Thermochimica Acta, 41 (1980) 297—304
Elsevier Scientific Publishing Company, Amsterdam — Printed in Belgium

VAPOUR PRESSURE OF α-IODONAPHTHALENE

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(Received 8 April 1980)

ABSTRACT

Using three different techniques, the vapour pressure of α-iodonaphthalene was measured in the temperature range 322—422 K. The pressure equation $\log P(\text{kPa}) = 8.82 \pm 0.29 - (3719 \pm 300)/T$, was determined. The enthalpy of vaporization change, $\Delta H^0_{298} = 69.4 \pm 4.0$ kJ mole^{-1}, was determined as the average of the results obtained by second- and third-law treatment of the experimental data. Antoine's constants, $A = 6.258$, $B = 2010$ and $C = 171$, were also derived.

INTRODUCTION

Some theoretical works and the physical properties of α-iodonaphthalene are reported in the literature, but apparently no vapour pressure measurements have yet been made for this compound. As part of our continuing research program for the study of halogenated naphthalene [1,2], the vapour pressure of this compound was determined. The measurements were carried out using the transpiration, torsion effusion and Knudsen effusion techniques.

EXPERIMENTAL AND RESULTS

The α-iodonaphthalene was supplied by Koch-Light with a stated purity of 99%, where the major impurities are due to iodine. The cells were always loaded in a dry box to avoid any interaction with moisture.

Transpiration

The basis of the method and the experimental procedure have been described elsewhere [3]. The vapour pressure values (P_i) were determined from the mass of sample (m_i) transported by a carrier gas and condensed in a cooled glass collector during the time (Δt) of the transpiration experiment by the relation

$$P_i = m_i/(m_i + P_0\varphi\, \Delta t M_i/RT_0)$$

where M_i is the molecular mass of the sample, R is the gas constant, φ is the

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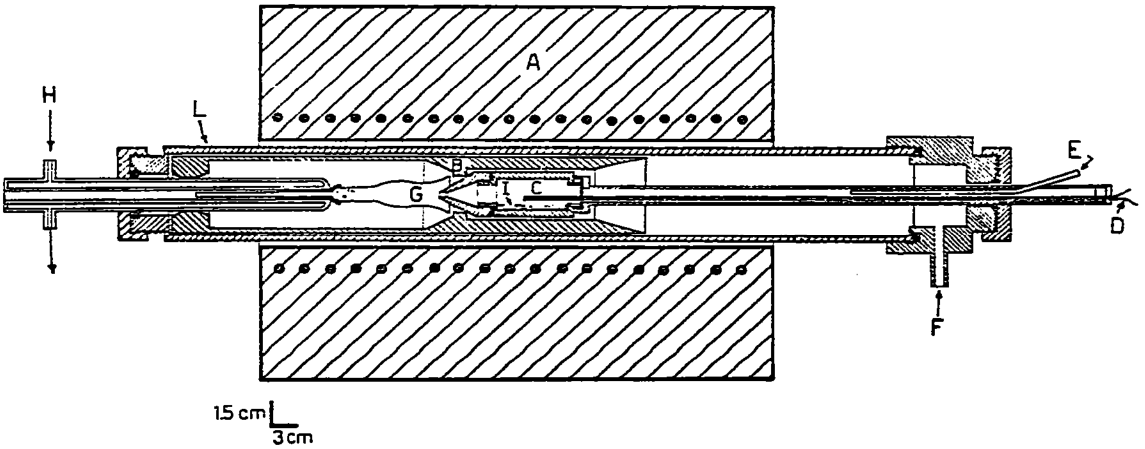

Fig. 1. Transpiration apparatus assembly. A, Furnace; B, stainless-steel support; C, sample container; D, thermocouple; E, inlet carrier gas; F, inlet auxiliary gas; G, collector; H, water-cooling inlet; I, sample; L, steel tube.

flow rate of the carrier gas measured at the inlet of the furnace, and P_0 and T_0 are the pressure and temperature, respectively, where the flow was measured. The experimental apparatus is illustrated in Fig. 1. Its geometry ensures the saturation of the carrier gas with the vapour of the investigated sample in the experimentally evaluated flow range 1.2—1.6 l min^{-1}. Under these conditions, diffusion effects were considered negligible.

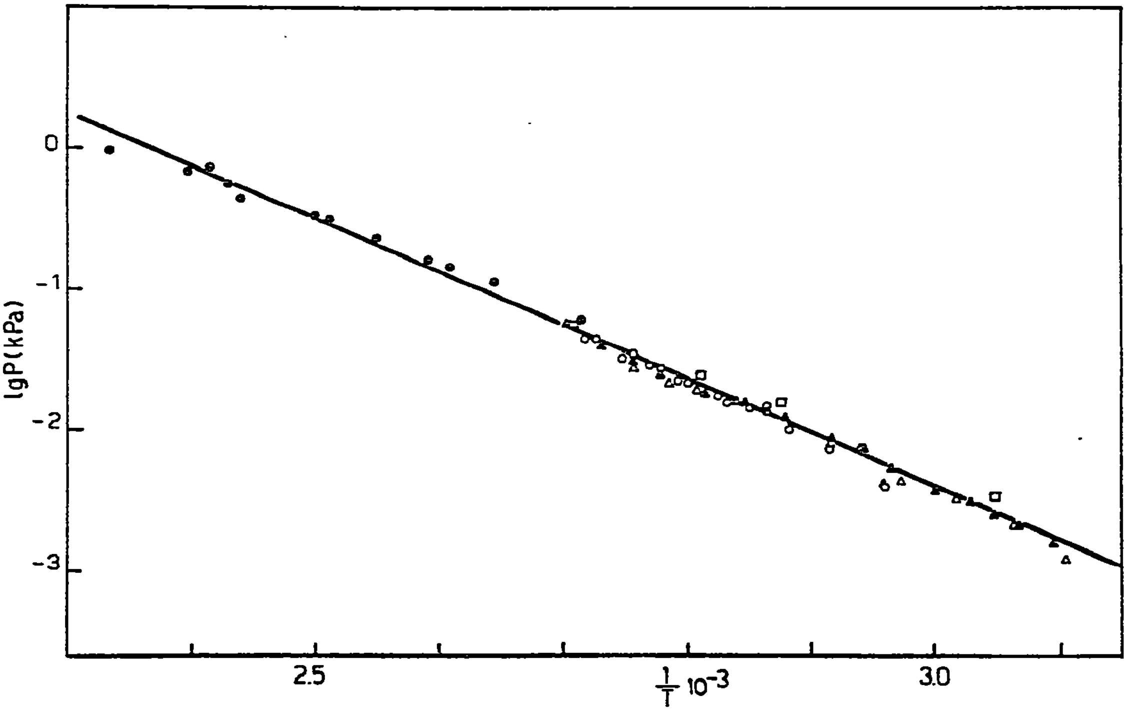

Fig. 2. Experimental vapour pressure values of α-iodonaphthalene. Transpiration technique, ●; Knudsen effusion technique, □; torsion effusion technique (cell A, ○; cell B, △; cell C, ▲).

The mass of the condensed vapour was determined by the mass gain of the collector. At each temperature a series of vapour pressure values were determined by varying the flow rate of the carrier gas and/or the time of the transpiration experiment. The average pressure data are summarized in Table

TABLE 1

Vapour pressure determined by transpiration method

T (K)	ϕ (ml min^{-1})	Condensed sample (mg)	Time (min)	P (kPa)	$-\Delta[(G^0_T - H^0_{298})/T]$ (J mole^{-1} K^{-1})	ΔH^0_{298} (kJ mole^{-1})
384	142	44.9	20	1.50	116.2	65.3
384	137	42.2	21	1.40	116.2	65.6
384	129	40.6	20	1.51	116.2	65.3
398	138	67.6	15	3.09	116.2	65.3
398	140	56.2	10	3.81	116.2	64.6
398	135	61.1	16	2.67	116.2	65.8
410	155	65.6	9	4.48	116.3	66.0
410	153	65.9	9	4.56	116.3	66.0
410	150	62.4	9	4.41	116.3	66.1
428	143	64.9	5	8.63	116.8	66.9
428	142	70.2	5	8.95	116.8	66.7
378	153	71.3	40	1.10	116.2	65.3
378	153	95.3	50	1.19	116.2	65.0
378	153	58.5	30	1.20	116.2	65.0
386	163	59.3	21	1.65	116.4	65.5
386	158	53.4	20	1.56	116.4	65.6
386	154	40.6	15	1.77	116.4	65.5
400	160	91.7	15	3.62	116.2	65.2
400	163	48.6	9	3.14	116.2	65.6
400	159	69.4	12	3.44	116.2	65.3
411	145	93.2	10	6.09	116.3	65.1
411	145	85.1	10	5.57	116.3	65.5
411	150	90.6	10.5	5.45	116.3	65.6
414	154	124.4	10	7.63	116.4	64.9
414	154	129.9	10.5	7.60	116.4	64.9
414	153	95.2	8	7.35	116.4	65.1
417	148	69.9	6	7.46	116.5	65.5
417	146	84.8	7.33	7.49	116.5	65.5
417	143	70.2	7	6.64	116.5	65.9
417	137	67.2	7	6.62	116.5	65.9
368	142	43.6	46	0.63	116.2	65.3
368	144	43.3	45	0.60	116.2	65.4
392	143	66.7	20	2.27	116.2	65.4
392	145	72.6	20	2.37	116.2	65.2
392	144	77.4	22	2.31	116.2	65.3
					Average	65.5 ± 0.5 *

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* The error is the standard deviation.

TABLE 2

Vapour pressure determined by torsion effusion method

T (K)	α (deg.)	$P \times 10^3$ (kPa)	$-\Delta[(G_T^0 - H_{298}^0)/T]$ (J mole^{-1} K^{-1})	ΔH_{298}^0 (kJ mole^{-1})
Cell A				
338	13	4.07	115.8	67.6
343	37	11.58	115.9	65.6
347	35	10.96	116.0	66.6
349	48	15.03	116.0	66.1
351	47	14.72	116.1	66.5
353	53	16.59	116.1	66.6
354	57	17.85	116.2	66.6
357	71	22.23	116.2	66.5
358	74	23.17	116.2	66.5
360	91	28.49	116.3	66.3
361	95	29.74	116.2	66.4
363	114	35.69	116.2	66.2
364	105	32.88	116.2	66.6
367	140	43.83	116.2	66.3
368	145	45.40	116.2	66.3
			Average	66.4 ± 0.5 *
Cell B				
322	11	1.26	115.7	67.5
326	19	2.18	115.7	66.9
331	29	3.32	115.8	66.7
336	39	4.47	115.9	67.0
338	37	4.24	115.8	67.5
340	66	7.58	115.9	66.3
343	70	8.02	115.9	66.7
347	112	12.82	116.0	66.2
349	124	14.20	116.0	66.2
352	144	16.49	116.1	66.4
354	150	17.18	116.2	66.7
356	157	17.98	116.2	66.9
359	184	21.07	116.2	67.0
363	237	27.14	116.2	67.0
			Average	66.7 ± 0.4 *
Cell C				
323	14	1.60	115.7	67.1
326	19	2.18	115.7	66.8
328	22	2.52	115.8	66.9
330	27	3.09	115.8	66.8
333	33	3.78	115.8	66.8
337	47	5.38	115.9	66.6
340	64	7.33	115.95	66.4
343	79	9.05	115.9	66.4
347	110	12.60	116.0	66.2
351	140	16.03	116.1	66.3
355	160	18.32	116.2	66.7
360	216	24.73	116.2	66.7
363	244	27.94	116.2	66.9
366	360	41.22	116.2	66.3
370	533	61.03	116.2	65.8
			Average	66.6 ± 0.4 *

* The error is the standard deviation.

1 and plotted in Fig. 2. Least-squares treatment of the data over the temperature range 368—422 K yields the following equation

$$\log P(\text{kPa}) = 7.49 \pm 0.21 - (3187 \pm 85)/T \tag{1}$$

where the associated errors are standard deviations.

Torsion effusion method

Details of the method and the experimental apparatus for this technique have been given elsewhere [4,5]. Different glass cells with different geometrical constants were employed. The vapour pressure values of α-iodonaphthalene were derived from the measured torsion angles (α) of the cell by the equation

$$P(\text{atm}) = K\alpha$$

where K is a constant which takes into account the geometrical constants of the cell and the torsion constant of the suspension Ni—Pt fibre. The instrument constant was experimentally determined before and after each vaporization run by loading the employed cell with high purity mercury whose vapour pressures are well known in the literature [6]. The temperature of the sample was measured by a calibrated thermometer (±0.2°C) in direct contact with the sample, as shown in Fig. 3. The vaporization of α-iodonaphthalene was investigated with three different cells over the temperature range 322—370 K. The pressure data so determined are reported in Table 2 and fitted in Fig. 2.

Least-squares treatment of the data taken in each experiment yields the following pressure—temperature equations

$$\text{cell A} \quad \log P(\text{kPa}) = 9.09 \pm 0.45 - (3822 \pm 160)/T \tag{2}$$

$$\text{cell B} \quad \log P(\text{kPa}) = 9.60 \pm 0.36 - (4025 \pm 123)/T \tag{3}$$

$$\text{cell C} \quad \log P(\text{kPa}) = 9.02 \pm 0.17 - (3809 \pm 54)/T \tag{4}$$

where the associated errors in the slopes and intercepts are standard deviations.

Knudsen effusion method

Some vapour pressure values of α-iodonaphthalene were determined by the Knudsen effusion technique [7]. The experimental apparatus is shown in Fig. 4.

Heating of the Knudsen cells, with different effusion holes (0.5 and 1.3 mm in diameter, respectively), was carried out using a water—glycerine bath thermostat and its temperature was measured by a calibrated thermometer inserted in an isothermal block in contact with the effusion cell. At any fixed temperature (T), the vapour pressure was derived from the mass loss of the sample (m) effused from the cell in the experimental time (Δt) from the relation

$$P(\text{kPa}) = 2.29K'm(T/M)^{1/2}/S\ \Delta t$$

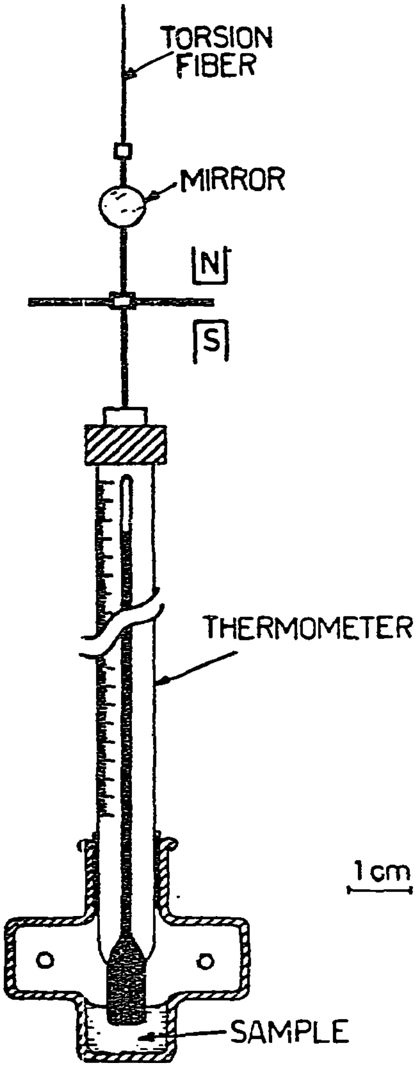

Fig. 3. Torsion effusion apparatus.

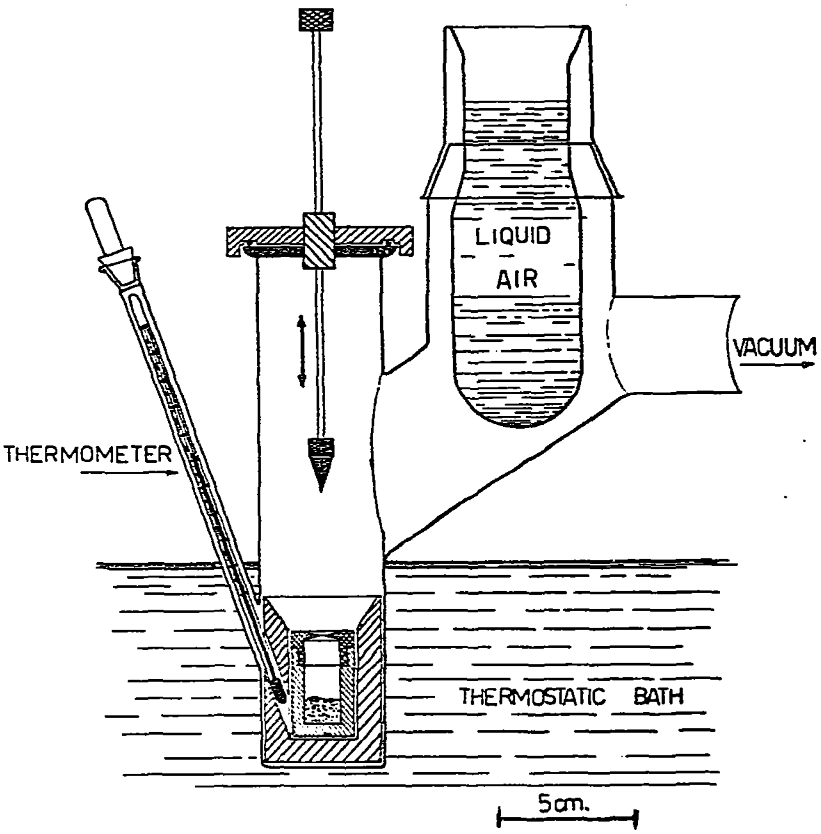

Fig. 4. Knudsen effusion apparatus.

where S and K' are the area and Clausing's factor, respectively, [8] of the effusion hole of the Knudsen cell and M is the molar weight of the vapour.

The vaporization time was evaluated by opening and closing the effusion hole of the thermostated cell under vacuum with a mechanical device. Calibration runs with pure mercury were also performed. The vapour pressure data obtained by assuming that α-iodonaphthalene is the only gaseous species in thermodynamic equilibrium with the liquid phase in analogy with α-chloronaphthalene [9] are reported in Table 3 and Fig. 2. In spite of the few experimental points, the data were treated by the least-square method, giving the following equation

$$\log P(\text{kPa}) = 8.32 \pm 0.16 - (3528 \pm 56)/T \qquad (5)$$

where the errors of the slope and intercept are standard deviations.

TABLE 3

Vapour pressure determined by the Knudsen effusion technique

T (K)	Exp. time (min)	Evap. mass (mg)	P (kPa)	$-\Delta[(G^0_T - H^0_{298})/T]$ (J mole^{-1} K^{-1})	ΔH^0_{298} (kJ mole^{-1})
348	60	126.9	1.56×10^{-2}	116.1	65.7
328	120	59.3	3.53×10^{-3}	115.8	65.9
369	20	146.4	5.55×10^{-2}	116.2	65.8
356	50	161.4	2.43×10^{-2}	116.2	66.0
				Average	65.8 ± 0.1 *

* The error is the standard deviation.

CONCLUSION

On the basis of the results obtained by three different techniques we propose the following vapour pressure equation for α-iodonaphthalene(l)

$$\log P(\text{kPa}) = 8.82 \pm 0.29 - (3719 \pm 300)/T \qquad (6)$$

The constants were evaluated by weighting the corresponding values obtained in each technique and their errors were estimated taking into account the uncertainties in the temperature measurements and the calibration factors. From the slope a second-law vaporization enthalpy, $\Delta H^0_{373} = 71.1 \pm 5.5$ kJ mole^{-1}, was derived.

The third-law ΔH^0_{298} values determined at each experimental temperature are reported in Tables 1—3. The free energy functions for α-iodonaphthalene (gas) were taken from the literature [10], whereas for the liquid they were considered equal to those previously derived for α-bromonaphthalene [1].

The average third-law value, $\Delta H^0_{298} = 66 \pm 2$ kJ mole^{-1}, where the error was estimated on the basis of uncertainties in the temperature measurements and the free energy function evaluations, is in agreement within the associated errors with the second-law value, $\Delta H^0_{298} = 72.1 \pm 5.5$ kJ mole^{-1}, corrected at 298 K using the enthalpic function reported in the literature [8,1]. On this basis we propose the value 69 ± 4 kJ mole^{-1} as ΔH^0_{298} associated with the vaporization process of α-iodonaphthalene.

The constants A and C of Antoine's equation were also determined from the slope and intercept of eqn. (7) obtained by least-squares treatment of the vapour data according to a procedure suggested by Thomson [11]

$$\log P(\text{kPa}) = A - (t_0 + C)(\log P - \log P_0)/(t - t_0) \qquad (7)$$

where t_0 and P_0 represent the temperature and pressure at the boiling point ($t_0 = 302°\text{C}$ [12] and $P_0 = 101.3$ kPa) and P is the pressure measured at the experimental temperatures t (°C). From the constants A and C, using Antoine's equation, $\log P = A - B/(t + C)$ (temperature in °C), for each experimental vapour pressure—temperature couple, a series of B values was evaluated, so the following Antoine's constants, $A = 6.258$, $C = 171$ and an average $B = 2010$, were derived.

ACKNOWLEDGEMENT

This work has been supported by Consiglio Nazionale delle Ricerche, Rome.

REFERENCES

1 M. Urbani, R. Gigli and V. Piacente, J. Chem. Eng. Data, 25 (1980) 97.
2 D. Ferro, M. Pelino and V. Piacente, Rev. Roum. Chim., in press.
3 V. Piacente, A. Desideri, L. Malaspina and A. Hallgass, Rev. Int. Hautes Temp. Refract., 10 (1973) 85.
4 R.D. Freeman in J.L. Margrave (Ed.), The Characterization of High Temperature Vapour, Wiley, New York, 1967.
5 V. Piacente and G. DeMaria, Ric. Sci., 39 (1969) 549.
6 R. Hultgreen, R.L. Orr and K.K. Kelley, Supplement to Selected values of Thermodynamic Properties of Metals and Alloys, Dep. Min. Technol., Univ. California, Berkeley, CA, 1967.
7 M. Knudsen, Ann. Phys., 28 (1909) 75.
8 S. Dushman, Scientific Foundation of Vacuum Technique, Wiley, New York, 1958, pp. 90—111.
9 O. Shuzo, Computer Aided Data Book of Vapour Pressure, Data Book Publishing Co. Tokyo, Japan, 1976.
10 D.G. Mc.Fee and J. Lielmezs, Thermochim. Acta, 30 (1979) 173.
11 G.W.N. Thomson, Chem. Rev., 39 (1946) 1.
12 R.C. Weast (Ed.), CRC Handbook of Chemistry and Physics, 1978—1979, 5th edn.