Table 4. Emperical Parameters for ^{13}C Chemical Shifts of Alkanes[a] and Amines[b]

S	B_S	A_{S2}	A_{S3}	A_{S4}	γ_S	δ_S	N_i
1	6.80	9.56	17.83	25.48	−2.99	0.49	$N = 22.58$
2	15.34	9.75	16.70	21.43	−2.69	0.25	$N = 2.02$
3	23.46	6.60	11.14	14.70	−2.07		$N = 0.20$
4	27.77	2.26	3.96	7.35	0.68		$N = 1.63$

[a] From reference 2, [b] From reference 4(a).

$$\begin{aligned}\delta_{COO} &= 182.09 + d_3 + d_4 + d_5\\ &= 182.09 + 2.56 - 0.55 - 3.33\\ &= 180.77\end{aligned}$$

The experimental values of δ_G, δ_α, and δ_{COO} are 60.16, 53.18 and 181.00 ppm, respectively.

The standard deviations between the shifts calculated by this approach and those determined experimentally for aminopolycarboxylate anions are 0.29 ppm for the carboxylate carbons, 0.40 ppm for the glycinate carbons, and 1.13 ppm for other carbons. We found the good agreement for carboxylate and glycinate carbons but less agreement for other carbons. The larger difference between calculated and experimental values might be originated from the conformational and/or electronic differences between compounds whose data are used as models for the parameterization.

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A New Method of Density Measurement

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Density is defined as a ratio of the sample mass to the volume occupied by that mass. In case of fine powderous or fine porous solid material, it is essential to eliminate a fake volume contributed from fine pores and internal voids in measuring the volume to obtain an accurate density. For this purpose, in the conventional method[1-4] the gas which fills these pores and internal voids is displaced with a wetting liquid such as water and the mass difference thereupon is measured to determine the gas phase volume inside the sample. In most of the experiment, however, a considerable amount of gas, dispersed as fine bubbles in the sample, can not be displaced completely by the liquid, thereby resulting in a negative deviation in the measured density.

In this brief note, a method of measuring an accurate density of powderous or porous substances is reported. In this new method, the void volume is measured with an inert gas using the BET adsorption apparatus.

Experimental

Meterial. Argon gas of 5 N purity is used as the displacing fluid and ambient gas in the BET apparatus. The powder sample is the perovskite-type mixed oxides ($LaNiO_3$, $La_{0.98}Sr_{0.02}NiO_3$, $La_{0.96}Sr_{0.04}NiO_3$, $LaFeO_3$, $La_{0.9}Sr_{0.1}FeO_3$), which are synthesized by the citrate precipitate method[5] from the component metal nitrates in this laboratory and sieved out between 230 and 270 meshes.

Apparatus and Measurement. The BET adsorption apparatus used in this work is a gravimetric one, which has been described in a previous paper[6]. The sensitivity of the microbalance was determined to be 2.23 μg/mV.

Description of the Method

A buoyancy effect is used to measure the volume of the sample with the microbalance in the BET system. Buoyancy effect results from the volume difference between the sample bucket and the counterbalancing magnet of the microbalance. The magnitude of the effect is expected to increase with the pressure of the gas inside the system according to the Archimedes' principle;

$$W = \frac{MP}{RT} \Delta V,$$

where W is a difference of the buoyant force of the bucket and magnet, arising from their volume difference ΔV, and all other symbols have their usual physical meanings. The buoyancy difference W is read off from the counterbalancing currents flowing through the solenoid surrounding the magnet, and then plotted against the gas pressure. From the slope of this plot ΔV can be obtained.

The value of ΔV determined in this way includes two contributions: one from the sample and the other from the unequal volume between the two arms of the balance itself. In order to calibrate for the latter effect, the experiments are carried out with the sample bucket loaded successively with 5 tiny glass bulbs of known volume. One of these calibration

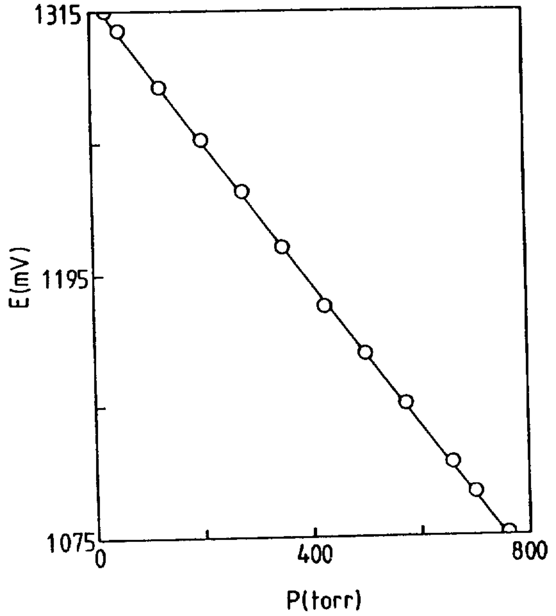

Figure 1. Calibration plot of the counterbalancing current vs. the gas pressure, when the sample bucket is loaded with a glass bulb of 0.377 cm^3.

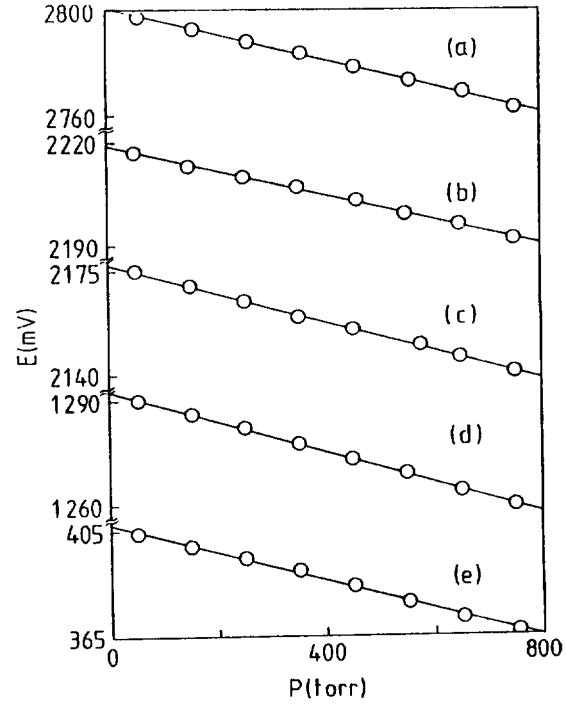

Figure 2. The plot of the counterbalancing current vs. the gas pressure, when the sample buckets is loaded with five samples, successively. (a), $LaNiO_3$; (b), $La_{0.96}Sr_{0.04}NiO_3$; (c), $La_{0.98}Sr_{0.02}NiO_3$; (d), $La_{0.9}Sr_{0.1}FeO_3$; (e), $LaFeO_3$.

results are shown in Figure 1, in which the volume of the bulb is 0.377 cm^3. All other results show similar features.

The calibrations result in the volume difference of 0.073 cm^3 in average, the magnet side being bulkier.

Table 1. The Densities Determined with Various Method

Sample	Density (g/cm^3)		
	This method	Conventional method	Lattice parameter method
$LaNiO_3$	6.976	6.713	7.216
$La_{0.98}Sr_{0.02}NiO_3$	6.996	6.643	
$La_{0.96}Sr_{0.04}NiO_3$	7.792	6.035	
$LaFeO_3$	6.666	5.997	6.643
$La_{0.9}Sr_{0.1}FeO_3$	7.241	6.538	

Results and Discussions

The buoyancy effect is measured for five perovskite-type mixed oxides and the data are shown in Figure 2. The volume difference ΔV is determined from these data, and the real volumes of the samples are obtained after the calibration. The results of the density obtained by this method are given in Table 1. The volumes determined by a conventional method[1] of replacing the void space air by liquid water and those determined from the lattice parameters[7] are also shown for comparison. Good agreement is obtained between the densities by this method and those by the lattice parameters, suggesting this method is suitable to determine the accurate density of fine powders. The densities by the conventional method are found to deviate negatively, and also expected to depend on the liquid used. It is concluded that this method determines the accurate density of fine powderous or porous substances. The method is especially of value when the sample reacts with displacing liquid. A flaw in this method might be the use of BET apparatus, a little intricate equipment.

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