Enthalpies of sublimation and vapour pressures of 11 polycyclic hydrocarbons

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(*Received 2 July 1979*)

Simultaneous torsion- and weighing-effusion techniques were used to measure the vapour pressure as a function of temperature. The enthalpies of sublimation were derived from the temperature dependence of the vapour pressures. Overall mean values for both techniques are: benzene, $\Delta H°(191.16 \text{ K}) = (51.7 \pm 2) \text{ kJ mol}^{-1}$; naphthalene, $\Delta H°(267.88 \text{ K}) = (74.4 \pm 0.5) \text{ kJ mol}^{-1}$; anthracene, $\Delta H°(351.28 \text{ K}) = (100.4 \pm 1) \text{ kJ mol}^{-1}$; phenanthrene, $\Delta H°(325.03 \text{ K}) = (90.5 \pm 1) \text{ kJ mol}^{-1}$; naphthacene, $\Delta H°(437.04 \text{ K}) = (128.1 \pm 2) \text{ kJ mol}^{-1}$; chrysene, $\Delta H°(405.82 \text{ K}) = (118.9 \pm 2) \text{ kJ mol}^{-1}$; triphenylene, $\Delta H°(395.15 \text{ K}) = (115.6 \pm 2) \text{ kJ mol}^{-1}$; 1,2-benzoanthracene, $\Delta H°(385.77 \text{ K}) = (113.5 \pm 1) \text{ kJ mol}^{-1}$; pentacene, $\Delta H°(512.60 \text{ K}) = (154 \pm 5) \text{ kJ mol}^{-1}$; 1,2:3,4-dibenzoanthracene, $\Delta H°(439.53 \text{ K}) = 139.1 \pm 2) \text{ kJ mol}^{-1}$; 1,2:5,6-dibenzoanthracene, $\Delta H°(449.48 \text{ K}) = (148.8 \pm 2) \text{ kJ mol}^{-1}$. Each temperature given is a mid-range value and is such that the vapour pressure of each substance is 0.4 Pa at that temperature.

1. Introduction

Fused polycyclic hydrocarbons have been extensively studied both theoretically and experimentally. Vapour pressures and enthalpies of sublimation, however, are scarce, especially for the higher members of the series. Besides, the available results are not always consistent, as they should be if they are to be used for atom–atom potential calculations. We therefore decided to determine the enthalpies of sublimation from the temperature dependence of the vapour pressure of this (ortho-fused) series, which has up to 5 benzene rings.

2. Experimental

SAMPLES

The benzene used was Uvasol-grade (Merck, Germany). For naphthalene and anthracene we used zone-refined material. Phenanthrene is known to contain up to 1 per cent of anthracene but we used a sample (Fluka, Switzerland) which contained less than 0.1 mass per cent of anthracene (U.V. spectroscopy). Chrysene was obtained from Merck and triphenylene from Aldrich (USA). The other samples were obtained from Fluka, and used without purification. No influence of impurities could be detected in the results. The sample of pentacene was vacuum-sublimated at 500 K; a grey-brown residue remained.

MEASURING PRINCIPLE

Use was made of the simultaneous torsion- and weighing-effusion technique. The apparatus has been described previously.[1] Recent minor improvements and automation of the measurements have increased reproducibility.

TREATMENT OF RESULTS

Vapour pressures obtained from simultaneous torsion-effusion measurements (subscript t) and weighing-effusion measurements (subscript w) were fitted separately to the equation:[2]

$$R \ln(p/p^\circ) = -\Delta G^\circ(\theta)/\theta + \Delta H^\circ(\theta)(1/\theta - 1/T), \tag{1}$$

in which θ is a reference temperature and p° a standard pressure (1 Pa). For each substance the value of the reference temperature θ is such that the vapour pressure is 0.4 Pa.

For measurements made over a large temperature range equation (1) can be extended with terms which contain as adjustable parameters $\Delta C_p^\circ(\theta)$ and the derivatives of $\Delta C_p^\circ(\theta)$ with respect to temperature. In our measurements over a temperature range of only 20 K the plot of $\ln(p/p^\circ)$ as a function of $1/T$ does not deviate significantly from a straight line. Therefore our results permit the evaluation of not more than two parameters, namely $\Delta G^\circ(\theta)$ and $\Delta H^\circ(\theta)$. If however $\Delta C_p^\circ(\theta)$ is obtained by other means, equation (1) can be extended with the term:

$$+\Delta C_p^\circ(\theta)\{\theta/T - 1 + \ln(T/\theta)\}.$$

In that case, the vapour pressure can be extrapolated with more confidence. Furthermore, the enthalpy of sublimation can be extrapolated to 298 K.

3. Results and discussion

In table 1 we give the experimental results expressed as θ, $\Delta G^\circ(\theta)$, and $\Delta H^\circ(\theta)$ of equation (1). The results for benzene and naphthalene have been published and discussed before[1] but are presented here again as members of the series of aromatic hydrocarbons. In the column 10 the value for p_w/p_t at θ_t is given. This value will differ[3,4] from 1 if the mean molecular mass of the vapour deviates from the molecular formula mass. The high value for benzene is attributed[1] to less accurate temperature control at low temperatures. The error ranges given in table 1 are such that we can reproduce the tabulated results after a period of several weeks or months. So the error ranges indicate the reproducibility obtainable in our laboratory. By checking the apparatus with naphthalene about twice a year, we are trying to keep systematic errors as small as possible. Naphthalene has been proposed by Ambrose[5] as a reference substance. In columns 12, 13, and 14 we have given the mean of the values for the two techniques. By inserting these values in equation (1) we have obtained table 2.

The results for benzene and naphthalene are in good agreement with literature values as discussed in reference 1. With the help of figures 1 and 2, in which $\Delta H^\circ(T)$ is

plotted as a function of temperature, it is possible to compare the results for anthracene and phenanthrene with the results of other investigations. The points with the reference Mortimer[6] were obtained by adding the enthalpies of fusion to Mortimer's enthalpies of vaporization. The enthalpy of fusion for anthracene was taken to be $29.37 \text{ kJ mol}^{-1}$, as given by Goursot.[7] In Landolt–Börnstein[8] the enthalpy of fusion of phenanthrene is given as $18.62 \text{ kJ mol}^{-1}$.

Enthalpies of sublimation are often required at 298.15 K: for instance for determining the enthalpy of formation or for calculating lattice energies by the atom–atom potential method. $\Delta H^\circ(298.15 \text{ K})$ can be calculated from

$$\Delta H^\circ(298.15 \text{ K}) = \Delta H^\circ(T) + \int_T^{298.15 \text{ K}} \Delta C_p^\circ(T) \, dT, \qquad (2)$$
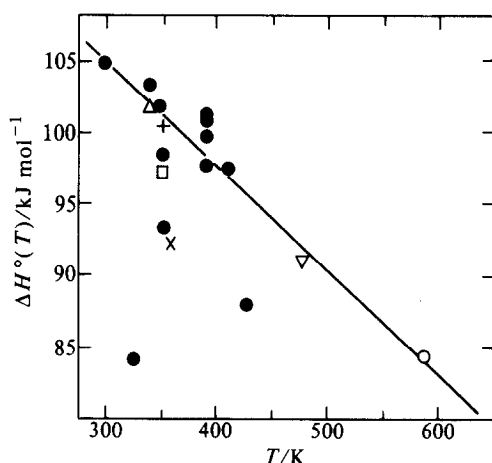

FIGURE 1. Enthalpy of sublimation $\Delta H^\circ(T)$ of anthracene. $\triangledown$, Brady;[14] $\times$, Inokuchi;[13] $\triangle$, de Kruif;[15] +, this work; ●, Malaspina;[16] ○, Mortimer;[6] □, Taylor.[17]
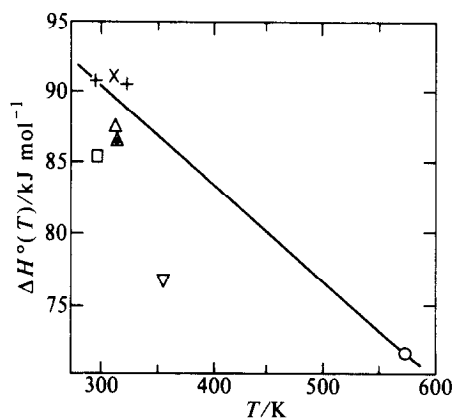
FIGURE 2. Enthalpy of sublimation $\Delta H^\circ(T)$ of phenanthrene. $\triangledown$, Brady;[14] $\times$, Inokuchi;[13] $\triangle$, de Kruif;[15] †, Morawetz;[19] ●, Bradley;[20] □, Sabbah;[18] ○, Mortimer;[6] +, this work.

TABLE 1. Experimental results at θ and extrapolated values at 298.15 K based on measurements in the temperature range T_1 to T_2. [a] References 9, 10, and 11; [b] reference 12; [c] references 5 and 12; [d] see figure 1; [e] see figure 2; [f] see figure 3: extrapolated values

	$\dfrac{T_1}{K}$	$\dfrac{T_2}{K}$	$\dfrac{\theta_t}{K}$	$\dfrac{\Delta G_t^\circ(\theta)}{J\,mol^{-1}}$	$\dfrac{\Delta H_t^\circ(\theta)}{kJ\,mol^{-1}}$	$\dfrac{\theta_w}{K}$	$\dfrac{\Delta G_w^\circ}{J\,mol^{-1}}$	$\dfrac{\Delta H_w^\circ(\theta)}{kJ\,mol^{-1}}$	$(p_w/p_t)(\theta_t)$
benzene	183	197	191.76	1461 ± 80	53.9 ± 1	190.57	1452 ± 40	49.4 ± 0.5	1.21
naphthalene	253	273	267.85	2041 ± 20	74.8 ± 0.5	267.90	2041 ± 10	73.9 ± 0.2	0.99
anthracene	337	361	351.32	2676 ± 50	100.6 ± 1	351.24	2676 ± 50	99.9 ± 1	1.01
phenanthrene	315	335	325.04	2476 ± 25	90.5 ± 1	324.99	2476 ± 25	90.5 ± 1	1.00
naphthacene	419	446	436.99	3329 ± 100	128.7 ± 2	437.07	3330 ± 100	127.5 ± 1	0.99
chrysene	390	417	405.70	3091 ± 100	119.2 ± 2	405.93	3092 ± 100	118.5 ± 1	0.98
triphenylene	381	406	395.26	3011 ± 100	115.9 ± 1	394.96	3009 ± 100	115.2 ± 2	1.03
1,2-benzo- anthracene	373	396	385.65	2938 ± 50	113.8 ± 1	385.80	2939 ± 50	113.1 ± 1	0.99
pentacene	495	530	512.59	3905 ± 200	154 ± 5	512.61	3905 ± 200	155 ± 5	1.00
1,2:3,4-dibenzo- anthracene	425	452	439.83	3351 ± 100	140.2 ± 1	439.23	3346 ± 50	138.0 ± 2	1.05
1,2:5,6-dibenzo- anthracene	436	462	449.65	3426 ± 50	141.6 ± 1	449.31	3423 ± 100	140.0 ± 2	1.03

TABLE 2. Pressure-temperature table obtained by inserting mean values of table 1 in equation (1)

p/Pa:	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
					T/K					
benzene	183.35	187.17	189.48	191.16	192.48	193.57	194.51	195.32	196.05	196.70
naphthalene	257.21	262.44	265.59	267.88	269.68	271.17	272.44	273.56	274.55	275.44
anthracene	337.66	344.34	348.36	351.28	353.57	355.47	357.09	358.51	359.77	360.90
phenanthrene	312.11	318.44	322.26	325.03	327.21	329.01	330.55	331.90	333.10	334.17
naphthacene	420.50	428.61	433.50	437.04	439.82	442.12	444.09	445.80	447.33	448.70
chrysene	390.46	397.99	402.53	405.82	408.41	410.54	412.37	413.96	415.38	416.66
triphenylene	380.17	387.51	391.94	395.15	397.67	399.76	401.53	403.09	404.47	405.71
1,2-benzoanthracene	371.22	378.36	382.66	385.77	388.21	390.24	391.97	393.47	394.81	396.02
pentacene	493.66	502.95	508.55	512.60	515.78	518.42	520.66	522.62	524.37	525.94
1,2:3,4-dibenzoanthracene	424.08	431.67	436.23	439.53	442.12	444.26	446.09	447.68	449.10	450.37
1,2:5,6-dibenzoanthracene	433.53	441.36	446.08	449.48	452.16	454.37	456.26	457.91	459.37	460.69

and if there is a transition between T and 298.15 K, the enthalpy of transition must be added. Unfortunately the required heat capacities of both solid- and gas-phase are not available, except for benzene and for naphthalene. As an approximation we shall therefore use

$$\Delta H^\circ(298.15\ \mathrm{K}) = \Delta H^\circ(T) + \Delta C_p^\circ(298.15\ \mathrm{K})(298.15\ \mathrm{K} - T). \tag{3}$$

For benzene the required (extrapolated) values can be obtained from the values given in references 9, 10, and 11; the result is $\Delta C_p^\circ(298.15\ \mathrm{K}) = -(27 \pm 3)\ \mathrm{J\ K^{-1}\ mol^{-1}}$. For naphthalene one can take the value of $\Delta C_p^\circ(298.15\ \mathrm{K}) = -59\ \mathrm{J\ K^{-1}\ mol^{-1}}$ given by Miller.[12] This value is consistent with the value $\Delta C_p^\circ(298.15\ \mathrm{K}) = -(60.5 \pm 10)\ \mathrm{J\ K^{-1}\ mol^{-1}}$ which we found by fitting Ambrose's[5] wide-range vapour pressures to equation (1) extended with the ΔC_p° term. The slope of the straight line in figure 1

TABLE 1—*continued*

	mean values		extrapolated values			
θ	$\Delta G°(\theta)$	$\Delta H°(\theta)$	$\Delta C_p°(298.15\ \mathrm{K})$	$\Delta H°(298.15\ \mathrm{K})$	$\Delta G°(298.15\ \mathrm{K})$	$p(298.15\ \mathrm{K})$
K	$\mathrm{J\ mol^{-1}}$	$\mathrm{kJ\ mol^{-1}}$	$\mathrm{J\ K^{-1}\ mol^{-1}}$	$\mathrm{kJ\ mol^{-1}}$	$\mathrm{kJ\ mol^{-1}}$	Pa
191.16	1456 ± 80	51.7 ± 2	-27 ± 3^a	44.4^b		
267.88	2041 ± 20	74.4 ± 0.5	-59 ± 5^c	72.6 ± 0.6	-6 ± 0.1	11.3 ± 0.4
351.28	2676 ± 50	100.4 ± 1	-77 ± 10^d	104.5 ± 1.5	17.8 ± 2	$(7.5 \pm 0.7) \times 10^{-4}$
325.03	2476 ± 25	90.5 ± 1	-73 ± 25^e	92.5 ± 2	9.9 ± 0.2	$(1.8 \pm 0.1) \times 10^{-2}$
437.04	3329 ± 100	128.1 ± 2	-112 ± 20^f	143.7 ± 5	46 ± 1	$(9.3 \pm 4) \times 10^{-9}$
405.82	3092 ± 100	118.9 ± 2	-112 ± 20^f	131.0 ± 4	36 ± 1	$(5.7 \pm 2) \times 10^{-7}$
395.15	3010 ± 100	115.6 ± 2	-112 ± 20^f	126.5 ± 4	32 ± 1	$(2.3 \pm 0.7) \times 10^{-6}$
385.77	2938 ± 50	113.5 ± 1	-112 ± 20^f	123.3 ± 3	29.3 ± 0.5	$(7.3 \pm 1.3) \times 10^{-6}$
512.60	3905 ± 200	154 ± 5	-140 ± 25^f	184 ± 10	74 ± 4	$(1.0 \pm 0.8) \times 10^{-13}$
439.53	3348 ± 100	139.1 ± 2	-140 ± 25^f	159 ± 6	50 ± 2	$(1.3 \pm 0.6) \times 10^{-9}$
449.48	3425 ± 50	140.8 ± 2	-140 ± 25^f	162 ± 6	54 ± 2	$(3.7 \pm 1.8) \times 10^{-10}$

(anthracene) corresponds to $\Delta C_p°(298.15\ \mathrm{K}) = -(77 \pm 10)\ \mathrm{J\ K^{-1}\ mol^{-1}}$. In the same way we obtain from figure 2 (phenanthrene), $\Delta C_p°(298.15\ \mathrm{K}) = -(73 \pm 25)\ \mathrm{J\ K^{-1}\ mol^{-1}}$. In figure 3 we plot $\Delta C_p°$ as a function of the number N of benzene rings. Assuming that the linear relation between $\Delta C_p°$ and N can be extended to the higher polycyclic hydrocarbons, we are now in a position to extrapolate the experimental work. The results are given in the last four columns of table 1. We did not detect (by DSC) any transitions between 298 K and θ for any of the substances for which the extrapolated values are given. Finally in figure 4 we plot $\Delta H°(298.15\ \mathrm{K})$ against N. The plot shows that the enthalpy of sublimation for the fused polycyclic hydrocarbons with a linear arrangement exceeds that for the ortho-fused isomers by $20\ \mathrm{kJ\ mol^{-1}}$. The increase in $\Delta H°$ has a constant value of $33.3\ \mathrm{kJ\ mol^{-1}}$ per benzene ring or $8.33\ \mathrm{kJ\ mol^{-1}}$ per carbon atom, which is about 17 per cent higher than the average value derived by Inokuchi[13] from a number of aromatic hydrocarbons.

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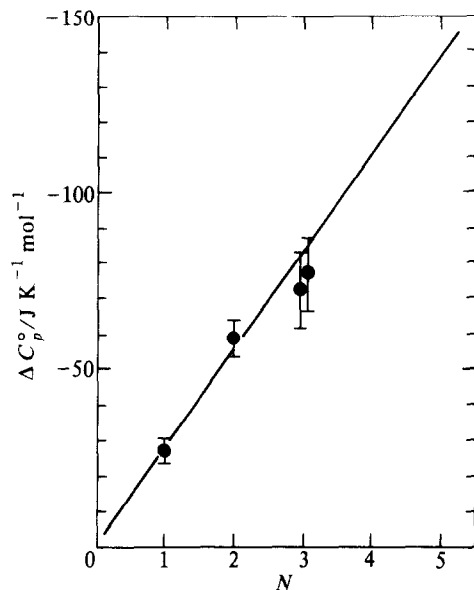13. Inokuchi, H.; Shiba, S.; Handa, T.; Akamatu, H. *Bull. Chem. Soc. Jpn.* **1952**, 25, 299.

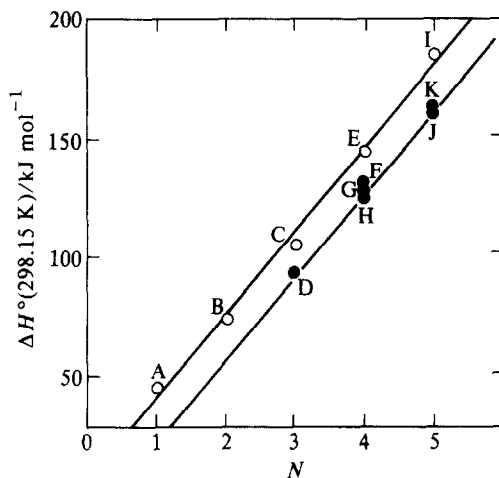FIGURE 3. ΔC_p° against number N of benzene rings.

FIGURE 4. Enthalpy of sublimation $\Delta H^\circ(298.15 \text{ K})$ against number N of benzene rings. $\bigcirc$, linear arrangement; $\bullet$, non-linear; A, benzene; B, naphthalene; C, anthracene; D, phenanthrene; E, naphthacene; F, chrysene; G, triphenylene; H, 1,2-benzoanthracene; I, pentacene; J, 1,2:3,4-dibenzoanthracene; K, 1,2:5,6-dibenzoanthracene.

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