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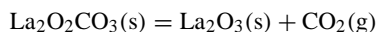
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Abstract

Thermochemistry in the decomposition of lanthanum dioxycarbonate, $\text{La}_2\text{O}_2\text{CO}_3(\text{s})$, was studied over the temperature region of 773–1190 K. The decomposition reaction can be written as



The equilibrium property of the above reaction was then studied by tensimetric measurement of the $\text{CO}_2(\text{g})$ pressure over the biphasic mixture of $\text{La}_2\text{O}_2\text{CO}_3(\text{s})$ and $\text{La}_2\text{O}_3(\text{s})$ at different temperatures. The temperature dependence of the equilibrium pressure of CO_2 thus measured could be given by

$$\ln p_{\text{CO}_2}(\text{Pa})(\pm 0.22) = -\frac{17\,502.2}{T} + 25.87 \quad (773 \leq T(\text{K}) \leq 1190)$$

From the above vapor pressure expression, the median enthalpy and entropy of the decomposition of the oxycarbonate from the second law analysis worked out to be $145.5 \pm 5.0 \text{ kJ mol}^{-1}$ and $119.2 \pm 5.0 \text{ J mol}^{-1} \text{ K}^{-1}$, respectively. The results are discussed in the light of available thermochemical data of the compound.

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Keywords: Lanthanum dioxycarbonate; Decomposition pressure measurements; Tensimetric method; Thermodynamic properties; Equilibrium pressure measurements

1. Introduction

Lanthanum dioxycarbonate, $\text{La}_2\text{O}_2\text{CO}_3(\text{s})$ is a stable intermediate in the thermal decomposition of lanthanum carbonate, $\text{La}_2(\text{CO}_3)_3$ [1]. The reported thermal analysis shows that the compound undergoes decomposition as $\text{La}_2\text{O}_2\text{CO}_3(\text{s}) = \text{La}_2\text{O}_3(\text{s}) + \text{CO}_2(\text{g})$ above 993 K. However, there is no reliable thermodynamic information on $\text{La}_2\text{O}_2\text{CO}_3(\text{s})$ to be used for the study of chemical equilibria in its reactive decomposition with other oxides forming their solid

solutions or compounds of double and multiple oxides of interest in reactor materials, superconductors, solid oxide fuel cell, etc. Analysis of such chemical equilibria that involve the gaseous product CO_2 would lead to the understanding of the thermodynamic properties of the product states. The reported values on the decomposition enthalpies of the dioxycarbonates of La, Nd, Sm, Gd, Dy, and Lu based on thermal analysis [2,3] suffer from too large and unsystematic variations among themselves. The decomposition enthalpy and entropy values of the La compound reported by the two recent studies [4,5] differ significantly from each other and also, from the results of thermal analysis [2,3].

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In view of the large uncertainties of the available thermodynamic data of $\text{La}_2\text{O}_2\text{CO}_3(\text{s})$ this study was taken up. The equilibrium property of dissociation of the compound was measured by monitoring the vapor pressure due the gaseous product CO_2 with the help of tensimetric technique.

2. Experimental

$\text{La}_2\text{O}_2\text{CO}_3(\text{s})$ was prepared by thermal decomposition of lanthanum carbonate $\text{La}_2(\text{CO}_3)_3(\text{s})$ of high purity (99.9%, Aldrich). Thermal analysis of the as procured compound showed the presence of some moisture that got released by 600 K and the carbonate decomposed to the stoichiometric oxycarbonate, $\text{La}_2\text{O}_2\text{CO}_3(\text{s})$ at 723 K in dry air. The thermogravimetric (TG) analysis also showed that the oxycarbonate decomposes to $\text{La}_2\text{O}_3(\text{s})$ at 1000 K in the air. However, when the decomposition of the freshly prepared oxycarbonate was carried out in $\text{CO}_2(\text{g})$ controlled at 1 bar pressure, the TG step corresponding to $\text{La}_2\text{O}_3(\text{s})$ formation was observed sharply at 1223 K. TG analysis in CO_2 atmosphere also showed initially small gain in mass of the oxycarbonate sample followed by

the sluggish loss at around 923 K. These might be due to initial uptake of CO_2 converting a small portion of the dioxycarbonate to the reported monooxycarbonate, $\text{La}_2\text{O}(\text{CO}_3)_2(\text{s})$ [6] that decomposed back to the dioxycarbonate at 923 K.

For the tensimetric study of the dioxycarbonate, the compound was freshly prepared and characterized by thermal and XRD analysis and stored in vacuum desiccator. Typically 500 mg powder sample was taken in a quartz reaction tube closed at its one end and placed horizontally locating the sample in isothermal zone of a resistance furnace which was equipped with controlled heating facility. The other end of the reaction tube was coupled to manometers by a gas tight joint. There were two manometers in parallel, respectively to cover low and high ranges of gas pressure to be monitored. The manometer of dibutyl phthalate oil could measure pressure up to 7500 Pa with the readability of 5 Pa, while the mercury manometer monitored the upper values of pressure. Both manometers were made out of Pyrex glass to render readability of the manometric fluid levels. The dead volume of the system, i.e the quartz reaction tube together with the connecting limbs of the two manometers, was less than 25 ml. The system was coupled to high vacuum system through

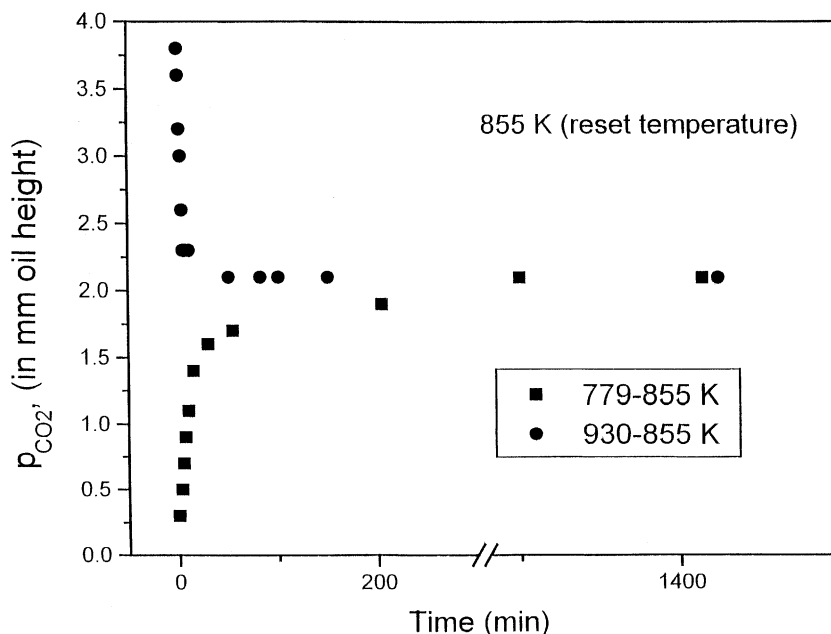
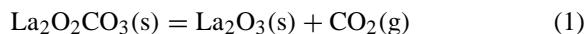


Fig. 1. The invariability of equilibrium pressure at 855 K as the sample is thermally cycled around this temperature.

quick fit stopcock. The system could hold static vacuum over several weeks to better than the measuring sensitivity of oil manometer. Sample temperature was measured with the help of a Pt–Pt13%Rh thermocouple which was calibrated at the melting points of pure metals as recommended in [7]. The temperature could be measured to an accuracy of ± 1 K.

After loading the sample in the tensimetric apparatus the system was evacuated under the dynamic vacuum of 1×10^{-8} bar. Under evacuation the sample temperature was raised to 773 K to let off any absorbed moisture from the sample. The conditioning was continued till the static pressure of the system measured by the oil manometer became constant. The system was then isolated from the vacuum pump for taking measurements. At first the attainment of equilibrium was examined for the following decomposition reaction:



The above-mentioned chemical path for decomposition was confirmed from the TG analysis. As the system was thermally cycled around a fixed temperature and the course of development of CO_2 pressure was monitored it was seen that the fluid level in the manometer ultimately converged to a constant value. A typical case is shown in Fig. 1. It was also seen that the gas pressure developed in the closed system when relieved temporarily, developed back to the same value at any fixed sample temperature. The attainment of pressure invariancy at a temperature following the thermal and mechanical perturbations was indicative of accomplishing thermodynamic equilibrium in the system.

3. Results and discussions

The equilibrium pressure of $\text{CO}_2(\text{g})$ at different temperatures of the sample was monitored in the temperature range of 773–1190 K. The lower limit of temperature was chosen by considering the measuring sensitivity of the oil manometer, while the upper limit was near 1 bar pressure. The measured pressures of $\text{CO}_2(\text{g})$ at various temperatures are shown in Table 1. Each of the pressure readings given in the table is actually the average value of several readings taken at large time intervals as the system attained equilibrium at a

Table 1

Equilibrium pressures of $\text{CO}_2(\text{g})$ measured over the biphasic mixture of $\text{La}_2\text{O}_2\text{CO}_3(\text{s})$ and $\text{La}_2\text{O}_3(\text{s})$ as a function of temperature

	<i>T</i> (K)						
	773	853	903	1003	1104	1124	1190
<i>p</i> _{CO₂} (Pa)	30	220	540	3985	18,400	29,145	10,0710

temperature typically within 12 h. This averaging was done to even out the effect of room temperature fluctuation on the manometric readings. It may be noted that the room temperature fluctuated within ± 2 K, which corresponded to an insignificantly small uncertainty in the recorded height of dibutyl phthalate oil (specific gravity 1.045 at 293 K), used. From the measurement the vapor pressure relation worked out to be

$$\begin{aligned} \ln p_{\text{CO}_2} (\text{Pa}) (\pm 0.22) \\ = -\frac{17502.2}{T} + 25.87 \quad (773 \leq T (\text{K}) \leq 1190) \end{aligned} \quad (2)$$

From the above vapor pressure equation, the calculated temperature of 1220 K for 1 bar of p_{CO_2} compares well with the thermogravimetric step of the decomposition observed at 1223 K under 1 atm of CO_2 pressure. The plot of $\ln p_{\text{CO}_2}$ as a function of $1/T$ is given in Fig. 2.

Using Eq. (2) and the free energies of formation of $\text{La}_2\text{O}_3(\text{s})$ and $\text{CO}_2(\text{g})$ from Barin [8], the free energy of formation of $\text{La}_2\text{O}_2\text{CO}_3(\text{s})$ can be derived as

$$\begin{aligned} \Delta_f G^\circ (\text{La}_2\text{O}_2\text{CO}_3(\text{s})) (\pm 5.0 \text{ kJ mol}^{-1}) \\ = -2323.8 + 0.39T \quad (773 \leq T (\text{K}) \leq 1190) \end{aligned} \quad (3)$$

From Eq. (2), the median enthalpy and entropy of the decomposition of the oxycarbonate from the second law analysis worked out to be $145.5 \pm 5.0 \text{ kJ mol}^{-1}$ and $119.2 \pm 5.0 \text{ J mol}^{-1} \text{ K}^{-1}$, respectively. These values compare well with the reported data of the respective thermodynamic quantities as 149 kJ mol^{-1} and $126 \text{ J mol}^{-1} \text{ K}^{-1}$ due to Watanabe et al. [4] even though the entropy of decomposition is marginally different. The enthalpy change for the decomposition reaction derived from differential thermal analysis (DTA) curves by Patil et al. [3] works out to be $322 \pm 48 \text{ kJ mol}^{-1}$ which differs significantly from our results as well as that of Watanabe et al. [4]. The difficulties in deriving the heat of reaction from DTA

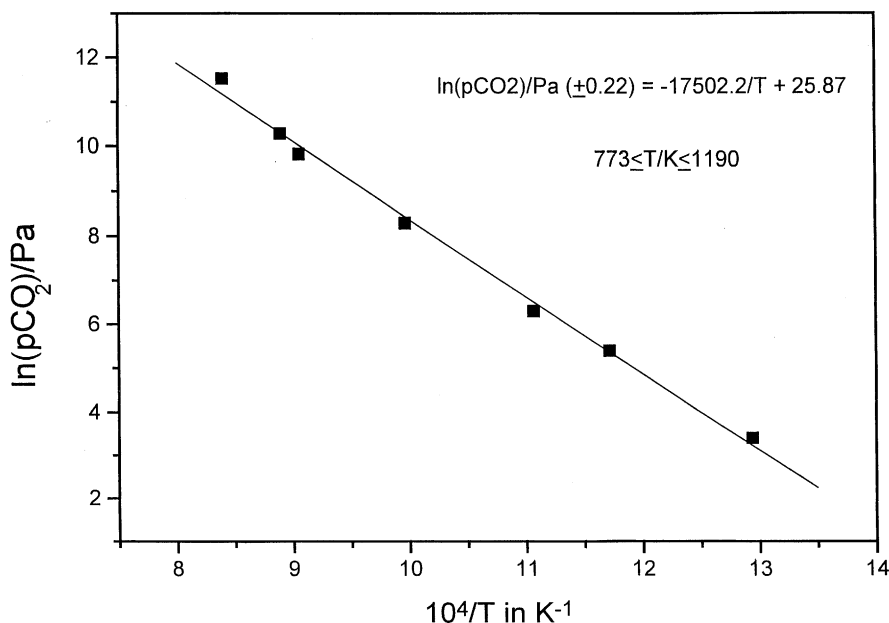


Fig. 2. Plot of $\ln p_{\text{CO}_2}$ (Pa) as a function of $1/T$.

curves have been well-documented [9–11]. Therefore, the enthalpy derived from equilibrium measurements in this work and by Watanabe et al. [4] can be considered to be more reliable. The entropy change for the decomposition reaction (1) derived from the measured heat capacity data of Olafsen and Fjellvag [5] works out to be $170.2 \pm 0.6 \text{ J mol}^{-1} \text{ K}^{-1}$ at 300 K. This value differs significantly from the entropy of decomposition at the median temperature (981 K) derived in this work. The discrepancy may, in part, result from the temperature dependence of formation entropy.

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