Saturated vapour pressure and enthalpy of sublimation of C_{84}

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The vapour pressure and sublimation enthalpy of HPLC-purified C_{84} have been determined by Knudsen cell mass spectrometry in the temperature range 658–980 K; the temperature–pressure equation is $\ln(p/\mathrm{Pa}) = (-24337\pm539)/(T/\mathrm{K}) + (25.15\pm0.64)$, 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 C_{60} and C_{70}. 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 C_{84} and partial-mole sublimation enthalpies of C_{76}, C_{78} and C_{84} 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 C_{60} and C_{70}) using a 10 mm × 25 cm Cosmosil Buckyprep column, toluene eluent, operated at 4.5 ml min^{-1} flow rate. The retention time of C_{84} was 24.95 min (C_{60} 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 C_{82} may be present since it is well-known to co-elute with C_{84} using this column and conditions, which are now the universal standard for separation of this fullerene). Sample **2** was obtained after HPLC removal of C_{60} and C_{70} 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 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 C_{60}^{+} 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.

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

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 C_{76}, C_{78} and C_{84} (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 C_{60} and C_{70} 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-

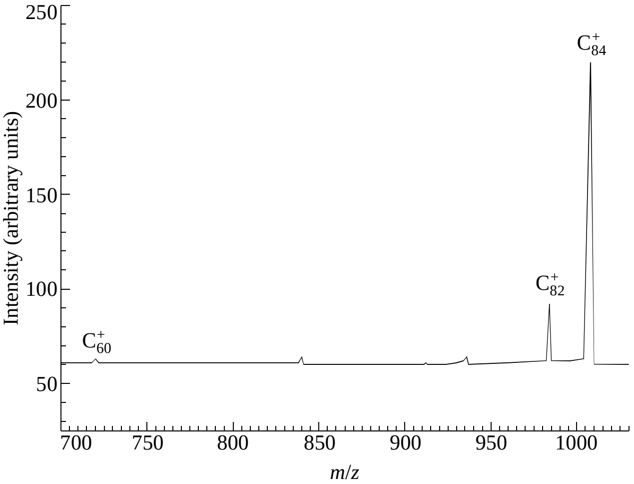

Figure 1 Electron impact mass spectrum of sample **1** at T = 980 K. Mass range 700–1030 amu.

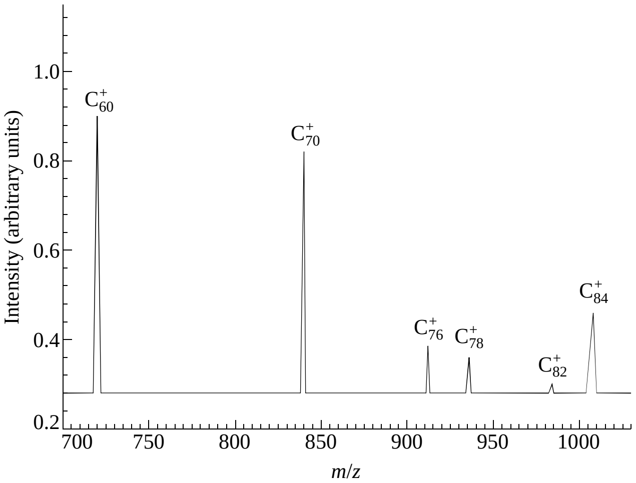

Figure 2 Electron impact mass spectrum of sample **2** at T = 822 K. Mass range 700–1030 amu.

Table 2 Vapour pressures and sublimation enthalpies of C_{60}, C_{70} and higher fullerenes.

Work	Fullerene	System	Temperature interval/K	$\lg(p/\mathrm{Pa}) = -B/T + A$		T/K	$\Delta_{\rm sub}H^0_{\rm T}$ / 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]	—	247±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

[a] The 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 C_{84}^+ ion current for sample **1** was measured in the temperature interval 658–980 K. The partial pressure values of C_{84} were obtained from comparison of the intensities of C_{84}^+, and of C_{60}^+ of the standard, using the known vapour pressure of C_{60}.[6] The correction for ionisation cross section was made using the additivity rule.[11] The recommended temperature variation of the saturated vapour pressure of C_{84} 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 C_{84} and disregard the influence of 10% of C_{82} (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 C_{84}^+ and Cs_2I^+ of the standard (CsI) using the known vapour pressure of Cs_2I_2.[12] The correction for ionisation cross sections was made using the additivity rule.[11] The temperature dependence of the partial pressure of C_{84} 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 $\ln[p(C_{84})/\mathrm{Pa}]$ *versus* $1/T$ for samples **1** and **2** are presented in Figure 3.

The values of the enthalpies of sublimation of C_{84} 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: C_{60}, 0.05%; C_{70}, 13%; C_{78}, 5.7%; C_{84}, 44% and C_{96}, 5.8%]. This mixture was assumed to behave as an ideal solution and the value obtained was regarded as the sublimation enthalpy of pure C_{84}. Our result for the sublimation enthalpy of separated C_{84} 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.

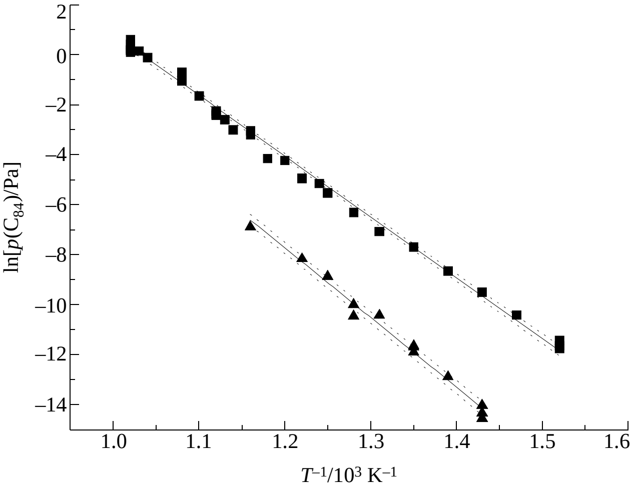

Figure 3 The plots of $\ln(p/\mathrm{Pa})$ *versus* $1/T$ for C_{84} over sample **1** (■) and over sample **2** (▲).

Using the data on the composition at the end of the experiment, the activity coefficient of C_{84} in sample **2** at 741 K was determined as $\gamma(C_{84}) = 0.05\pm0.02$ (Table 1). These results roughly satisfy a regular solution equation (1):

$$\Delta_{\rm sol}\bar{H}^0_{\rm T}(C_{84})_{\rm m} = RT\ln[\gamma(C_{84})] \qquad (1)$$

where $\Delta_{\rm sol}\bar{H}^0_{\rm T}(C_{84})_{\rm m}$ is the partial molar enthalpy of dissolution.

We also determined the saturated vapour pressures and partial molar sublimation enthalpies of C_{76} and C_{78} for the higher fullerene mixture (see Table 2).

Results for C_{60} and C_{70} 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 C_{60} and C_{70} 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 C_{60} and C_{70}. 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.* C_{84}, C_{78} and C_{76}, which are less volatile than C_{60} and C_{70}.

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