

Saturated vapour pressure and enthalpy of sublimation of C₈₄

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The vapour pressure and sublimation enthalpy of HPLC-purified C₈₄ have been determined by Knudsen cell mass spectrometry in the temperature range 658–980 K; the temperature–pressure equation is $\ln(p/\text{Pa}) = (-24337 \pm 539)/(T/\text{K}) + (25.15 \pm 0.64)$, and the mean sublimation enthalpy at 853 K is 202 ± 4 kJ mol⁻¹.

There has been considerable interest in the thermodynamic properties of pure C₆₀ and C₇₀. The enthalpies of formation, heat capacity, enthalpies of sublimation and the saturated vapour pressures have been reported.^{1–7}

However, separation and purification of higher fullerenes C_n ($n > 70$) still remains a complicated and time- and labour-consuming procedure, and this hinders investigations of their physical and chemical properties. Only a few papers have been published on the thermodynamic studies of higher fullerenes and their mixtures.^{8,9}

Here we report our determination of the sublimation enthalpy of pure C₈₄ and partial-mole sublimation enthalpies of C₇₆, C₇₈ and C₈₄ determined from a mixture of higher fullerenes.

Sample preparation. Two samples were investigated. Sample 1 was prepared as follows. The crude fullerenes were Soxhlet-extracted with chloroform from the fullerene-containing soot. The extract was then dissolved in toluene and purified directly by HPLC (without pre-separation of C₆₀ and C₇₀) using a 10 mm×25 cm Cosmosil Buckyprep column, toluene eluent, operated at 4.5 ml min⁻¹ flow rate. The retention time of C₈₄ was 24.95 min (C₆₀ elutes at 7.8 min under the same conditions). The product from the initial separation was recycled (same conditions) to remove traces of other fullerenes present due to tailing during the initial run. The re-purified material showed (HPLC) complete absence of other fullerenes (except that traces of C₈₂ may be present since it is well-known to co-elute with C₈₄ using this column and conditions, which are now the universal standard for separation of this fullerene). Sample 2 was obtained after HPLC removal of C₆₀ and C₇₀ from the fullerene-containing soot extract.

Knudsen cell mass spectrometry study. A magnetic sector MI-1201 mass spectrometer (Russia) equipped with a high temperature ion source (electron impact ionization, EI) was used in the sublimation studies; details of the instrumentation are described elsewhere.¹⁰ A weighed amount (3–4 mg) of the sample was placed into the first chamber of the twin effusion

Table 1 Composition of sample 2 before and after evaporation.

Fullerene	Mole fraction	
	Before evaporation	After evaporation
C ₆₀	0.05	0.10
C ₇₀	0.12	0.24
C ₇₆	0.19	0.14
C ₇₈	0.23	0.16
C ₈₄	0.41	0.36

cell. Both Ni and Pt effusion cells were incorporated in different series, the hole diameters being 0.5 and 0.25 mm, respectively. The evaporation/effusion surface ratios were estimated to be not less than 400 and 100, respectively. Prior to our experiments with the twin cells, they were checked for the equivalence of flows from the two chambers. [60]Fullerene was placed into both chambers, and C₆₀⁺ ion currents were measured and found to be equal. Either [60]fullerene or caesium iodide, used as standards in the experiments with samples 1 and 2, respectively, were placed into the second chamber of the twin cell. The cell was resistively heated and the temperature was measured with a Pt/Pt-Rh thermocouple.

The EI mass spectra of samples 1 and 2 are presented in Figures 1 and 2, respectively.

The composition of sample 2 was estimated from the HPLC data, assuming equivalence of the extinction coefficients of C₇₆, C₇₈ and C₈₄ (Table 1). The amount of residue after completion of the vapour pressure measurements comprised 10–15% of the starting sample (5–8 mg). The residue dissolved partially in toluene and the solution obtained was analysed by HPLC, which showed a relative increase in C₆₀ and C₇₀ contents compared to the initial composition. This contradicts expectation based on their higher volatilities and arises in part due to the known thermal degradation of higher fullerenes to lower ones, and possibly also from differential solubilities in the toluene-

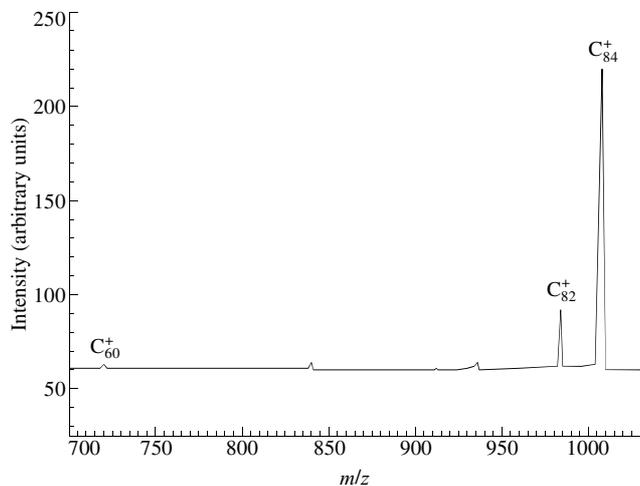


Figure 1 Electron impact mass spectrum of sample 1 at $T = 980$ K. Mass range 700–1030 amu.

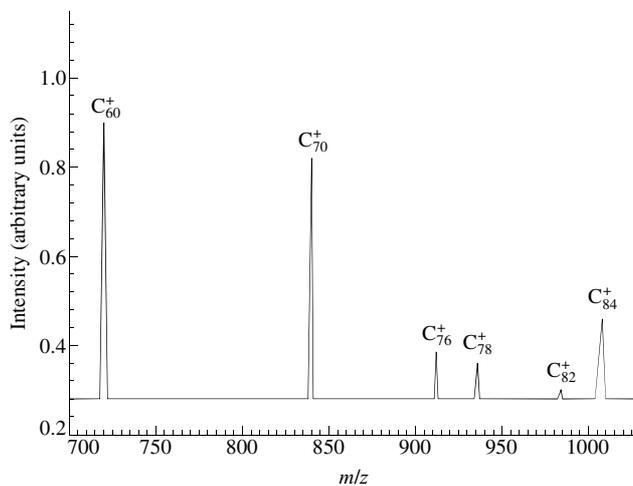


Figure 2 Electron impact mass spectrum of sample 2 at $T = 822$ K. Mass range 700–1030 amu.

Table 2 Vapour pressures and sublimation enthalpies of C₆₀, C₇₀ and higher fullerenes.

Work	Fullerene	System	Temperature interval/K	$\lg(p/\text{Pa}) = -B/T + A$		T/K	$_{\text{sub}}H_T^0/\text{kJ mol}^{-1}$
				B/K	A		
This	C ₇₆	mixture	700–862	11586±913	10.32±1.21	756	222±17
This	C ₇₈	mixture	700–862	11588±842	10.25±1.12	756	222±16
8	C ₈₄	mixture	800–950	12902±1306	15 ^a	—	2 47±25
9	C ₈₄	pure	920–1190	10950±300	10.92±0.30	950	210±6
This	C ₈₄	pure	658–980	10570±234	10.92±0.28	853	202±4
This	C ₈₄	mixture	700–862	12101±949	11.15±1.26	756	231±18

^aThe parameter of the temperature equation was estimated without errors.

insoluble carbonaceous residue. This residue, widely observed in fullerene thermolysis, is believed to be composed of degraded or polymerised material.

The temperature dependence of C₈₄⁺ ion current for sample **1** was measured in the temperature interval 658–980 K. The partial pressure values of C₈₄ were obtained from comparison of the intensities of C₈₄⁺, and of C₆₀⁺ of the standard, using the known vapour pressure of C₆₀.⁶ The correction for ionisation cross section was made using the additivity rule.¹¹ The recommended temperature variation of the saturated vapour pressure of C₈₄ in the temperature range 658–980 K, and the corresponding value of the sublimation enthalpy, are presented in Table 2.

We consider the pressure equation already mentioned and the sublimation enthalpy to describe the thermodynamic characteristics of pure C₈₄ and disregard the influence of 10% of C₈₂ (always present unless a two-stage HPLC secondary Buckylutcher column is used).

For sample **2** the temperature dependence was measured in the temperature range 700–862 K. The partial pressures were determined from the measured ion currents of C₈₄⁺ and Cs₂I⁺ of the standard (CsI) using the known vapour pressure of Cs₂I.¹² The correction for ionisation cross sections was made using the additivity rule.¹¹ The temperature dependence of the partial pressure of C₈₄ and the corresponding partial molar enthalpy of sublimation are also presented in Table 2. The error values were taken from the least square correlation as $t_{0.95}\sigma$, where $t_{0.95}$ is the Student coefficient and σ is the standard deviation. The plots of $\ln[p(\text{C}_{84})/\text{Pa}]$ versus $1/T$ for samples **1** and **2** are presented in Figure 3.

The values of the enthalpies of sublimation of C₈₄ obtained from the pure sample and from the higher fullerene mixture were compared with the sublimation enthalpy of Moalem *et al.*⁸ and that of Piacente *et al.*⁹ (Table 2). The former result was determined in the study of a mixture of higher fullerenes [the composition estimated from surface analysis by laser-induced desorption (SALI) mass spectrometry was as follows: C₆₀, 0.05%; C₇₀, 13%; C₇₈, 5.7%; C₈₄, 44% and C₉₆, 5.8%]. This mixture was assumed to behave as an ideal solution and the value obtained was regarded as the sublimation enthalpy of

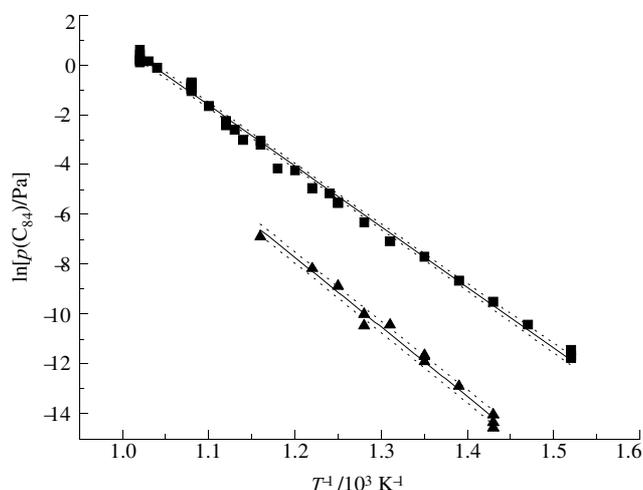


Figure 3 The plots of $\ln(p/\text{Pa})$ versus $1/T$ for C₈₄ over sample **1** (■) and over sample **2** (▲).

pure C₈₄. Our result for the sublimation enthalpy of separated C₈₄ differs considerably from the values obtained for the mixture (see Table 2). This suggests that the higher fullerene mixture cannot be considered as an ideal solution.

Using the data on the composition at the end of the experiment, the activity coefficient of C₈₄ in sample **2** at 741 K was determined as $\gamma(\text{C}_{84}) = 0.05 \pm 0.02$ (Table 1). These results roughly satisfy a regular solution equation (1):

$$_{\text{sol}}\bar{H}_T^0(\text{C}_{84})_{\text{m}} = RT \ln[\gamma(\text{C}_{84})] \quad (1)$$

where $_{\text{sol}}\bar{H}_T^0(\text{C}_{84})_{\text{m}}$ is the partial molar enthalpy of dissolution.

We also determined the saturated vapour pressures and partial molar sublimation enthalpies of C₇₆ and C₇₈ for the higher fullerene mixture (see Table 2).

Results for C₆₀ and C₇₀ were rather unexpected. Values of their activities were *ca.* 10⁻³, but the sublimation enthalpies were very close to the values obtained for pure substances.^{6,7} This can be ascribed to diffusion in the solid phase, *i.e.* the diffusion process controls the evaporation rate of the volatile component. It results in the decrease in concentration of volatile components C₆₀ and C₇₀ in the surface layer and leads, subsequently, to underestimated values of the activities of these components and underestimation of the partial molar sublimation enthalpies of C₆₀ and C₇₀. This effect would appear not to influence the results on the vapour pressure and sublimation enthalpy of the major components of the mixture, *i.e.* C₈₄, C₇₈ and C₇₆, which are less volatile than C₆₀ and C₇₀.

We are grateful to the Russian Foundation for Basic Research (grant nos. 97-03-003391a and 97-03-33682a) and the Russian Research Program 'Fullerenes and Atomic Clusters' for the partial financial support of this work.

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Received: Moscow, 7th May 1998

Cambridge, 8th June 1998; Com. 8/03647K