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LETTERS

Preliminary Study on the Vapor Pressure of C_{84} Fullerene

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The equilibrium pressures over C_{84} were measured over a large temperature range, 920−1190 K, by the torsion effusion method. The data obtained are well represented by the following selected linear equation: $\log(p/\text{kPa}) = (7.92 \pm 0.30) - (109\,50 \pm 300)/T$. Considering the vapor phase constituted by only $C_{84(g)}$, the sublimation standard enthalpy of this compound, $\Delta_{\text{sub}}H°(950) = 210 \pm 6$ kJ mol^{-1}, as derived by second-law treatment of the experimental data, is proposed.

While the vapor pressure of C_{60} and C_{70} fullerenes has been measured by several authors, apparently, up to now, no data were reported for the vapor pressure of C_{84}. In an ongoing research program on the sublimation thermodynamics of fullerenes,[1,2] this work has been undertaken with the aim of measuring the vapor pressure of C_{84} by the torsion effusion method. The experiments have been performed employing the very same torsion assembly already described.[3] Two conventional graphite torsion cells having different sizes of their effusion holes (cell A with 1.0 mm and cell B with 0.3 mm of their nominal diameters) were used. The instrument calibration constant, K, for each cell was obtained by vaporizing pure reference substances in experiments carried out before and after each vaporization run of C_{84}. The resulting K values were $(1.67 \pm 0.09) \times 10^{-2}$ and $(3.64 \pm 0.13) \times 10^{-2}$ kPa·rad^{-1} for the cells A and B respectively. They were determined as the average of several values of the p/α ratio, where p is the well-known vapor pressure of a calibrating substance (lead and silver[4] in this work) and α is the corresponding torsion angle of the assembly. The associated errors, which are the semidispersions, produced a displacement in the logarithm of the absolute pressure values lower than about ±0.08.

The C_{84} sample, supplied by Technocarbo (06130, Plan de Grasse, France), is a black powder, stated to be 99.9% pure with respect to other fullerenes, as checked by chromatographic analysis, and to possibly contain a small amount of toluene from crystallization. SEM analysis and several reflections observed in X-ray diffraction patterns indicated that the original sample is constituted by a crystalline powder.

The heating of C_{84} samples produced weight losses, ranging from 2 to 6% of their original masses in an approximated temperature range of 500−600 K; these losses were considered to be due to the vaporization of the small amount of the residue solvent (toluene used for the crystallization firmly inserted in the solid structure) and/or of amounts of other undetermined impurities as mixtures of polycyclic aromatic hydrocarbons probably produced during the preparation of the fullerene. Except for this initial vaporization, no further vaporization of the samples was observed up to about 950 K. Starting from this temperature the vapor pressure of C_{84} was detectable by our torsion assembly. In an initial step of the vaporization the measured vapor pressure values were well reproducible and show a $\log p$ vs $1/T$ linear behavior. When approximately 30−40% of the sample was vaporized, the vapor pressure exhibits a very slowly decreasing trend. These last values were not well reproducible but seemed to lie on new $\log p$ vs $1/T$ lines with continuously changing slopes slightly lower than that obtained in the first sublimation step. When the vapor pressures

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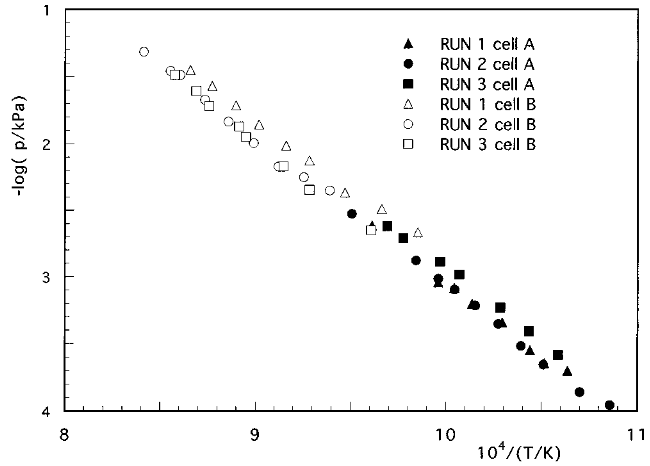

Figure 1. Experimental torsion vapor pressures of C_{84}.

TABLE 1: Vapor Pressures of C_{84} Fullerene

			$\log(p/\mathrm{kPa}) = A - B/(T/\mathrm{K})$	
run	no. of points	ΔT/K	A^a	B^a
		Cell A		
1	8	940−1040.5	7.78 ± 0.35	108 31 ± 347
2	10	921−1052	7.94 ± 0.22	109 99 ± 215
3	7	944.5−1032	7.83 ± 0.25	107 65 ± 248
		Cell B		
1	9	1015−1155	7.49 ± 0.24	103 39 ± 263
2	9	1065−1189	8.13 ± 0.38	112 26 ± 429
3	8	1041−1166	8.38 ± 0.25	115 20 ± 274

[a] The quoted errors are the standard deviations.

decreased to values below the limit of detectability of our apparatus, the residues, about 3−5% of the original weight of the samples, appeared to be amorphous, as observed by the X-ray diffraction analysis. The residue did not present detectable pressure up to ~1300 K (upper limit of the used furnace).

It is interesting to note that the SEM image of this residue showed the appearance of a substance, probably constituted by carbon black, more compact than that very aeriform noted as residue of the C_{60} vaporization.[1] This substance, partly present in the original sample as observed by SEM and partly produced during its sublimation, became layered on its surface so that only in the first step of the vaporization does the sublimation of clean pure C_{84} occur. When the residual crystals were covered with this substance, the C_{84}(g) pressure decreased and their values were no longer significant. Therefore we took into account only the points measured in the first step of each vaporization run which were considered to be representative of the vapor pressure of C_{84} fullerene.

The results, obtained in six runs employing about 30 mg of sample in each experiment, are shown in Figure 1 and summarized in Table 1 as log p vs $1/T$ equations derived by least-squares fitting of the data determined in each run.

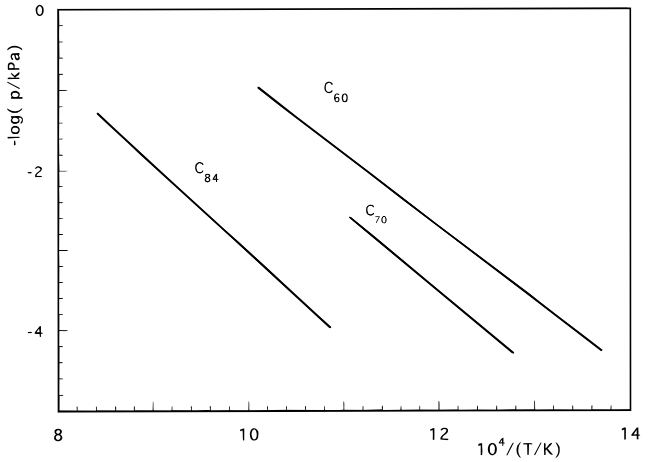

Figure 2. Comparison of the vapor pressures of C_{70}, C_{60}, and C_{84} fullerenes.

From these equations, by weighting their slopes and intercepts proportionally to the number of experimental points, the following final equation valid in the temperature range 920−1190 K was selected:

$$\log(p/\mathrm{kPa}) = (7.92 \pm 0.30) - (109\ 50 \pm 300)/(T/\mathrm{K}) \quad (1)$$

The errors were estimated considering an uncertainty of about 20% in the absolute pressures (originated by the uncertainties on the aforementioned instrument constant and on the torsion angle measurements) and of about 3 K in the temperature values.

The selected eq 1 is reported in Figure 2 for comparison with those obtained in the C_{60} and C_{70} studies.[1,2] It is interesting to note the lower volatility of the C_{84} with respect to the other fullerenes. Some determinations of the weight loss rate of the sample, employing the Knudsen equation,[5] allowed the evaluation of the mean molecular weight of vapor. The resulting values, ranging from 980 to 1145 (where the uncertainty associated with each value is about ±50), show the congruency of the vaporization. From the slope of eq 1 the sublimation enthalpy of C_{84}, $\Delta_{\mathrm{sub}}H°(950) = 210 \pm 6$ kJ mol^{-1}, was derived.

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