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Thermochemistry of decomposition of $RE_2O_2CO_3$ (RE = Sm, Eu)

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ABSTRACT

Thermochemistry in the decomposition of samarium di-oxycarbonate, $Sm_2O_2CO_3(s)$ and europium di-oxycarbonate, $Eu_2O_2CO_3(s)$ was studied over the temperature regions of 755–987 K and 773–989 K, respectively. The equilibrium properties of the decomposition reactions were obtained by tensimetric measurement of the $CO_2(g)$ pressure over the biphasic mixture of $RE_2O_2CO_3(s)$ and $RE_2O_3(s)$ at different temperatures (RE = Sm, Eu) and also by thermogravimetric analysis of the decomposition temperature at 1 atmosphere of CO_2 pressure. The temperature dependence of the equilibrium pressure of CO_2 thus measured could be given by

$$\ln p_{CO_2}(\mathrm{Pa})\,(\pm 0.13) = \frac{-15722.8}{T} + 26.83 \quad (755 \le T(\mathrm{K}) \le 987)\ \text{for}$$

$Sm_2O_2CO_3$ decomposition and

$$\ln p_{CO_2}(\mathrm{Pa})\,(\pm 0.13) = \frac{-18615.7}{T} + 29.90 \quad (773 \le T(\mathrm{K}) \le 989)\ \text{for}$$

$Eu_2O_2CO_3$ decomposition.

From the above vapor pressure expressions, the median enthalpy and entropy of the decomposition of the oxycarbonates were calculated by the second law analysis and their thermodynamic stabilities were derived. The results are discussed in the light of available thermochemical data of the compounds.

1. Introduction

Rare earth di-oxycarbonates, $RE_2O_2CO_3(s)$ are stable intermediates in the thermal decomposition of rare earth oxalates or carbonates [1]. However, there is no reliable thermodynamic information on $RE_2O_2CO_3(s)$ 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 cells, etc. Analysis of 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 of the decomposition enthalpies of the di-oxycarbonates of La, Nd, Sm, Gd, Dy, and Lu based on thermal analysis [2,3] suffer from too large and unsystematic variations among themselves. The only reported thermodynamic data for $Sm_2O_2CO_3$ is the enthalpy change for its decomposition to Sm_2O_3 which has been derived from the DTA curve [3]. Thermodynamic data for $Eu_2O_2CO_3$ have not been reported so far.

It is well known that the enthalpy changes derived from the dynamic measurements in DTA are not very reliable. We have determined the thermodynamic stabilities of $La_2O_2CO_3$, $Gd_2O_2CO_3$ and $Nd_2O_2CO_3$ [4,5] by thermogravimetric as well as tensimetric methods. Therefore, continuing our studies on the rare earth oxy carbonates, the thermodynamic investigations of $Sm_2O_2CO_3(s)$ and $Eu_2O_2CO_3(s)$ decomposition were taken up. The equilibrium properties of dissociation of these compounds were measured by monitoring the vapor pressure due to the gaseous product CO_2 with the help of a tensimetric apparatus.

2. Experimental

Samarium oxalate was prepared from 99.9% pure Sm_2O_3 by dissolving the oxide in nitric acid and precipitating the oxalate using oxalic acid. Similarly europium oxalate was prepared from Eu_2O_3. $Sm_2O_2CO_3$ and $Eu_2O_2CO_3$ were prepared by thermal decomposition of the respective oxalates. Thermogravimetric (TG) and differential thermal analysis (DTA) studies were carried out using a simultaneous TG/DTA apparatus ((SETARAM 92-16.18), France) in carbon dioxide atmosphere at a heating rate of 5 K/min. The recorded temperature scale of the TG profiles was precalibrated by noting the melting temperatures of pure silver and gold.

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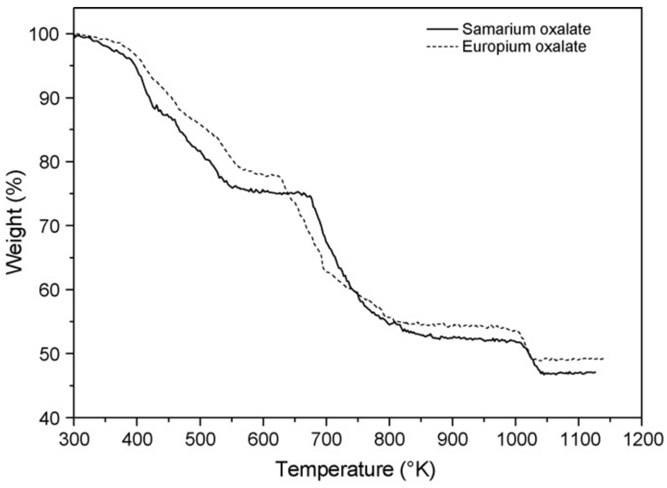

Fig. 1. Thermogravimetric plot of samarium oxalate and europium oxalate in CO_2 (g) atmosphere at a heating rate 10 °C/min.

Powder XRD patterns of all the samples were recorded on a Philips X-ray Diffractometer (PW 1710) with Ni-filtered Cu K(radiation, using silicon as an external standard. For tensimetric study of the di-oxycarbonates, the compounds were freshly prepared and characterized by thermal and XRD analyses and stored in a vacuum desiccator. Typically 500 mg powder samples were taken in a quartz reaction tube closed at its one end and placed horizontally locating the sample in the 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 di-butyl phthalate could measure pressure up to 7500 Pa with an accuracy of ±5 Pa, while the mercury manometer monitored the upper values of pressure with an accuracy of ±10 Pa. Both manometers were made of pyrex glass to render a 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 a high vacuum system through a Quickfit stopcock. The system could hold static vacuum over several weeks to better than the measuring sensitivity of the oil manometer. The sample temperature was measured with a Pt–Pt13%Rh thermocouple which was calibrated at the melting points of pure metals as recommended [6]. The temperature could be measured to an accuracy of ±1 K.

3. Results and discussion

3.1. Thermal analysis

Thermogravimetric curves for the decomposition of samarium oxalate and europium oxalate (Fig. 1) show the presence of some moisture that got released by 400 K. Sm oxalate started decomposing to the stoichiometric oxycarbonate, $Sm_2O_2CO_3$(s) at 670 K in CO_2 atmosphere and in case of Eu oxalate this temperature was about 620 K. Thermogravimetric analysis also showed that Sm oxycarbonate decomposes to Sm_2O_3(s) at 1025 K in CO_2(g) controlled at 1 bar and $Eu_2O_2CO_3$(s) decomposes to Eu_2O_3(s) at 1010 K in CO_2(g) controlled at 1 bar.

3.2. Characterization by XRD

The XRD patterns of $Sm_2O_2CO_3$ and $Eu_2O_2CO_3$ given in Fig. 2. The XRD pattern of $Eu_2O_2CO_3$ indicates that it is not formed in highly crystalline state. The observed d-values of $Sm_2O_2CO_3$ agreed well with the reported d-spacings of JCPDS file No. 37-0807 (Hexagonal symmetry with lattice parameters a = 3.945 Å and c = 15.448 Å). Similarly the XRD pattern of $Eu_2O_2CO_3$ agreed with the reported d-values of JCPDS file No. 25-0334 (Tetragonal symmetry with lattice parameters a = 3.99 Å and c = 12.88 Å).

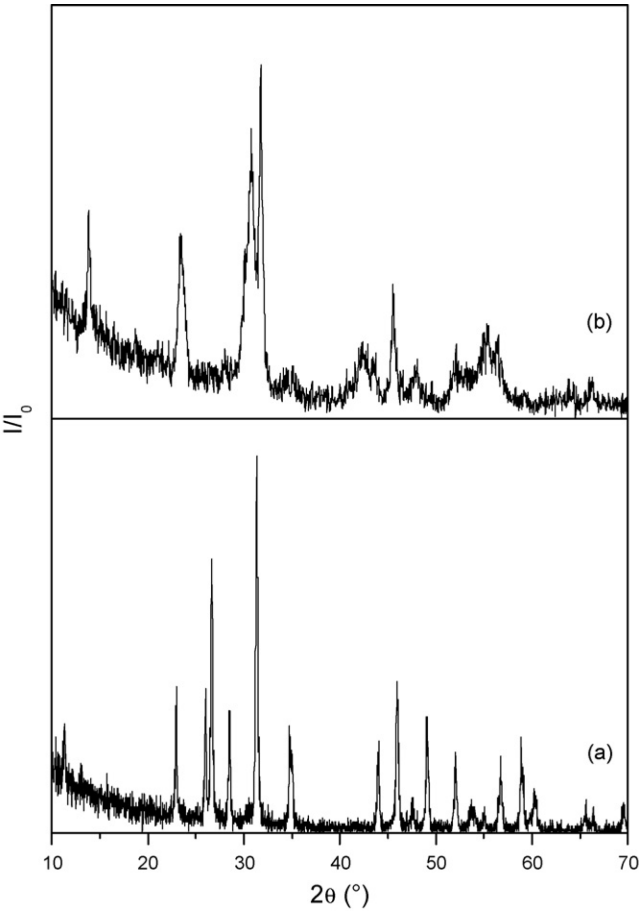

Fig. 2. XRD pattern of (a) $Sm_2O_2CO_3$ and (b) $Eu_2O_2CO_3$.

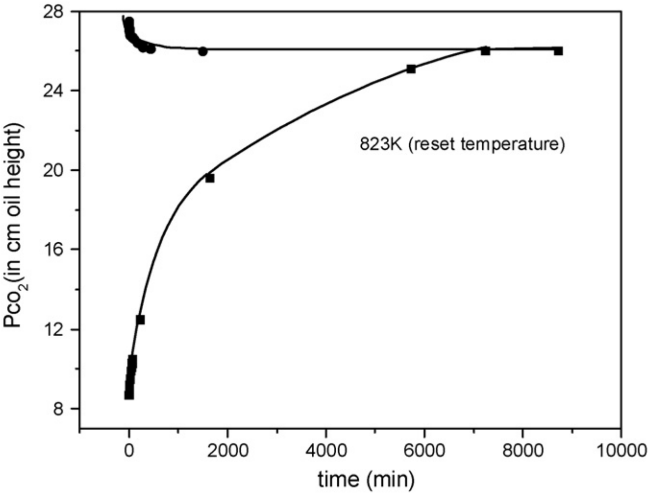

Fig. 3. Reversibility of p_{CO_2} over $Sm_2O_2CO_3(s) + Sm_2O_3(s)$ phase mixture at 823 K.

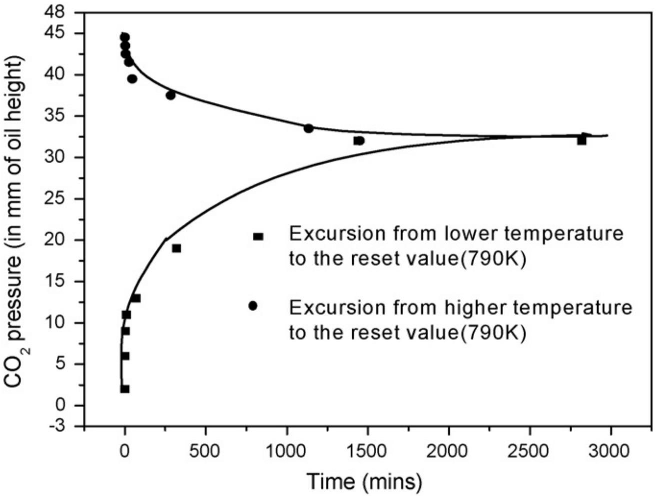

Fig. 4. Reversibility of p_{CO_2} over $Eu_2O_2CO_3(s) + Eu_2O_3(s)$ phase mixture at 790 K.

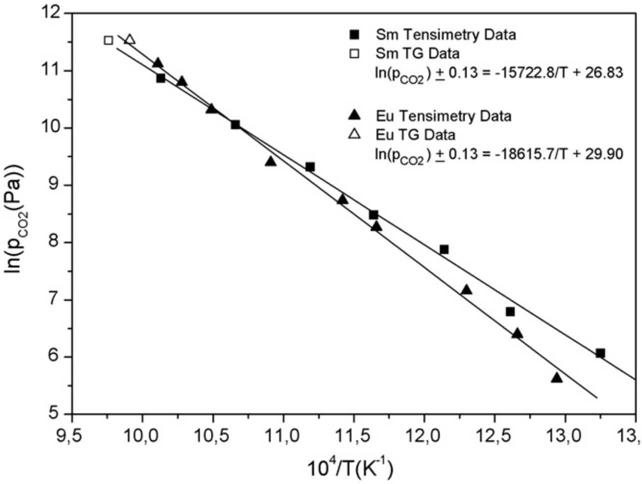

Fig. 5. Equilibrium pressure of $CO_2(g)$ over $Sm_2O_2CO_3(s) + Sm_2O_3(s)$ and $Eu_2O_2CO_3(s) + Eu_2O_3(s)$ phase mixtures.

3.3. Tensimetric studies

After loading the oxycarbonate sample in the tensimetric apparatus the system was evacuated under the dynamic vacuum of 1×10^{-8} bar. Under vacuum the sample temperature was raised to 755 K to desorb any moisture from sample. The conditioning was continued until the static pressure of the system measured by the 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 reactions:

$$Sm_2O_2CO_3(s) = Sm_2O_3(s) + CO_2(g) \quad (1)$$

$$Eu_2O_2CO_3(s) = Eu_2O_3(s) + CO_2(g) \quad (2)$$

The above-mentioned chemical path for decomposition was confirmed by TG analysis (Fig. 1). 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. Typical results for Sm_2O_2 CO_3 and $Eu_2O_2CO_3$ are shown in Figs. 3 and 4. It was also seen that the gas pressure developed in the closed system when released 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 perturbation was indicative of accomplishing thermodynamic equilibrium in the system.

The equilibrium pressures of $CO_2(g)$ at different temperatures of the sample were monitored in the temperature range of 755–987 K for $Sm_2O_2CO_3$ and 773–989 K for $Eu_2O_2CO_3$. 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 system attained equilibrium at a given temperature typically within 12 h. This averaging was done to even out the effect of room temperature fluctuation on the manometric reading. It may be noted that the room temperature fluctuated within ±2 K, which corresponds to insignificantly small uncertainty in the recorded height of manometric fluid used in this study, viz., dibutyl phthalate oil (specific gravity of 1.045 at 293 K).

From these measurements the vapor pressure relation worked out to be

$$\ln p_{CO_2}(\mathrm{Pa})\,(\pm 0.13) = \frac{-15722.8}{T} + 26.83 \quad (755 \le T(\mathrm{K}) \le 987), \quad (3)$$

for $Sm_2O_2CO_3$ decomposition and

$$\ln p_{CO_2}(\mathrm{Pa})\,(\pm 0.13) = \frac{-18615.7}{T} + 29.90 \quad (773 \le T(\mathrm{K}) \le 989), \quad (4)$$

for $Eu_2O_2CO_3$ decomposition.

The calculated temperature of 1028 K (from Eq. (3)) for 0.1 MPa of p_{CO_2} compares well with the thermogravimetric step of the decomposition observed at 1025 K under 0.1 MPa of CO_2 pressure for $Sm_2O_2CO_3(s)$ (Fig. 1). Similarly, the calculated temperature of 1013 K (from equation (4)) for 0.1 MPa of p_{CO_2} compares well with the thermogravimetric step of the decomposition observed at 1010 K under 0.1 MPa of CO_2 pressure for $Eu_2O_2CO_3(s)$ (Fig. 1). The plots of $\ln p_{CO_2}$ as a function of $1/T$ for the decomposition of $Sm_2O_2CO_3$ and $Eu_2O_2CO_3$ are given in Fig. 5.

3.4. Thermochemical data

From the vapor pressure equations of respective oxycarbonates, the mean enthalpies and entropies of the decomposition of the oxycarbonates from the second law analysis were worked out and are given in Table 1 along with the reported data of respective thermodynamic quantities. As can be seen from Table 1, the enthalpy change for the decomposition of $Sm_2O_2CO_3$ derived from thermal analysis (DTA) curves by Patil et al. [3] works out to be 105 ± 16 kJ mol^{-1}, which differs significantly from the result of this work, viz. 131 ± 5 kJ mol^{-1}. The enthalpy of decomposition of $Eu_2O_2CO_3$, derived from this work is 155 ± 5 kJ mol^{-1}. There is no reported data for this compound for comparison.

Table 1
Enthalpies and entropies of decomposition of $Sm_2O_2CO_3(s)$ and $Eu_2O_2CO_3(s)$

Ln_2O_2 CO_3 (s) = Ln_2O_3 (s) + CO_2(g)		T (K)	Δ_rH (kJ mol^{-1})	Δ_rS (J K^{-1} mol^{-1})
Ln = Sm	This work	755–987	131 ± 5	127 ± 5
	Patil et al. [3]	1023	105 ± 16	
Ln = Eu	This work	773–993	155 ± 5	153 ± 5

The difficulties in deriving the enthalpy of reaction from DTA curves have been well-documented [7,8]. The precision and accuracy of these results are very poor. It is difficult to derive the enthalpies of overlapping reactions and careful calibration in the temperature of the reaction is required. The calibration constant often depends on the nature of the sample, the type of the reaction and several other factors. Therefore, the enthalpy derived from the equilibrium measurements in this work can be considered to be more reliable. In this work, equilibrium has been established during the tensimetric measurements (Figs. 3 and 4). The temperatures of the decomposition of the dioxycarbonates in 0.1 MPa CO_2, obtained from TG/DTA also agree well with those derived from the equilibrium measurements.

Using Eqs. (3) and (4), and the Gibbs energy of formation of Sm_2O_3(s), Eu_2O_3(s) and CO_2 (g) from Barin [9], Gibbs energies of formation of the oxycarbonates could be derived as

$$\Delta_f G^0(\mathrm{Sm_2O_2CO_3(s)}\ (\pm 5.0\,\mathrm{kJ\,mol^{-1}}) = -2347.7 + 0.42\ T \quad (755 \le T(K) \le 987) \tag{5}$$

$$\Delta_f G^0(\mathrm{Eu_2O_2CO_3(s)}\ (\pm 5.0\,\mathrm{kJ\,mol^{-1}}) = -2190.3 + 0.44\ T \quad (773 \le T(K) \le 989) \tag{6}$$

4. Conclusions

Thermochemical data on rare earth oxycarbonates ($Sm_2O_2CO_3$ and $Eu_2O_2CO_3$) have been derived from tensimetric measurements of equilibrium CO_2 pressures. Thermogravimetric studies have also been carried out to corroborate the derived data. Care has been taken to establish equilibrium conditions during the measurements. In view of these arguments, the thermodynamic data on rare earth dioxycarbonates reported in this work can be considered to be more reliable than available literature values and can be used for the thermodynamic evaluations of reactions involving the oxycarbonates.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tca.2008.08.008.

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