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Vapour pressure of C_{60} by a transpiration method using a horizontal thermobalance

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Abstract

A horizontal thermal analysis system was adopted for the measurement of vapour pressure of C_{60} using the vapour transport technique. The experimental precautions taken in order to ensure measurement of equilibrium vapour pressure by the transpiration method are described. The equilibrium nature of these measurements was ensured by the existence of plateau regions in the isothermal plots of apparent vapour pressure as a function of flow rate of the carrier gas. To verify the applicability of this TG based transpiration method, vapour pressure of CsI was measured to be $\log(p/\mathrm{Pa})=11.667\pm0.013-(9390\pm0.078)/T$ (K) over the range 737–874 K yielding a value of 195.6 kJ mol^{-1} for the third-law enthalpy of sublimation, $\Delta H^0_{\mathrm{sub},298}$ of CsI, the value which compares well with the literature data. The vapour pressure measurements on C_{60} over the range 789–907 K could be represented by $\log(p/\mathrm{Pa}) = 9.018 \pm 0.061 - (7955 \pm 0.280)/T(\mathrm{K})$. Third-law treatment of the data yielded a value of 183.5±1.0 kJ mol^{-1} for $\Delta H^0_{\mathrm{sub},298}$ of C_{60} which is in good agreement with some of the other vapour pressure measurements in the literature, if subjected to third-law processing using the same set of free energy functions reliably reported in the literature. © 1998 Elsevier Science B.V.

1. Introduction

Following the discovery of fullerenes in 1985 by Kroto et al. [1], considerable work on their synthesis and characterization were reported in the literature [2–4]. Notable among the physico-chemical measurements made on the fullerenes were the vapour pressure measurements which clearly demonstrated the metastability of the fullerenes in comparison with other polymorphic forms of carbon. However, the number of reports in the literature [5–12] on the vapour pressure of C_{60}, C_{70} and their solid solutions are quite a few which included techniques such as the conventional transpiration Quartz Crystal Microbalance (QCM), Knudsen Cell Mass Spectrometry (KCMS), Knudsen Effusion Weight Loss (KEWL) and Optical Absorption Spectra (OAS) measurements. Despite a reasonable number of such vapour pressure measurements employing diverse techniques, there is a considerable scatter in the vapour pressure data and in the values of the standard enthalpy of sublimation, $\Delta H^0_{\mathrm{sub},298}$ for even the well-studied fullerene C_{60}. Hence, the present investigation was undertaken in order to assess the reliability of the vapour pressure data by employing a modified transpiration method. Since this method facilitates adaptation of a commercial thermoanalyser functioning in the

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horizontal configuration as a transpiration apparatus, the reliability of such a technique needs to be established by measurements on a well characterised material whose vapour pressure is well assessed in the literature. This was accomplished by carrying out vapour pressure measurements on cesium iodide and comparing the results with the literature values prior to the initiation of vapourisation studies on the fullerene C_{60}.

2. Experimental

2.1. Materials

Reagent grade CsI of purity better than 99.9% (supplied by Aldrich Chemicals, USA) pulverised to a mesh size of between 200 and 350 was used for the transpiration runs.

The Kratschmer's carbon arc method [2,3] was used to produce the fullerenes. The soot so obtained by arcing the graphite electrodes was extracted by using Soxhlet extractor followed by chromatographic separation on an alumina column. Toluene/Hexane mixtures which was used as the eluent was removed by vacuum annealing of the product at 523 K for 24 h. The purity of C_{60} was ascertained by XRD and UV-Vis spectroscopy within 1 mass% limit of detection of impurity phases, namely C_{70} and other higher fullerenes by these techniques. For a more stringent analysis of purity, the fullerene sample was subjected to HPLC technique which showed that the fullerene C_{60} was of 99.8% purity with the impurity phases of toluene and C_{70} to be <0.2% threshold of detection by HPLC.

2.2. Transpiration apparatus

A horizontal thermal analysis system (Model – Seiko 320) was adopted for vapour pressure measurements. A Pt-13% Rh/Pt thermocouple (Type-R) which formed an arm of the microbalance beam was used for temperature measurement in the vicinity of the sample located in the uniform temperature zone (UTZ) of a compact tubular furnace. A flat Pt crucible was used to spread the samples in order to maximise surface-to-volume ratio. High purity (better than 99.999%) helium was used as the carrier gas. Since the flow rate for the gas is the most important parameter in the transpiration measurement, the flow rates were monitored by a capillary type glass flowmeter. This capillary type glass flowmeter was in turn calibrated by the soap-bubble method using a horizontal calibrated burette [13]. A wet test meter (Model – Toshniwal, India) which was also used for total volume measurement at the outlet was in turn calibrated with the help of the glass capillary flowmeter. Though the precision in the flow rate measurements by the glass capillary flowmeter was ±0.5%, the overall precision in the integral volume flow was of the order of ±2% of the total volume of the carrier gas.

The horizontal design of the thermal analysis system facilitated the minimisation of errors in weight measurement due to convection while the location of the sample and reference pan in the same UTZ of the furnace minimised errors arising from effects such as buoyancy and thermal expansion of the beam. A narrow tube of the furnace was helpful in achieving saturation of the carrier gas with the vapourizing species at moderately lower flow rates. The high purity of the helium gas (which was independently monitored for its oxygen content using a solid electrolyte oxygen sensor [14]) minimised the possible weight gain due to oxidation of fullerene to its sub-oxide [15]. Since the vapour pressures were proposed to be derived from weight-loss measurements, other sources of errors that could be incurred by processes such as desorption of volatiles also needed to be minimised by preheating the sample in the range 373–573 K for 1 to 2 h. In addition, correction factor was generated for apparent mass gain as a function of time at different isothermal temperatures in the range 700–1000 K under flow rates of 6 to 18 dm^3/h in the blank runs carried out with empty sample and reference pans under helium atmosphere. It was found that the correction amounted to an average value of 9.04 μg per hour for an apparent isothermal weight gain in the blank runs encompassing the ranges of temperature and helium flow rates as mentioned above. The scatter in the correction factor between the extremes of temperature and flow rate ranges mentioned here was found to be only $\pm 0.9\ \mu g/h$ ($\approx 10\%$). Hence, a constant correction factor was employed for the weight losses which were resulting from mainly transpiration phenomena. The lower temperature limit of vapour pressure studies was restricted to that temperature at which this scatter in correction would tend to be <1% of the measured weight loss.

In the preliminary transpiration runs where CsI was employed for the purpose of establishing the horizontal thermoanalyser as a transpiration apparatus, adequacy of the quantity of the sample as well as its exposed surface area for saturating the carrier gas with the vapour was also tested, besides identifying the plateau region (in the plot of apparent isothermal vapour pressure against flow rate). It was found that a quantity of ca. 20 mg of CsI was required to be spread on a platinum foil-tray of nearly double the surface area of the standard sample crucible in order to give a flow-rate-independent plateau (between 10.4 and 12.4 dm^3/h at the highest temperature of 874 K). In the remaining three sets of experiments with CsI at lower temperatures, a flow rate of 10.9 dm^3/h was used which should be lying within the broader plateau regions (these being lower temperature measurements). However, 10 mg of fullerene sample spread as a thin layer in the standard sample pan was found to be adequate to give rise to plateau region in the plot of isothermal apparent pressure vs. flow rate. In addition, efforts to establish plateau not only at the highest temperature of vapourisation studies, but also at the lowest and middle temperatures were made for C_{60}, being the material taken up for reassessment. The general experimental procedure is the same for the runs with both CsI and C_{60}. The furnace was purged with the carrier gas at a flow rate of 10 dm^3/h at room temperature prior to heating. A heating rate of 10°C/min was employed to raise the temperature to 473 K at which it was maintained for ca. 1 to 2 h. After this step, the temperature was raised to the experimental temperature at the rate of 100°C/min. Once the set temperature was reached, the sample was maintained at the same isothermal temperature for the required time followed by natural cooling. Each time a fresh sample was loaded for vapourisation studies instead of recycling the same sample for obvious reasons of avoiding errors owing to sintering, surface depletion, oxidation, etc. For the configuration and sample size (10 mg) employed for C_{60}, the same flow rate of 12.4 dm^3/h was found to be in the middle of the plateau region determined independently for three different isothermal temperatures, namely 791, 844 and 907 K. Nearly five sets of experimental runs were carried out on C_{60} for different isothermal temperatures.

3. Results

If W is the mass loss of the sample at the isothermal temperature T, which was caused by the flow of V_c (dm^3) of the carrier gas, the apparent vapour pressure p could be calculated using the Dalton's law of partial pressure for ideal gas mixtures as given by

$$p^{\mathrm{app}} = WRT/MV_c \tag{1}$$

where M is the molecular weight of the sample.

3.1. Vapour pressure of CsI

Weight losses amounting to 3290 and 3550 µg were observed at a temperature of 874 K for the passage of carrier gas exactly for 60 min, each time corresponding to flow rates of 10.9 and 12.3 dm^3/h, respectively. By using Eq. (1) and assuming CsI to be essentially monomeric (with negligible dimer concentration below the melting point of 904 K [16,17]), values of 8.43 and 8.21 Pa, respectively, could be calculated for the vapour pressure. For subsequent runs at lower temperatures, a flow rate of 10.9 dm^3/h was employed so as to be within the plateau. Weight losses of 320, 640 and 2100 µg were observed for the passage of the carrier gas for 8, 4 and 2 h at 737, 777 and 830 K, respectively, at the same flow rate (10.9 dm^3/h). Together with the runs at 874 K, values of 0.09, 0.36, 2.25 and 8.43 Pa could be calculated for the vapour pressure of CsI (monomeric) at 737, 777, 830 and 874 K, respectively. These values (shown in Fig. 1) could be fitted into the least-squares expression

$$\log(p/\mathrm{Pa}) = 11.667 \pm 0.013 - (9390 \pm 0.078)/T(\mathrm{K}) \tag{2}$$

valid over the range 737 to 874 K.

3.2. Vapour pressure of C_{60}

A plot of the apparent vapour pressure p^{app} against flow rate at three different temperatures 791, 844 and 907 K is shown in Fig. 2. From this figure, the plateau regions characterising the equilibrium vapourisation

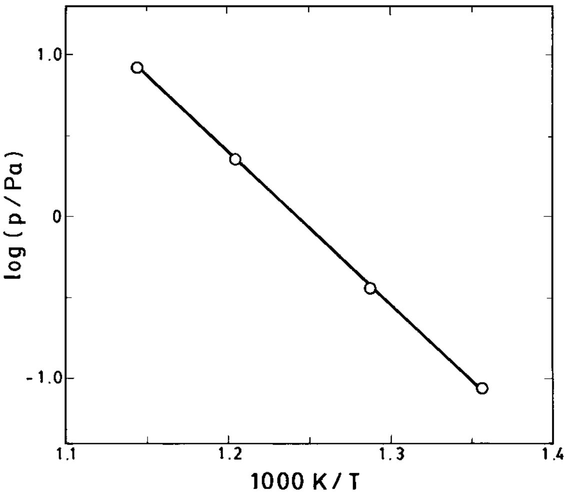

Fig. 1. Experimental vapour pressure results on CsI(s).

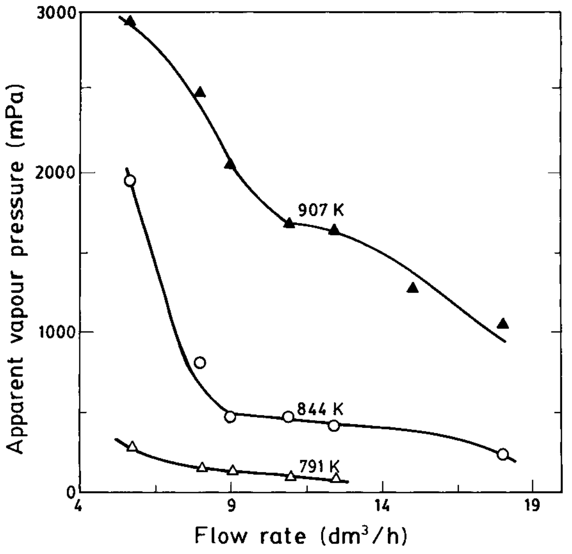

Fig. 2. Plot of apparent isothermal vapour pressure of C_{60} as a function of flow rate.

Table 1
Vapour pressure of C_{60} by TG transpiration method

Run No.	T (K)	Mass loss (μg) [a]	V_c (dm^3)	Pressure, p (mPa)
1	789.3	93.14	9.551	88.9
2	791.0	278.05	31.491	80.7
3	791.0	293.45	36.848	72.8
4	810.3	209.04	10.369	188.7
5	814.3	209.44	10.373	190.0
6	821.7	209.64	10.364	192.0
7	844.0	459.04	10.767	415.7
8	844.0	419.04	8.670	471.3
9	844.0	509.04	10.527	471.5
10	873.4	881.14	10.522	845.1
11	904.2	1481.34	10.546	1467.4
12	907.0	1899.04	12.182	1633.6
13	907.0	1691.04	10.549	1680.0

[a] Data are given correct to two decimal places which are one digit more than the significant figures for computational purposes.

was identified to be between the flow rates of 10.9 to 12.4 dm^3/h at 907 K and 9.0 to 12.4 dm^3/h for 791 and 844 K. The variation in the vapour pressure values at least over a narrower range of flow rates between 10.9 to 12.4 dm^3/h (for all the three temperatures) is seen (cf Fig. 2) to be not more than 2 to 5% of the mean values. A major part of this variation could be accounted for by the 2% uncertainty in the flow calibration alone. Since the mass loss measurements subsequent to the determination of the plateau regions were carried out using a flow rate almost in the middle of the plateau (10.9 dm^3/h), the values of p^{app} could be approximated to be the true equilibrium vapour pressure p as calculated from Eq. (1) by substituting the values of mass loss W in the respective experimental run. The results of mass loss, total volume of the carrier gas V_c and equilibrium pressure p determined by transpiration experiments are summarised in Table 1. A least-squares expression for the values of $\log p$ plotted against reciprocal temperature as shown in Fig. 3 is given by

$$\log(p/\mathrm{Pa}) = 9.018 \pm 0.061 - (7955 \pm 0.280)/T(\mathrm{K}) \quad (3)$$

4. Discussion

4.1. Vapour pressure of CsI(s)

The results of the vapour pressure measurements on CsI using an inert gas (namely He) as the carrier, shown in Fig. 1, was represented by Eq. (2). These measurements were carried out essentially to verify whether the modified transpiration method (adopting a horizontal thermobalance) could yield reliable vapour pressure data for a well characterised material whose

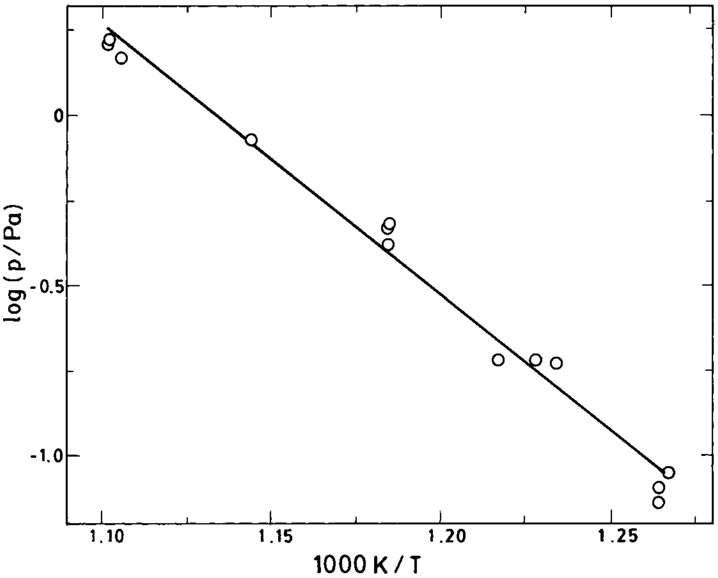

Fig. 3. Temperature dependence of the equilibrium vapour pressure of C_{60}.

vapour pressure values were well established in the literature. Measurement of vapour pressure on standard metal powders might be prone to interference by the ubiquitous oxygen impurity in the inert carrier gas. Many other substances with vapour pressures which are amenable for measurement by transpiration weight loss were found to exhibit complex vapourisation behaviour owing to the stability of their polymeric forms in the gaseous state. It was found that CsI exhibited vapourisation as monomer with only 2% of dimer concentration near its melting point of 904 K [17] and with negligible dimer concentration up to 873 K [16]. The vapour pressure of CsI was a subject of study from 1921 onwards until recent years by employing diverse techniques including the conventional boiling point method. The vapour pressure measurements on this material prior to 1982 was reviewed by Viswanathan and Hilpert [18] and hence is omitted here. Including the study using the KCMS by Viswanathan and Hilpert, there are at least three reports in the literature on the vapour pressure of CsI subsequent to 1982. A comparison of Eq. (2) from the present work with the results from these three investigations is warranted to uphold the applicability of the modified transpiration method for measuring the vapour pressure. Table 2 shows that there is a reasonable agreement among the values of p (Pa) at an overlapping temperature of 800 K between the present work and those from the recent literature. To assess the temperature dependent errors in the vapour pressure results, third-law method was employed for the four data points shown in Fig. 1. For this purpose, free-energy functions, FEFs, were computed from the $S^0_{\mathrm{f},298}$ and C^0_{p} values listed for CsI (s and g) in the recent Thermochemical Tables by Knacke et al. [19]. Corresponding to the four values of p (CsI) at 737, 777, 830 and 874 K, values of 194.9, 195.6, 195.8 and 196.0 kJ mol^{-1} were derived for the standard enthalpy of sublimation, $\Delta H^0_{\mathrm{sub},298}$ which is averaged to give 195.6±0.5 kJ mol^{-1} (Table 2). It is seen that all the four values in Table 2 for $\Delta H^0_{\mathrm{sub},298}$ lie within a band of 4 kJ.

4.2. Vapour pressure of C_{60}

The vapour pressure expression given by Eq. (3) from the present work is compared with those from seven other reliable reports [6–12] from the recent literature. Since different investigators had employed different techniques ranging from KCMS and KEWL, on one hand, and the transpiration and optical absorption measurements on the other over different ranges

Table 2
Comparison of vapour pressure and sublimation enthalpy of CsI (s, monomer)

S.No.	Method	log(*p*/Pa)=*A*−*B*/*T*(K)		*p* (Pa) at 800 K	$\Delta H^0_{sub,298}$ [a]	References
		A	−*B*			
1	KCMS	11.99	9573	1.1	191.1	[18]
2	KEWL and transpiration	12.59	10029	1.1	193.1	[16]
3	Transpiration	11.95	9549	1.0	193.1	[17]
4	TG transpiration	11.67	9390	0.9	195.6	This work

[a] Third-law values.

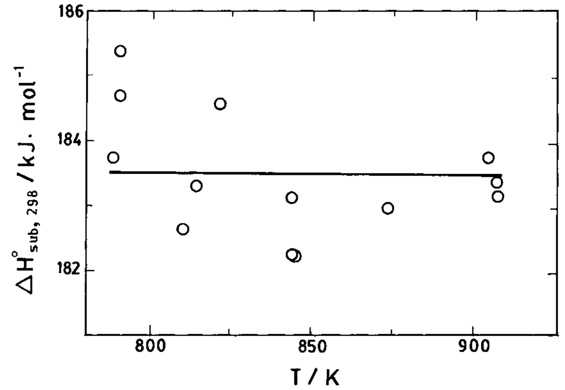

Fig. 4. Third-law plot of the enthalpy of sublimation for C_{60}; the horizontal line is the mean result.

of temperature, a meaningful comparison is possible only if the same set of FEFs are used in the evaluation of $\Delta H^0_{sub,298}$ for all the eight sets of vapour pressure data. Fortunately, Korobov and Sidorov [9] had compiled the thermodynamic functions for C_{60}(s) from 10 to 1000 K using precise heat capacity data. They had also evaluated FEFs for C_{60} gas from the experimental vibrational wave numbers derived from IR, Raman, neutron scattering, high-resolution energy-loss techniques, etc. from the literature. Making use of the FEFs for C_{60}(s) and C_{60}(g) as listed, in conjunction with the relation

$$\Delta H^0_{sub} = \Delta G^0_{vap} - T\Delta \mathrm{FEF} \qquad (4)$$

for the vapourisation process, values of ΔH^0_{sub} of C_{60} were calculated for the 13 points in Table 1 and were plotted against experimental temperature (third-law plot) as shown in Fig. 4. There is a very slight temperature dependence in the values of $\Delta H^0_{sub,298}$ which shows the absence of significant temperature-dependent errors in the present work. The same set of FEFs from Korobov and Sidorov [9] were applied to the vapour pressure values at the two extremes of the temperature range of each technique (given in Table 3) in order to calculate ΔH^0_{sub}. The value 183.5±1.0 kJ mol^{-1} for ΔH^0_{sub} from the present work is in good agreement with four other investigations, but is somewhat different from those reported by Popovic et al. [10] and Piacente et al. [11] using KCMS and from Gong et al. [12] by optical absorption measurements. In the earlier reports on the vapour pressure of C_{60}, the emphasis was more on the comparison of ΔH^0_{sub} at the mean temperature of measurement T_{mean}, values of which could differ considerably from one to the other. Uniform application of the same set of FEFs to all the reported values has thus facilitated a meaningful comparison of $\Delta H^0_{sub,298}$. It is not possible to carry out such a third-law analysis on the data given in some of the literature reports [20–24] owing to lack of reporting of original *p* values. However, it is interesting to compare the ΔH^0_{sub} at T_{mean} for some of these measurements. Thus, the value of 163 kJ mol^{-1} at 840 K by Chen et al. [20] using DSC and TGA, 139 kJ mol^{-1} at 600 K by Tokmakoff et al. [21] using desorption kinetics, 180 kJ mol^{-1} at 907 K by Dai et al. [22] using UV-visible absorption, 155 kJ mol^{-1} at 859 K by Coheur et al. [23] using UV-visible absorption and 171 kJ mol^{-1} (temperature not specified) by Ruoff using valence molecular connectivity theory, etc. could be compared with the values of 193, 181, 159, 191, 158, 175, 175 and 152 kJ mol^{-1} at the respective T_{mean} for the eight investigations listed in Table 3 in the same sequence. As mentioned, comparison of ΔH^0_{sub} at T_{mean}, for different values of T_{mean}, could cause confusion and is therefore omitted in Table 3.

Table 3
Comparison of vapour pressure of C_{60} with literature data

S.No.	Technique employed	$\log(p/\text{Pa})=A-B/T(\text{K})$		P(Pa) at 800 K	$\Delta H^0_{\text{sub},298}$ [a]	References
		A	$-B$			
1	QCM and transpiration	11.609	10059	0.1	184.1±3.1	[6]
2	KCMS	11.185	9475	0.2	183.2±3.5	[7]
3	KEWL	9.587	8281	0.2	180.6±1.5	[8]
4	KCMS	11.875	9963	0.3	181.1±2.6	[9]
5	KCMS	10.490	8267	1.4	168.5±1.2	[10]
6	KEMS and torsion effusion	11.280	9154	0.7	169.3±6.9	[11]
7	Optical absorption spectra	10.565	9136	0.1	179.2±3.5	[12]
8	TG transpiration	9.018	7955	0.1	183.5±1.0	This work

[a] Third-law values.

Many authors [5,9–11,23] had made the observation that the impurities in C_{60} could give rise to erroneous values of p. These impurities would include C_{70} as well as traces of solvent such as toluene, used in the extraction of C_{60} from the soot. Taking note of this, the purity of C_{60} used in the present work was ascertained to be better than 99.8% through various analytical techniques including HPLC (cf Section 2). Pan et al. [5] recommended preheating of the sample to above 440 K for greater than 12 h to achieve stable vapourisation. In the present study, during the course of synthesis of the sample, a vacuum heat treatment at 523 K for 24 h should have yielded the desired stable vapourisation conditions. Further, the samples were generally heated to temperatures between 373 and 573 K for 1–2 h (as mentioned earlier). Sundar et al. [25] had indicated that amorphisation might become significant at temperatures comparable to 973 K which could lead to lower vapour pressure values. In addition, there are possibilities of deterioration of C_{60} owing to a host of reactions such as intercalation [26–28], photo-polymerisation [29,30] and oxidation [31] by traces of ubiquitous oxygen (present even in the highly pure He stream) which could be facilitated by higher temperatures. Hence, the high-temperature experiments on C_{60} were limited to just about 1 h.

Thus, the conflicting factors such as the need to heat at higher temperatures to achieve stable vapourisation and the need to avoid high temperature heating in order to minimize the deterioration of C_{60} requires careful planning of the experimental runs. In the light of these factors, the vapour pressure data from the present work should be considered as quite reliable with the proposed value of 183±1 kJ mol^{-1} for $\Delta H^0_{\text{sub},298}$ of C_{60}.

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