

## Vaporization Studies on Buckminsterfullerene

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A Knudsen cell mass spectrometric study of pure  $C_{60}$  was carried out in the temperature range 600–800 K to obtain the vapor pressure and enthalpy of sublimation. The measured appearance potential for  $C_{60}^+$  ( $8.1 \pm 0.5$  V) is in good agreement with the recommended value ( $7.6 \pm 0.2$  V) for the ionization potential of  $C_{60}$ . The enthalpy of sublimation was found to be  $181.4 \pm 2.3$  kJ/mol at 700 K by the second law method. The vapor pressure of  $C_{60}$  is given as a function of temperature by the equation  $\log(p/\text{Pa}) = -9777 \pm 138/T(\text{K}) + 11.582 \pm 0.126$ .

### Introduction

A simple method for the preparation of bulk quantities of fullerenes, first reported by Kratschmer et al.<sup>1</sup> a year ago, has opened up an exciting area of research on the physical and chemical properties of these fascinating molecules. The international interest is reflected in the large number of reports on the spectroscopic (IR, UV-vis, Raman, and NMR), electrochemical, and structural (XRD) properties of  $C_{60}$  as well as on their derivatives and compounds. However, very limited attention has been given to thermodynamic properties. There have been two measurements on heats of sublimation,<sup>2,3</sup> but both of them were made on mixtures of fullerenes. Further, no vapor pressure data have been reported. In this paper we report for the first time the vapor pressure of pure  $C_{60}$  as a function of temperature as well as its heat of sublimation. The principal technique used in this study is Knudsen cell mass spectrometry, which has earlier been employed in our laboratory in our studies on selenium and tellurium clusters<sup>4</sup> and on the vaporization thermodynamics of metal tellurides.<sup>5-9</sup>

### Experimental Section

The procedure used for the preparation of  $C_{60}$  was similar to the contact arc method described by Haufler et al.<sup>10</sup> The arc was struck between two graphite electrodes in a helium atmosphere of 200 Torr, and the graphite soot collected was subjected to Soxhlet extraction by using toluene or carbon tetrachloride as the solvent. The extract was evaporated using a rotary evaporator to obtain solid samples consisting mainly of  $C_{60}$  and  $C_{70}$ . This mixture was separated by column chromatography by using a neutral alumina column, and  $C_{60}$  was eluted with hexane. The samples were characterized by HPLC, UV-vis as well as IR spectroscopy, and XRD. The details of characterization are given

elsewhere.<sup>3</sup> The purity of the substance was also checked by mass spectrometry.

A VG Micromass 30BK mass spectrometer (electron impact ion source, single focusing, 90° sector magnetic analyzer) was used for vapor pressure measurements. The molecular beam effusing out of the Knudsen cell was ionized by electrons of 38-eV energy. The ions were accelerated to 3 kV and measured by a secondary electron multiplier. For determining the appearance potential, ionization efficiency curves were obtained by measuring the ion intensities as a function of electron energy at constant temperature. The electron impact energy scale was calibrated against the first ionization potentials of Ag, In, Hg, Ar, and He.<sup>7</sup> The relevant data were acquired and processed by an IBM compatible PC.

Alumina Knudsen cells (i.d. = 7.5 mm, o.d. = 10.0 mm, height = 10.0 mm, and orifice diameter = 0.51 mm) were used to contain the samples. The Knudsen cell with the sample (normally half to three-fourths of the cell) was kept inside a molybdenum cup which was heated by electron bombardment. Temperatures were measured by a chromel–alumel thermocouple touching the base of the Knudsen cell. The thermocouple was calibrated against the melting point of silver.

Two samples from independent preparations were used in these experiments. Sample 1 was annealed at 500 K for about 12 h while sample 2 was preheated at 800 K for about 3 h. In each experiment the ion intensities were measured as a function of time from those temperatures where a detectable signal was obtained, and the sample was taken to the next temperature (either higher or lower) only after ensuring equilibrium conditions for a reasonable period of time (normally 30–40 min). Such stable reading at each temperature was chosen for obtaining the temperature dependence of the ion intensities. The samples were weighed (along with the Knudsen cell) in a Mettler microbalance (sensitivity 10  $\mu\text{g}$ ) before and after the experiment to obtain the weight loss during the experiment. Experiments were carried out with samples of different initial weights and for different durations. Prior to each experiment with  $C_{60}$ , an experiment with silver (NBS standard) was carried out.

### Results and Discussion

In the mass spectrum of the equilibrium vapor, major peaks were observed in the mass ranges 720–722 and 360–361. The peaks in the mass range 720–722 were attributed to  $C_{60}^+$  on the basis isotopic abundance. The peaks in the mass range 360–361 may be due to fragmentation of  $C_{60}$  molecules or doubly positive ions of  $C_{60}$ . No other peak with significant ion intensity was detected up to a mass of 1020. Particular care was taken to detect any  $C_{70}$  present. The ratio of  $I_{60}^+/I_{70}^+$  at the highest temperature (800 K) was around 4000. Such a large value for the ratio indicates the purity of  $C_{60}$  and the effectiveness of the separation procedure. An appearance potential of  $8.1 \pm 0.5$  eV obtained for the ion  $C_{60}^+$  is in good agreement with the ionization energy value of  $7.61 \pm 0.2$  eV given in the assessment of Kroto et al.<sup>11</sup>

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TABLE I: Details of Weight Loss Experiments with Silver and C<sub>60</sub>

	sample no.	expt no.	initial weight, mg	weight loss, mg	$Q \times 10^6$	$k' \times 10^2$	$aC \times 10^3$
Ag		1	73.44	6.79	6.370	1.36	1.71
		2	59.17	6.43	7.198	1.60	1.65
C <sub>60</sub>	1 <sup>a</sup>	1	6.62	2.59	1.277	0.108	1.68
		2 <sup>b</sup>	4.03	0.51	1.167	0.099	1.68
		3	10.82	4.13	1.176	0.099	1.68

<sup>a</sup>Samples 1 and 2 belong to two different preparation lots. <sup>b</sup>Sample 1 was reweighed after experiment 1 and used for experiment 2.

TABLE II: Vapor Pressure of C<sub>60</sub>(g) over Pure C<sub>60</sub>

sample no.	expt no.	run no.	temp range, K	$\log(p/\text{Pa}) = -A/T(\text{K}) + B$		$p$ , Pa	
				$A^b$	$B^b$	700 K	800 K
1	1	1	690-800	9587 ± 94	11.279 ± 0.024	3.83 × 10 <sup>-3</sup>	0.197
		2	600-800	9573 ± 52	11.157 ± 0.032	3.03 × 10 <sup>-3</sup>	0.155
2	3	3	650-800	9370 ± 95	11.149 ± 0.038	5.80 × 10 <sup>-3</sup>	0.273
		4	650-800	9370 ± 72	11.155 ± 0.033	5.88 × 10 <sup>-3</sup>	0.277
		a	600-800	9777 ± 138	11.582 ± 0.126	4.12 × 10 <sup>-3</sup>	0.229

<sup>a</sup>Recommended equation is obtained by pooling all the individual points. <sup>b</sup>The errors are standard deviations.

The ion intensity measured at any temperature can be related to pressure by the equation<sup>12</sup>

$$p = k'IT \quad (1)$$

In eq 1  $k' = (k/\sigma sh)$ , where  $k$  is the instrument calibration constant,  $\sigma$  the ionization cross section,  $s$  the detector response, and  $h$  the isotopic abundance. The conventional procedure of obtaining  $k'$  by using a standard substance (like silver whose vapor pressure is well-known) may not be applicable in the present case on account of the nonavailability of a reliable ionization cross-section value for C<sub>60</sub>. Hence, the following procedure was adopted to obtain the vapor pressure of C<sub>60</sub>.

The weight loss  $w$  due to Knudsen effusion for time  $t$  is given by the equations<sup>12</sup>

$$w = Q \int_T IT^{1/2} dt \quad (2)$$

$$Q = k'(aC)(M/2\pi R)^{1/2} \quad (3)$$

where  $a$  is the orifice area,  $C$  the Clausing factor,  $M$  the average molecular weight,  $T$  the temperature, and  $R$  the universal gas constant. The constant  $Q$  was calculated from eq 2 by using the weight loss during the experiment and area under the curve  $IT^{1/2}$  vs time. Since experiments with silver yield  $k'$  (using measured  $I(\text{Ag}^+)$  and known  $p(\text{Ag})$ ), this can be substituted in eq 3 to obtain  $aC$ , the product of the orifice area and the Clausing factor. This, being independent of the sample, can now be used in eq 3 to calculate  $k'$  for C<sub>60</sub> and hence its partial pressure via eq 1.

Figure 1 gives a typical plot of  $\log(IT^{1/2})$  vs time. As can be seen from the plot, the reproducibility of ion intensities at each temperature is reasonably good. A similar trend was observed in other experiments. Table I summarizes the details of the weight loss experiments and the constants derived from them. Table II gives the results of least-squares-fitted  $\log p$  vs  $1/T$  plots. The agreement between the pressures obtained in various runs is reasonably good. The recommended pressure equation for C<sub>60</sub> was obtained by a least-squares fitting of all the points obtained in all the experimental runs.

Figure 2 gives a typical plot of  $\log(IT)$  vs  $1/T$  for two temperature dependence runs obtained in a particular experiment. Second law<sup>12</sup> enthalpy of sublimation was obtained from the slope of the least-squares-fitted  $\log(IT)$  vs  $1/T$  data and are given in Table III. The recommended value (181.4 ± 2.3 kJ/mol) is the average of all the runs. This is slightly higher than the value obtained by us earlier<sup>3</sup> over a mixture of C<sub>60</sub> and C<sub>70</sub> (176 ± 2

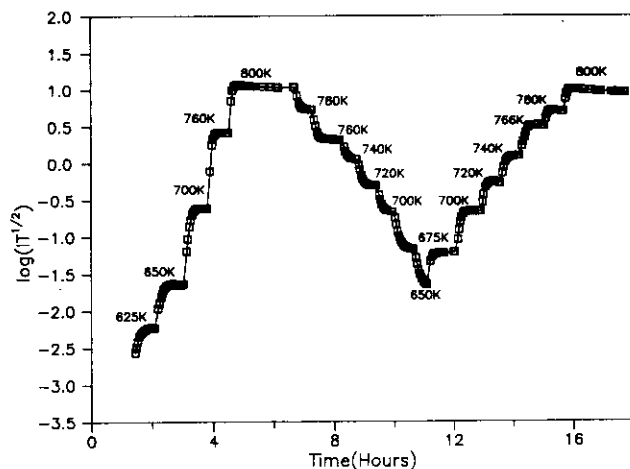


Figure 1. Plot of  $\log(IT^{1/2})$  vs time (weight loss experiment for C<sub>60</sub>: sample 2).

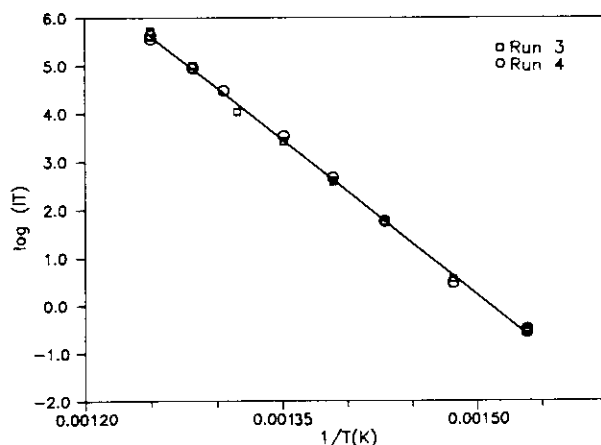


Figure 2. Temperature dependence of  $I(\text{C}_{60}^+)$ . Experimental points obtained for sample 2 (□, run 3; ○, run 4).

TABLE III: Second Law Enthalpy of Sublimation of Pure C<sub>60</sub>

sample no.	expt no.	run no.	temp range, K	$T_M$ , K	$\Delta H^\circ(\text{sub}, T)$ , <sup>b</sup> kJ/mol
1	1	1	690-800	745	183.6 ± 1.8
		2	600-800	700	183.3 ± 1.0
2	3	3	650-800	725	179.4 ± 1.8
		4	650-800	725	179.4 ± 1.4
		a	600-800	700	181.4 ± 2.3

<sup>a</sup>Recommended value is the average of the individual runs, and the error is the standard deviation of the mean. <sup>b</sup>The errors are standard deviations.

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kJ/mol). Pan et al.<sup>2</sup> report a somewhat lower ( $167.8 \pm 5.4$  kJ/mol) value, but their measurements were also on a mixture of C<sub>60</sub> and C<sub>70</sub>. The present measurements were carried out with pure C<sub>60</sub>, and the agreement between different samples and runs suggests that our value is reliable. The trend toward a lower enthalpy of sublimation in mixtures of C<sub>60</sub> and C<sub>70</sub> and the small magnitude of the difference are consistent with the picture of a

solid solution held together by van der Waals forces.

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