Density Measurement of Powdery and Porous Substances with a Gravimetric BET Adsorption Apparatus

Han-Sung Kim, Hyun-Woo Cho, Kwang-Soon Lee[†], and Woon-Sun Ahn*

Department of Chemistry, Sung Kyun Kwan University, Suwon 440-746
[†]Department of Chemistry, Song Sim College For Women, Buchon 422-743. *Received April 21, 1992*

An accurate method of density measurement is proposed. The method makes use of a gravimetric adsorption apparatus and is quite suitable for powdery and porous solid samples. The sample volume is determined by measuring its buoyancy with microbalance and the mass is measured in vacuum in the absence of buoyancy effect. Densities of inorganic compounds, such as alumina and perovskite, and some organic compounds are determined with the proposed method, and the results are compared with the values either determined with conventional methods or obtained from literatures.

Introduction

The density of material, a ratio of the sample mass to the volume, is one of the fundamental properties. However, the result of measurement is subjected to a considerable error especially when the sample is fine powdery or porous solid. The density of solid sample is commonly determined with a conventional liquid displacement method[1-4], in which the real volume is measured by the volume of the liquid which is displaced by the sample. In most measurements, however, a considerable amount of gas dispersed as fine bubbles and trapped in fine capillary pores can not be readily displaced by the liquid, hence an overestimated value of the sample volume is resulted. This inaccuracy in the sample volume measurement combined with the buoyancy effect which comes in when the sample mass is measured in the air results in an inaccurate density. This inaccuracy is significant especially when the sample is fine powdery or fine porous solid. In the gas volume measuring method, the known mass of sample is placed in a known volume of container and the volume of an inert gas which fills the pores and the free space is measured to obtain the sample volume. This method is also subject to a considerable error due to the inherent inaccuracy in the gas volume measurement. X-ray data for lattice dimension is also used to calculate the density. A correction for the lattice defects is neglected usually in calculating the density.

This paper is a supplement to a note previously reported in this journal[5]. The theoretical basis of the proposed method is the same, but the method is described in detail with the insertion of experimental basis in order to show the reliability of the method. Variety of samples ranging from organic to inorganic compounds are used for density measurement, and the results are found very satisfactory.

Experiments

Samples. Alumina samples are obtained by immersing aluminium foils with oxide film grown on it in an acid solution to dissolve off the metal. The oxide left thereupon is very fragile and porous, and is known to have an γ'-alumina structure.

The perovskite-type mixed oxide samples are synthesized by the citrate precipitation method[6] from the metal nitrates in this laboratory. The crystal structures of synthesized oxides are confirmed with SEM and XRD. Other organic and inorganic samples are commercially obtained reagent grades.

Sensitivity of the balance. A gravimetric adsorption apparatus with a Nernst-Donau type quartz beam microbalance is used[7,8]. It has been described in a previous paper[8]. The sensitivity of the microbalance is determined by counterbalancing the standard weight. Alnico wire is used as the counter weight around which magnetic field is generated by the controlled electric current passing through a solenoid, wound right around the outer wall of the encasing tube. Gold weights of known mass ranging from 372 μg through 3183 μg are used as standard weights for calibration of the balance. A good linearity between the voltage of the counterbalancing current and the mass of the standard weights was obtained. The sensitivity of the balance calculated from this linearity was 2.23 μg/mV.

Blank volume of the balance. Whenever the mass of a sample is measured with a balance, there arises a buoyancy effect due to the unequal volume distribution between two arms of the balance beam. The magnitude of this buoyancy effect is a function of the pressure of the gas surrounding the balance according to the Archimedes' principle. It can be given by the following equation, assuming the ideal behavior of the gas.

$$W=\frac{M\Delta V}{RT}P$$

where, M is the molar mass of the gas, ΔV the volume difference between two arms of the balace beam, and other symbols have their usual physical meanings. The buoyancy is the difference in weights measured in the fluid and in vacuum. Argon is used as a fluid gas. The buoyancy is measured at various pressures and plotted against the pressure. A straight line should be resulted in according to the above equation, with the slope of $M\Delta V/RT$. From the slope ΔV can be calculated.

The value of ΔV determined in this way includes two contributions: one from the sample and the other from the unequal volume distribution of the balance between two arms. In order to estimate the latter effect, following experiments are carried out with the sample bucket loaded successively with 5 tiny glass bulbs of known volume. The chamber arm,

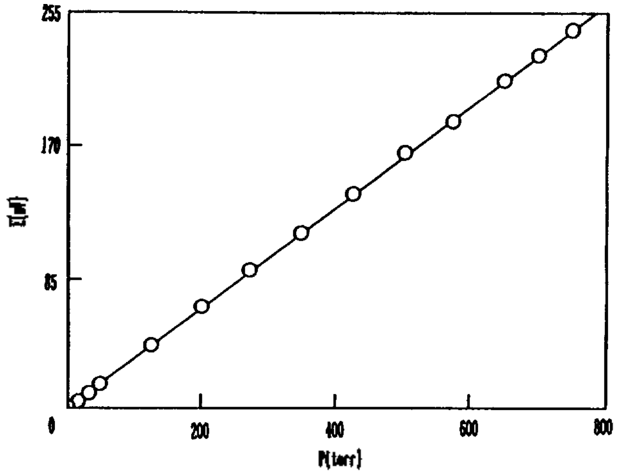

Figure 1. Buoyancy *vs.* the gas pressure, when the sample bucket is loaded with a glass bulb of 0.377 cm^3.

Table 1. Blank Volume of the Balance

Bulb	1	2	3	4	5
Volume of bulb (cm^3)	0.377	0.378	0.388	0.440	0.567
ΔV (cm^3)*	0.309	0.306	0.321	0.364	0.487
Blank volume	−0.068	−0.072	−0.067	−0.076	−0.080

*Values are the volumes measured without blank volume correction.

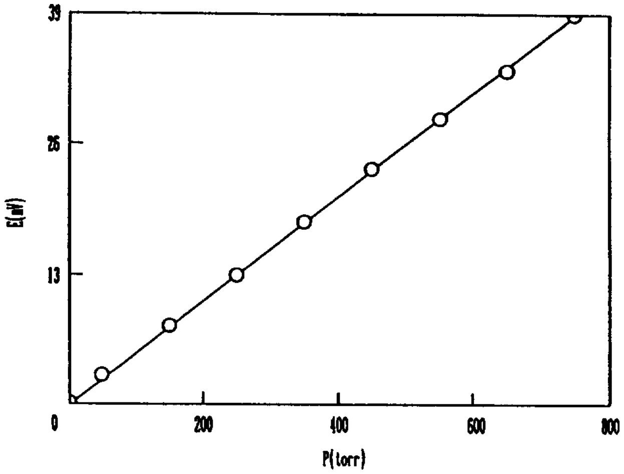

Figure 2. Buoyancy *vs.* the gas pressure, when the sample bucket is loaded with $La_{0.97}Sr_{0.03}NiO_3$.

Table 2. The Densities Determined with Various Method

Sample	Density (g/cm^3)			
	This	Conventional	Lattice parameter[9]	Literature[10,11]
$LaNiO_3$	6.84	6.71	7.22	
$La_{0.99}Sr_{0.01}NiO_3$	6.81			
$La_{0.98}Sr_{0.02}NiO_3$	7.00	6.64		
$La_{0.97}Sr_{0.03}NiO_3$	6.83			
$La_{0.96}Sr_{0.04}NiO_3$	6.84	6.04		
$La_{0.94}Sr_{0.06}NiO_3$	6.82			
$La_{0.99}Ba_{0.01}NiO_3$	7.57			
$LaFeO_3$	6.67	6.00	6.64	
Aluminium foil with oxide film (1)	2.98			
Aluminium foil with oxide film (2)	3.16			
γ'-alumina (3)	2.56			
Mannitol ($C_6H_{14}O_6$)	1.53			1.52
Thiourea (H_2NSCNH_2)	1.40			1.41
Anthracene ($C_{14}H_{10}$)	1.21			1.28
Si_3N_4	3.15			3.20
α-SiC	3.37			3.21
α-alumina	4.14			4.00
$BaCO_3$	4.38			4.29
TiB_2	4.69			4.50
TiN	5.45			5.21
NiO	6.74			6.67

inside of which the sample bucket is suspended, is immersed in ice water, and kept the temperature of the system at 0℃ during the measurement. The displacing gas, argon, is introduced slowly through a variable leak valve (capable of controlling the inlet gas at the rate of 10^{-10} cm^3/sec through 100 cm^3/sec). With a glass bulb of 0.377 cm^3 loaded on the sample bucket, the counterbalancing voltage is measured as a function of the gas pressure. The buoyancy is calculated and plotted against the gas pressure as shown in Figure 1. Similar measurements are repeated with other glass bulbs successively. These results are used to calculate the volume contribution of the balance itself. This contribution, shown in Table 1, is a blank volume to be corrected to the volume of the sample measured in the course of the density measurement. The blank volume obtained in this way is −0.073 cm^3 in average. The negative sign means that the counterweight side of the balance is bulkier.

Results and Discussions

The sample mass is measured in vacuum in order to eliminate buoyancy and gas adsorption effects. For this purpose the mass of the sample is measured in air and the corresponding voltage which counterweight the sample is measured with the microbalance at first. Then the system with the sample loaded on the balance is evacuated down to 10^{-5}-10^{-6} torr. The counterweighing voltage is measured with the sample in this completely desorbed state. The difference between the voltage in air and in vacuum can be attributed to the elimination of the buoyancy and adsorption effects. The mass equivalent of this voltage difference is calculated and subtracted from the mass in the air to obtain an accurate mass in vaccum.

The smaple volume is determined from the buoyancy measured in the course of its mass measurement. The buoyancy effect measured for perovskite $La_{0.97}Sr_{0.03}NiO_3$ is shown in Figure 2. The effects of other samples are not shown as they give similar straight lines. The densities obtained from the masses and volumes measured in this was are given in Table 2. The densities determined by the conventional method of liquid displacement, those calculated from lattice parameters[9] and the literature values[10,11] are also listed for comparison. The densities measured with the conventional liquid displacement method are found to give smaller values, as expected. Fairly good agreement is obtained in general between the values of the proposed method and those calculated from the lattice parameters[9]. Also, the values of this method agree very well with the literature values[10,11]. The proposed method is simple, intuitive, and yet gives quite an accurate result. This method will be especially of value when the sample is in powdery, porous form, or is reactive to displacing liquids.

Acknowledgement. This work is supported financially by the Ministry of Education, through the Basic Research Institute Program.

References

1. V. R. Choudhary and S. H. Vaidya, *Research and Industry*, **26**, 1 (1981).
2. D. Geldart, *Chem. Eng. Sci.*, **34**, 155 (1979).
3. W. H. Salzberg, J. I. Morrow, S. R. Cohen, and M. E. Green, "Physical Chemistry Laboratory", Part I, Chapter 8, Macmillan Publishing Co., Inc., New York, 1978.
4. S. Lowell and Joan E. Shields, "Powder Surface Area and Porosity", Chapter 21, Champman and Hall, New York, 1984.
5. W. Ahn, K. Lee, H. Cho, and J. Kim, *Bull. Korean Chem. Soc.*, **11**, 572 (1990).
6. D. J. Anderton and F. R. Sale, *Powder Metallurgy*, No. 1, 14 (1979).
7. S. P. Wolsky and E. J. Zdanuk, "Ultra Micro Weight Determination in Controlled Environments", Interscience Publishers, 1969.
8. W. Ahn, E. Yoo, H. Cho, and J. Kim, *Bull. Korean Chem. Soc.*, **9**, 244 (1988).
9. T. Nakamura, G. Petzow, and L. J. Gauckler, *Mat. Res. Bull.*, **14**, 649 (1979).
10. J. A. Dean, "Lange's Handbook in Chemistry", 12th Ed., McGraw-Hill, 1979.
11. S. Budaveri *et al.*, "The Merck Index", 11the Ed., MERCK & CO., INC., 1989.

Thermochemical Behaviour of Some Salicyaldehyde G-P Complexes of Fe (III), Co (II), Cu (II) and Zn (II)

M. A. H. Hafez* and M. N. H. Moussa

Department Chemistry, Faculty of Science, Mansoura University, Mansoura, Egypt

Received May 15, 1991

Through two different techniques TGA and DSC the thermal decomposition processes of salicyaldehyde G-P complexes having the general formula: $[MCl_2(L)_2]^{2+}\ 2Cl^-$; where L = salicyaldehyde carbohydrazone pyridinum cation, and M = Fe (III), Co (II), Cu (II) and Zn (II), have been studied. From the obtained thermogravimetric curves the following parameters n, E_a, A, ΔS^*, ΔH^* and ΔG^* were evaluated. The effect of the nature of the metal ions present in the complexes studied upon the calculated thermodynamic parameters was reported. A suitable mechanism for the thermal decomposition process was suggested.

Introduction

The thermal behaviour of the complexes plays a very important role for chemist to understand the mechanism of the thermal process. This thermal behaviour is based on the qualitative and quantitative analysis of the DTA and TG curves respectively[1-5]. The aim of the present work is to describe the thermochemical behaviour of some complexes, discuss the differences in their thermal stabilities and also to find a suitable mechanism for the thermal decomposition process.

Experimental

Syntheses of the complexes studied were carried out as mentioned previously[6]. The stoichiometry of the solid compounds obtained was confirmed by the results of the elemental analysis, molar conductance of solution of the complex (see Table 1), and magnetic measurements.

The thermal decomposition has been studied in a Pt crucible by thermo-analyser [TGA-DTA (1600℃) GDTA 15, Setram Lyon-France and DSC 777 Lyon-France] using linear temperature programmer with a constant heating rate of 5 ℃/min. Sample weight used was in the range of 20-37.2 mg.

Results and Discussion

Analysis of the DTA Curves. All the DTA curves obtained showed four different peaks. For example, in the case of the cobalt-complex the following peaks were observed:

1. A sharp endothermic peak at 254.3℃ which corresponds to the dechlorination of the chloride ions. This was confir-

---

*To whom all correspondence should be addressed.