(T/\text{K})$$

$$T = (777-865) \text{ K}. \quad (12)$$

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

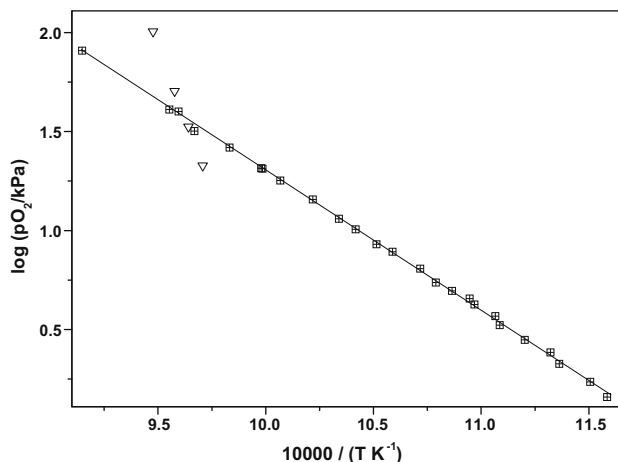
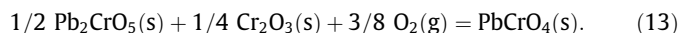


FIGURE 6. Variation of oxygen partial pressure over $\text{Pb}_2\text{CrO}_5(\text{s})$ – $\text{PbCrO}_4(\text{s})$ – $\text{Cr}_2\text{O}_3(\text{s})$ phase field. ∇ Gadalla and Abadir [13], \boxtimes (This work).

The oxygen pressures of the following equilibrium were measured as a function of temperature by the manometric method:



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:

$$(\log p_{\text{O}_2}/\text{kPa}) \pm 0.0130 = 8.3621 - 7060/\text{TK}^{-1} \\ T = (863 \text{ to } 1093) \text{ K}. \quad (14)$$

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 equation (14). Gadalla and Abadir [13] reported equilibrium oxygen pressures over $\text{PbCrO}_4(\text{s})$ – $\text{Pb}_2\text{CrO}_5(\text{s})$ – $\text{Cr}_2\text{O}_3(\text{s})$ 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 $\Delta_r G^\circ(T)$ for the reaction (13) can be represented as

$$\Delta_r G^\circ(T) = \Delta_f G_m^\circ \text{PbCrO}_4(\text{s}) - 1/2 \Delta_f G_m^\circ \text{Pb}_2\text{CrO}_5(\text{s}) \\ - 1/4 \Delta_f G_m^\circ \text{Cr}_2\text{O}_3(\text{s}) = (3/8)RT \ln p_{\text{O}_2}. \quad (15)$$

Using the data on $\Delta_f G_m^\circ \text{Pb}_2\text{CrO}_5(\text{s})$ from equation (11), $\Delta_f G_m^\circ \text{Cr}_2\text{O}_3(\text{s})$ from reference [18], $\Delta_f G_m^\circ \text{PbCrO}_4(\text{s})$ was computed from oxygen pressure data given by equation (14) and is given by

$$\Delta_f G_m^\circ \text{PbCrO}_4(\text{s}) \pm 0.17/(\text{kJ} \cdot \text{mol}^{-1}) \\ = -909.8 + 0.3111(T/\text{K}) \quad T = (863 \text{ to } 1093) \text{ K}. \quad (16)$$

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 $\Delta H_{f,298}^\circ$ 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 $\text{Pb}_5\text{CrO}_8(\text{s})$, $\text{Pb}_2\text{CrO}_5(\text{s})$, and $\text{PbCrO}_4(\text{s})$ 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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