MedCrave
Step into the World of Research

Material Science & Engineering International Journal

Short Communication

Open Access

Measurement of the standard free energy change of chemical reactions by the chemical equilibration technique using a thermogravimetric apparatus: a novel approach

Abstract

The current work aims at determining the standard free energy change (∆G°) as a function of temperature (T), using the chemical equilibration technique. A novel approach was made to find the equilibrium state with the assistance of a Thermogravimetric Analyzer. The ∆G° for lead carbonate dissociation reaction $PbCO_3(s)=PbO(s)+CO_2(g)$ was calculated as an example. The weight of $PbCO_3$started decreasing at specific temperature termed as equilibrium temperature. At this temperature $\Delta G=0$ and the equilibrium relation between ∆G° and the equilibrium constant K applied. Below this temperature, when there was no change in weight, $\Delta G>0$, and above this temperature, when the weight kept changing for continued dissociation of $PbCO_3$ (s), $\Delta G<0$. The obtained ∆G° for $PbCO_3(s)$ matched closely with the information found within in the literature.

Keywords: standard free energy, chemical equilibration technique, thermogravimetric analysis, thermodynamic data

Volume 1 Issue 1 - 2017

Aniket K Dutt,[1,2] Dinabandhu Ghosh[2]

[1]Department of Materials Science & Engineering, University of North Texas, USA
[2]Department of Metallurgical and Materials Engineering, Jadavpur University, India

Correspondence: Aniket K Dutt, Department of Materials Science & Engineering, University of North Texas, Denton, TX 76203, USA, Email aniketdutt@my.unt.edu

Received: March 03, 2017 | **Published:** April 21, 2017

Introduction

A thermogravimetric analyzer (TGA) measures the change in the mass of a reacting sample as function of time at any specified temperature or as a function of both temperature and time, which are conventionally used in the kinetic analysis of the reaction under study. Commonly, the change in the mass is converted into the fractional (or, percentage) conversion of the sample. A set of data of fractional conversion vs time helps to graphically detect the correct rate controlling mechanism by referring to the governing equations of differentrate controlling mechanisms such as gas film diffusion, product layer diffusion, and the interfacial reaction. However, it is not much heard of that a thermogravimetric analyzer has ever been used for any thermodynamic measurements. In the last decades, researchers used different approach like thermo barometry, EMF, and calorimetry methods for the determination of thermodynamic data.[1–10] Berman[1] used thermo barometry techniques to measure the thermodynamic data of minerals.[1] O'Neill et al.[8] studied the Gibbs free energies of formation of RuO_2, OsO_2 and IrO_2 using an electrochemical method with calcia–stabilized zirconia (CSZ) solid electrolytes.[8]

The current work aims at adapting the apparatus to the determination of the standard (Gibbs) free–energy change of a chemical reaction as a function of temperature, in the form $\Delta G°=A+BT$, where $A=\Delta H°$ and $B=-\Delta S°$, by using the chemical equilibration technique. An attempt was made to verify this new method by comparing the results obtained by it with the known, published data of the standard free–energy changes for the dissociation of two solid carbonates $CaCO_3$ and $PbCO_3$.Particularly, the reaction $PbCO_3(s)=PbO(s)+CO_2(g)$ was studied in details. It is proposed that if the new method is found to be successful, it can be extended to measuring the standard free–energy change of many other reactions for which the data have not yet been available.

Principle

The principle of determining the standard free energy change ($\Delta G°$) by the chemical equilibration technique in the thermogravimetric analyzer (TGA) is elucidated with the help of an example of the dissociation of lead carbonate expressed as

$$PbCO_3(s)=PbO\ (s)+CO_2(g);\ \Delta G°=A+BT\ (1)$$

Here, both A and B, which are standard enthalpy change ($\Delta H°$) and negative standard entropy change ($-\Delta S°$), respectively, are treated as unknown, and it is required to evaluate them experimentally so that the measured value of $\Delta G°$ can be expressed in the above common form of two–term equation.

The two most important variables in the current method are the temperature (T) and the partial pressure of carbon dioxide (p_{CO2}). These are mutually dependent because of the fact that the thermodynamic equilibrium constant of Reaction (1), $K_{(1)}$, expressed by the ratio ($a_{PbO}\cdot a_{CO2}$) / (a_{PbCO3}), is solely governed by p_{CO2}, the activities (a_i) of the two pure condensed phases ($PbCO_3$ and PbO) being 1 and a_{CO2}being equal to p_{CO2}. In the thermogravimetric apparatus, a chosen p_{CO2} (1 or less) is maintained by letting pure CO_2 (for p_{CO2}=1atm) or a mixture of CO_2 and Ar(for p_{CO2}<1atm), Ar (argon) being the diluent, flow over the solid sample ($PbCO_3$) continuously to ensure equilibration between the gas and solid while the furnace is heating and the temperature is slowly rising. Now, there is a unique temperature at which Reaction (1) comes to equilibrium with respect to the applied p_{CO2}, satisfying the thermodynamic condition of $\Delta G=0$ for equilibrium. Below this temperature, ΔG is greater than 0 (criterion for the impossibility of reaction), and above this temperature, ΔG is less than 0 (criterion for the spontaneity of reaction). The manifestation of the condition $\Delta G<0$ in the TGA is the occurrence of Reaction (1) leading to the release of CO_2 from the sample and the accompanying decrease in the mass of the sample. Thus, starting from the room temperature up to this unique temperature there is no change in the mass of the sample and the mass (weight) vs temperature curve, a TGA output, will remain flat for this particular temperature span. Just above the unique temperature, the mass of the sample will start decreasing and there will be a consequent descent of the curve, which will continue descending with the increasing temperature till the sample lasts. Thus, at this unique temperature (T_1, say), Reaction (1) will attain equilibrium (ΔG=0) under the applied p_{CO2} ($p_{CO2\ (1)}$, say). Alternatively, one can write, ΔG°_{T1}=–RT_1ln K_{T1}=–RT_1ln $p_{CO2\ (1)}$, where the value of R, the universal gas constant, is 8.314J/mol. K. Knowing both $p_{CO2\ (1)}$ and T_1 experimentally, the value of ΔG° at the temperature T_1, ΔG°_{T1}, is obtained. Similarly, by applying several other chosen partial pressures of CO_2 (with the help of CO_2–Ar mixtures produced at varying proportions) and by repeating the experiment, ΔG° at several other temperatures (T) can be found. These values of ΔG° when plotted against T will give ΔG° in the form of $A+BT$, where A and B are now known quantities.

Experimental

Commercially available powder $PbCO_3$(s) and $CaCO_3$ (s) were used for this work. To measure the weight change in the powder material with temperature and pressure thermogravimetric analyze (Bysakh, Okay) was used. The powdered sample of $PbCO_3$(s) and $CaCO_3$(s) was placed into the crucible. A heating rate of 10K/min was used for the experiment. A gas mixture of Ar and CO_2 was used for experiments. Gas mixture is passed through silica gel moisture trap to get rid of the moisture. For $PbCO_3$, three different values of p_{CO2} were considered: 0.4atm, 0.5atm, and 0.75atm. These partial pressures were established by mixing CO_2 and Ar ($p_{CO2+}p_{Ar}$=1atm) in the ratio 2:3 (for p_{CO2}=0.4atm), 1:1 (for p_{CO2}=0.5atm), and 3:1 (for p_{CO2}=0.75atm). However, for the experiment with $CaCO_3$, pure CO_2 (p_{CO2}=1atm) alone was considered. (Figure 1) shows the schematic of TGA experimental set–up.

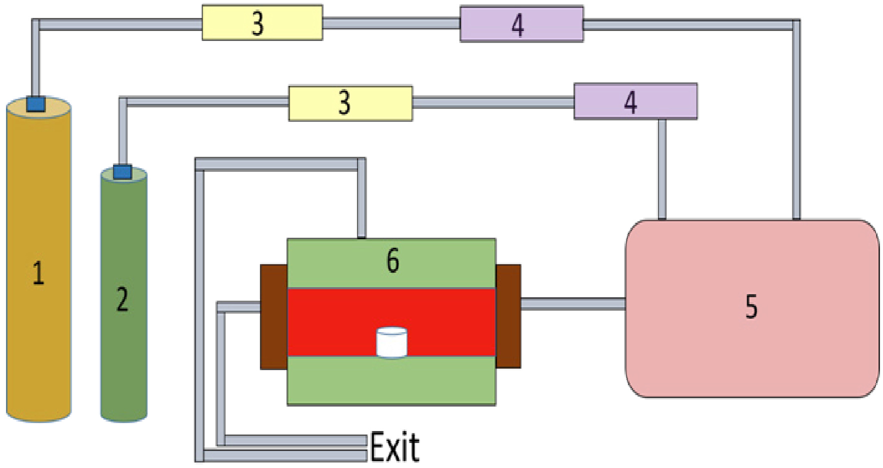

Figure 1 Schematic diagram of the experimental set-up: 1. CO_2 cylinder; 2. Ar cylinder; 3. Flow meter; 4. Moisture trap; 5. Mixer and gas channeling arrangement; 6. TGA

Result and discussion

$CaCO_3$

The weight vs temperature plot obtained from the TGA run on the dissociation of $CaCO_3$, the dissociation reaction

$CaCO_3$(s)=CaO(s)+CO_2(g) (2)

Under 1atm of CO_2, is shown in (Figure 2). Barring some small fluctuations in the curve because of gas flow disturbance, the temperature at which there is a monotonic descent of the curve is clearly noticeable and is found to be 853°C (1126 K). Now, according to the published data,[11] the standard free–energy change for Reaction (2) is

ΔG°=178500–159.1 T J (3)

This gives T=178500/159.1=1122 K=849°C for ΔG=ΔG°=0, noting that this is a case of standard state equilibrium because not only the two solids ($CaCO_3$ and CaO) but CO_2 also is at the standard state (1atm). This means that according to the published data, the onset of the descent of the curve should have been at 849°C. The agreement between the TGA result and the published one is thus very close.

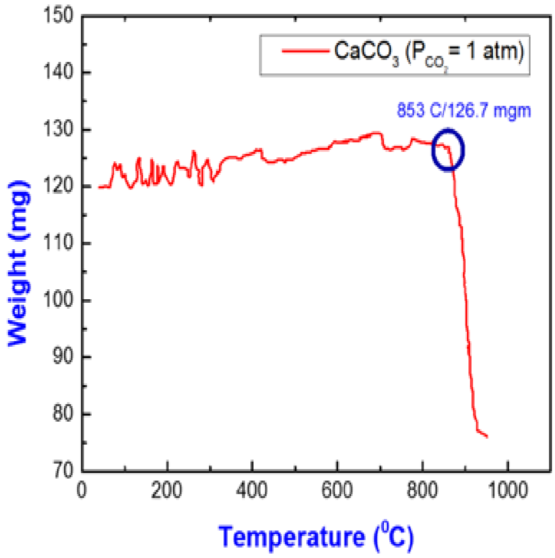

Figure 2 Weight versus temperature plot for the dissociation of $CaCO_3$ under 1atm CO_2.

Citation: Dutt AK, Ghosh D. Measurement of the standard free energy change of chemical reactions by the chemical equilibration technique using a thermogravimetric apparatus: a novel approach. *Material Sci & Eng Int J.* 2017;1(1):5‒8. DOI: 10.15406/mseij.2017.01.00002

PbCO3

The weight vs temperature plots obtained from the TGA run on the dissociation of $PbCO_3$ (Reaction (1)) for the three different values of p_{CO2}, 0.4atm, 0.5atm, and 0.75atm, are shown in (Figures 3 A, B, C), respectively. The corresponding temperatures for the onset of the descent of the curve, in a monotonic and noticeable manner, are 280±4°C (553±4K), 287±3°C (560±3K), and 300±6°C (573±6K), respectively. This allows one to find the values of $\Delta G°$ at these temperatures by using the relation $\Delta G° = –RT \ln K = –RT \ln p_{CO2\ (applied)}$. These values are listed in (Table 1).

In (Figure 4), a plot of $\Delta G°$ vs T is made and a good linear fit is found, which yields the following expression for the standard free energy change of Reaction (1):

$\Delta G° = 82955–142.37\ T$ J (4)

In comparison, the published data[11] for Reaction (1) is

$\Delta G° = 86700–149\ T$ J (5)

The two results differ by only about 4%, which may be considered quite satisfactory, and the standard free–energy data thus measured by the thermogravimetric analyzer may be considered reliable. This method may be extended to measure the standard free energy changes for the dissociation of $CrCO_3$(s), $NiCO_3$(s), $TiCO_3$(s), and WCO_3(s) and for similar other gas–solid reactions (dissociation of oxides, nitrides, *etc*) for which data are not yet available in the literature.

Table 1 Equilibrium temperatures for different applied partial pressures of CO_2, as obtained from the TGA, and the corresponding $\Delta G°$ values, for the reaction $PbCO_3(s)=PbO(s)+CO_2(g)$

Exp. no.	Sample	P_{CO2}(Atm)	Equilibrium temp.°c(K)	$\Delta G°$ (J)
1	$PbCO_3$(s)	0.4	280±4(553±4)	4212.77±25
2	$PbCO_3$(s)	0.5	287±3(560±3)	3227.18±14
3	$PbCO_3$(s)	0.75	300±6(573±6)	1370.49±12

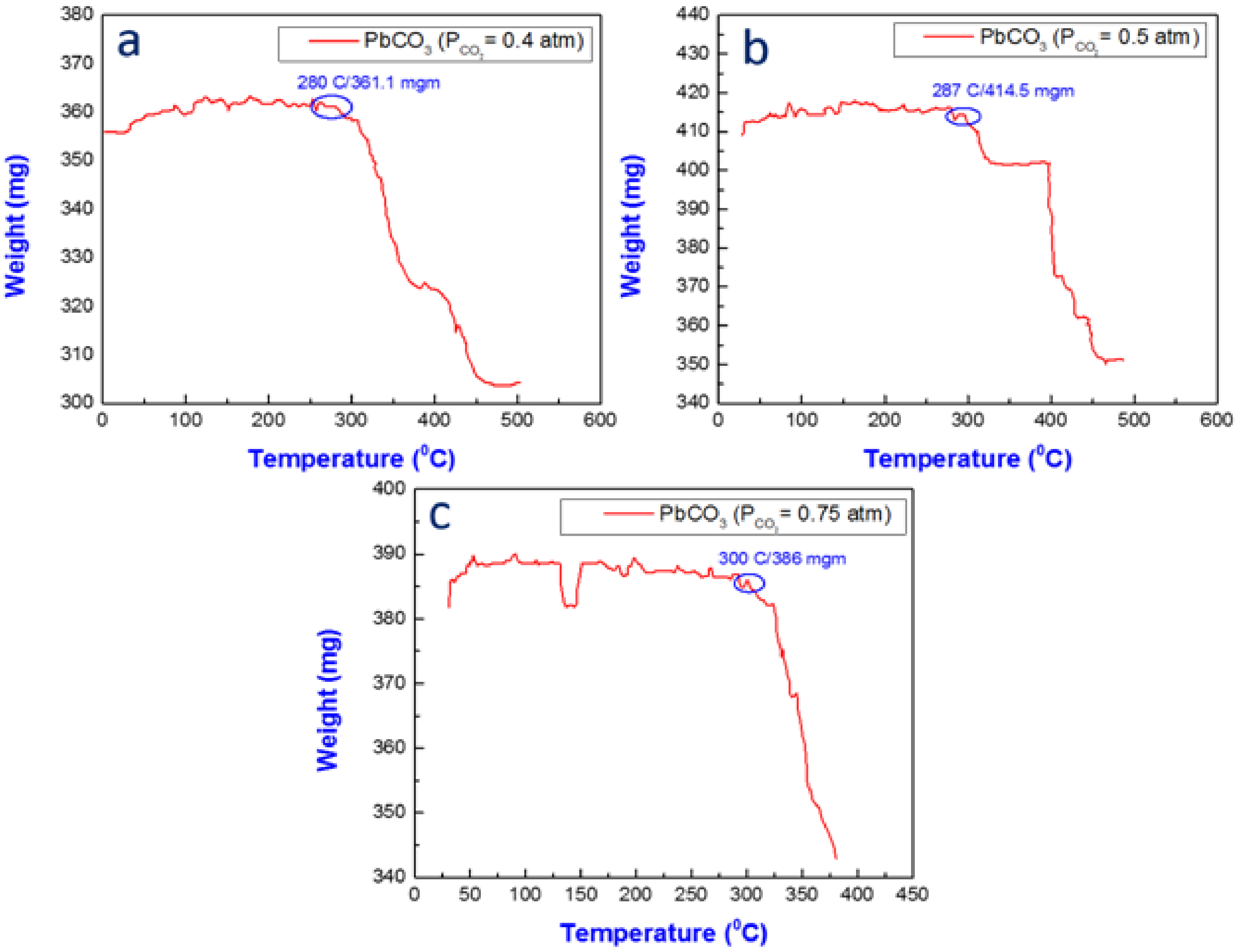

Figure 3 Weight versus temperature plot for the dissociation of $PbCO_3$ under (a) 0.4atm p_{CO2} (b) 0.5atm p_{CO2} and (c) 0.75atm p_{CO2}.

Citation: Dutt AK, Ghosh D. Measurement of the standard free energy change of chemical reactions by the chemical equilibration technique using a thermogravimetric apparatus: a novel approach. *Material Sci & Eng Int J.* 2017;1(1):5–8. DOI: 10.15406/mseij.2017.01.00002

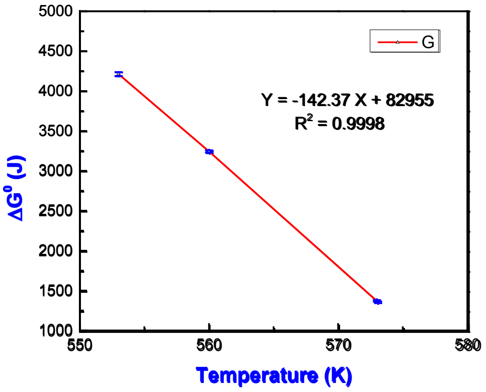

Figure 4 Plot of standard free energy change (ΔG°) vs temperature (T) for the reaction $PbCO_3(s) = PbO(s)+CO_2(g)$.

Conclusion

The salient features of the current work are as follows:

A. The thermogravimetric analyzer (TGA) has been traditionally used for kinetic studies. The current work aims at adapting the apparatus to the determination of the standard (Gibbs) free–energy change of a chemical reaction as a function of temperature, by using the chemical equilibration technique.

B. An attempt was made to verify this new method by comparing the results obtained by it with the known, published data of the standard free–energy changes for the dissociation of two solid carbonates $CaCO_3$ and $PbCO_3$.

C. The standard free energy change for the reaction $PbCO_3$ (s)=PbO (s)+CO_2 (g) was measured by the current method and the result obtained compared well with the published data:

$\Delta G^\circ = 82955 - 142.37\ T$ J (current work)

$\Delta G^\circ = 86700 - 149\ T$ J (published in data book).[11]

The two results differ by only about 4%. Hence, the standard free–energy data thus measured by the thermogravimetric analyzer may be considered reliable.

D. This method may be extended to measure the standard free energy changes for the dissociation of $CrCO_3$(s), $NiCO_3$(s), $TiCO_3$(s), and WCO_3(s) and for similar other gas–solid reactions (dissociation of oxides, nitrides, *etc*) for which data are not yet available in the literature.

Acknowledgements

None.

Conflict of interest

The author declares no conflict of interest.

References

1. Berman RG. Thermobarometry using multi–equilibrium calculations: a new technique, with petrological applications. *Canadian Mineralogist*. 1991;29:833–855.
2. Fitzner K. Diffusivity activity and solubility of oxygen in liquid bismuth. *Thermochimica Acta*. 1980;35:277.
3. Ganesan R, Gnanasekaran T, Srinivasa RS. Determination of standard molar Gibbs free energy of formation of Bi2O3 over a wide temperature range by EMF method. *The Journal of Chemical Thermodynamics*. 2003;35:1703.
4. Isecke B, Osterwald J. Gleichgewichtsuntersuchungen am System Wismut–Sauerstoff. *Zeitschrift für Physikalische Chemie*. 1979;115(1):17–24.
5. Kameda K, Yamaguchi K. Activity Measurements of Liquid Ag–Bi Alloys by an EMF Method Using a Zirconia Electrolyte. *Journal of the Japan Institute of Metals and Materials*. 1991;55(5):536–544.
6. Kameda K, Yamaguchi K, Kon T. Activity of Liquid Ti–Bi Alloys Measured by an EMF Method Using Zirconia Electrolyte. *Journal of the Japan Institute of Metals*. 1992;56:900.
7. Mehrotra G, Frohberg M, Kapoor M. Standard Free Energy of Formation of Bi2O3. *Zeitschrift für Physikalische Chemie*. 1976;99:304–307.
8. O'Neill HSC, Nell J. Gibbs free energies of formation of RuO2, IrO2, and OsO2:A high–temperature electrochemical and calorimetric study. *Geochim Cosmochim Acta*. 1997;61(24):5279–5293.
9. Rao AR, Tare V. Determination of the Melting Point and Heat of Fusion of Bi2O3 by the Solid Electrolyte Technique. *J Electrochem Soc India*. 1973;22:20.
10. Rao AR, Tare V. Free energy of formation of Bi_2O_3. *Scripta Metallurgica*. 1971;5:807.
11. Kubaschewski O, Alcock CB, Spencer P. *Materials thermochemistry*. 6th ed. USA: Pergamon Press; 1993.

Citation: Dutt AK, Ghosh D. Measurement of the standard free energy change of chemical reactions by the chemical equilibration technique using a thermogravimetric apparatus: a novel approach. *Material Sci & Eng Int J*. 2017;1(1):5–8. DOI: 10.15406/mseij.2017.01.00002