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Note

Vapour pressure of phthalic anhydride

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While searching for accurate vapour pressure data of phthalic anhydride, a careful evaluation indicated large inconsistencies among the existing data. This necessitated a redetermination of the vapour pressure. For this purpose, the carrier gas entrainment method was adopted and the results are presented in this communication.

EXPERIMENTAL

Reagent grade phthalic anhydride was further purified by resubliming it twice. The observed melting temperature was 404.0 ± 0.5 K. All other chemicals were of reagent quality and were used without further purification.

The pyrex glass transpiration apparatus (Fig. 1) was designed primarily to measure the volatility of air-sensitive organo-metallic compounds. Provision was made to move the sample container(B), a distance of about 15 cm from the hot zone to the cold without disturbing the rest of the set up.

A nichrome resistance wire (~1 mm diameter) wound on a pyrex tube of 40.0 mm diameter and 30.0 cm long served as the furnace. This furnace had an

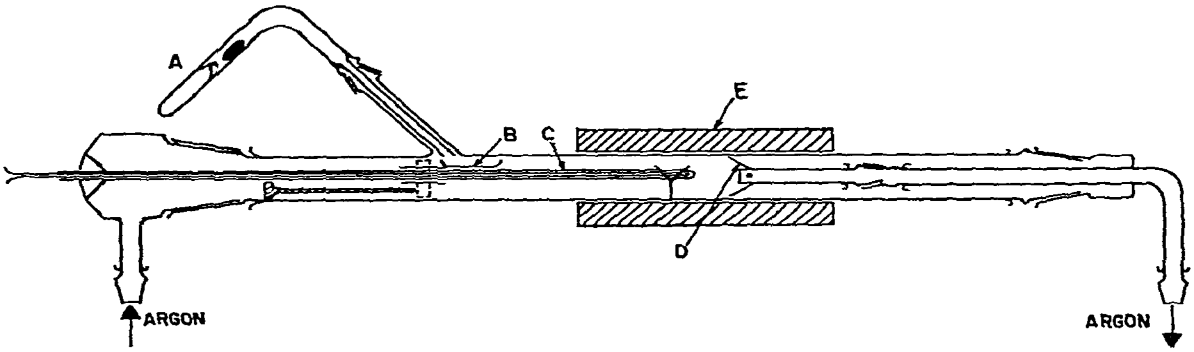

Fig. 1. Transpiration apparatus. A, Sample in break seal; B, sample boat attached to magnetically operated carriage; C, chromel–alumel thermocouple; D, collector assembly; E, furnace.

TABLE 1

COMPARISON OF MASS TRANSPORT RATE DETERMINED BY DIFFERENT ANALYTICAL TECHNIQUES

Temperature	*Mass transported*		
	Mass gain of the collector	*Mass loss of the boat*	*From titrimetry*
420.5	28.0		28.1
413.1	23.5		22.9
361.7	3.9	3.96	
357.6	6.7	6.85	

isothermal zone (± 0.5 K) of 5 cm near the centre where the sample was positioned during the run. The set temperature was maintained to ± 0.5 K with a Eurotherm temperature controller (Model PID/SCR) and the temperature of the sample was measured by a calibrated chromel–alumal thermocouple.

In a typical experiment, about 1.0 g of the sample was spread uniformly inside the boat(B). For measurements up to 370 K, the sample was initially positioned in the cold zone during the time required for the furnace to attain the set temperature with the argon carrier flowing at the predetermined rate. Then the sample was pushed into position and thermal equilibration of the sample was allowed (about 10–15 min) before the carrier gas volume was recorded on a Baird and Tatlock wet test meter. For higher temperatures, the sample was located in the hot zone position from the beginning and during the heating up period, argon carrier gas was admitted from the collector (D) side so that no vapour could enter and be deposited in the collector. After thermal equilibration, the argon carrier flow direction was reversed.

The number of moles of the argon carrier passed was calculated from the wet test meter readings, previously calibrated against a glass capillary flow meter[5], and the ambient temperature. The moles of phthalic anhydride vapour transported by this argon carrier were calculated from the weight loss of the sample in the boat, as well as from the increase in weight of the collector. To ascertain the reliability of the data, on a few occasions, in addition, the phthalic anhydride transported was determined by dissolving the deposit in the collector in a known excess of standard alkali solution followed by acidimetric titration. There was good agreement among the data obtained by these procedures (Table 1).

RESULTS AND DISCUSSION

Assuming the vapours to be ideal, the partial pressure of the phthalic anhydride (P_{ph}) was calculated by the expression

$$P_{\mathrm{ph}} \equiv \frac{n_{\mathrm{ph}}}{n_{\mathrm{ph}} + n_{\mathrm{Ar}}} P \qquad (1)$$

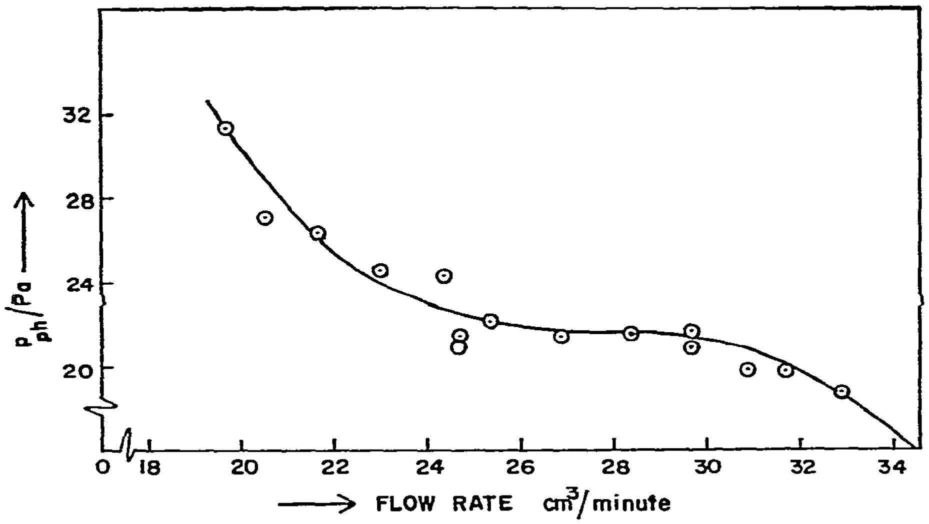

Fig. 2. Apparent vapour pressure of phthalic anhydride vs. argon flow rate.

TABLE 2

VAPOUR PRESSURE OF SOLID PHTHALIC ANHYDRIDE

Temperature (K ± 0.5)	*$10^3/T$ (K)*	*Moles of the vapour, n_{ph} transported per dm^3 of argon carrier ($\times 10^6$)*	*P_{ph} (Pa)*	*log (P_{ph}) (Pa)*
333.0	2.999	0.88	2.2	0.334
333.6	2.998	0.92	2.3	0.3560
341.0	2.933	1.61	3.9	0.595
351.6	2.844	4.27	10.5	1.020
353.7	2.827	3.98	9.8	0.990
361.2	2.769	8.72	21.4	1.330
363.6	2.750	8.64	21.2	1.326
375.0	2.667	24.8	60 8	1.783
375.4	2.764	27.3	66.9	1.825
382.0	2.618	38.4	94.1	1.973
395.7	2.527	105.9	260.1	2.415
395.9	2.526	105.9	259.9	2.414
403.8	2.476	167.8	411.9	2.614

where n_{ph} and n_{Ar} are, respectively, the moles of phthalic anhydride collected and argon passed, and p is the total gaseous pressure in the reaction zone.

The P_{ph} thus calculated in general corresponds to an apparent vapour pressure of phthalic anhydride and would be equal to the true equilibrium value only if this P_{ph} is flow-independent for the given set up. This flow-independent plateau region was experimentally established (Fig. 2) and in all subsequent runs, an argon flow in the region of 26.28 cm³/min was used.

The vapour pressures of phthalic anhydride thus determined between 330 and 440 K are presented in the Tables 2 and 3. In Fig. 3, a plot of log P vs. $1/T$ is presented

TABLE 3

VAPOUR PRESSURE OF LIQUID PHTHALIC ANHYDRIDE

Temperature (K ± 0.5)	*$10^3/T$ (K)*	*Moles of the vapour, n_{ph}, transported per dm^3 of argon carrier ($\times 10^4$)*	P_{ph} *(Pa)*	*log* P_{ph} *(Pa)*
411.7	2.429	2.40	589.5	2.770
411.7	2.429	2.48	608.1	2.783
419.4	2.384	3.62	887.8	2.948
420.1	2.380	3.36	823.3	2.915
431.9	2.315	6.32	1552.0	3.190
432.9	2.310	5.73	1406.7	3.148
440.2	2.271	8.28	2042.8	3.310
440.5	2 270	8 08	1993.8	3.299

along with the earlier data of Crooks and Feetham[4] for comparison. The break in the log P vs. $1/T$ plot corresponding to melting occurs at 405.5 ± 2.0 K.

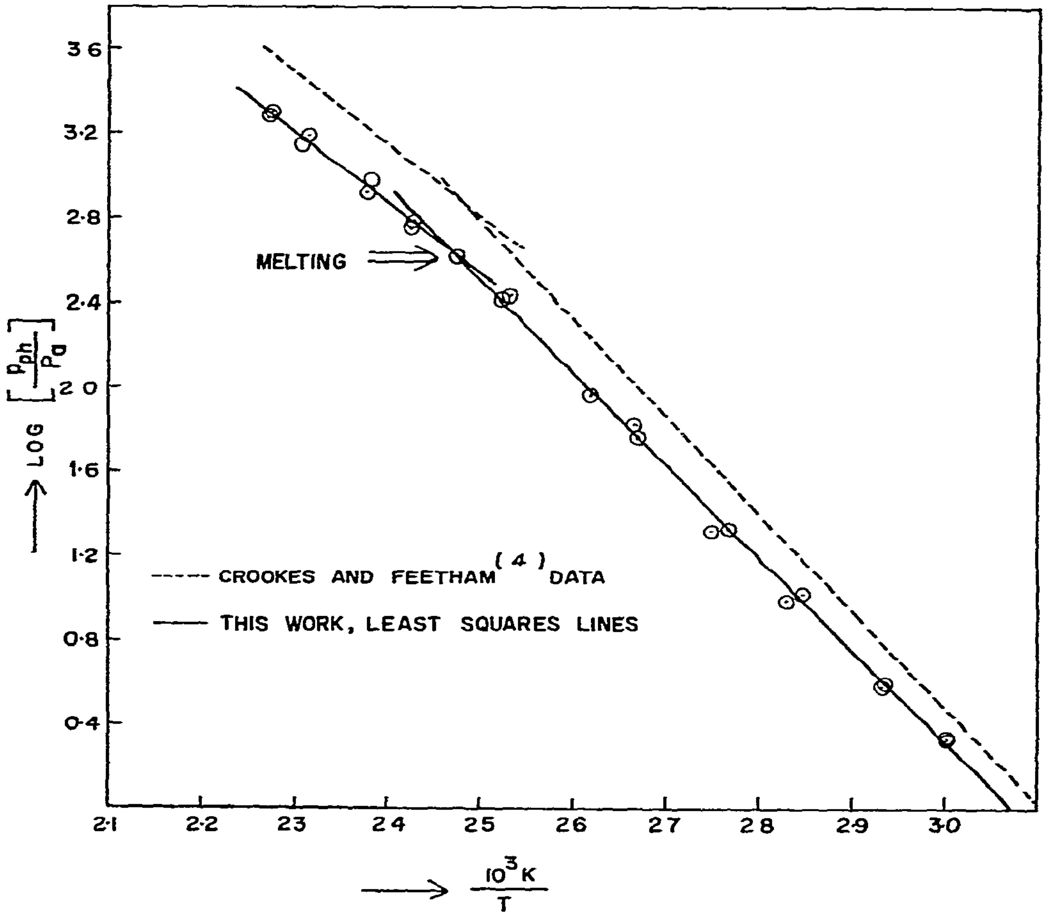

Fig. 3. Vapour pressure of phthalic anhydride vs. temperature.

Linear least squares fit of the data gave the eqns. (2) and (3) for the solid–vapour and liquid–vapour equilibria, respectively.

$$\log(P_{\mathrm{ph}}/\mathrm{Pa}) = (-\,4.400 \pm 0.061)\frac{10^3\mathrm{K}}{T} + (13.524 \pm 0.169) \quad 330 \leq T/\mathrm{K} \leq 404 \quad (2)$$

$$\log(P_{\mathrm{ph}}/\mathrm{Pa}) = (-\,3.337 \pm 0.129)\frac{10^3\mathrm{K}}{T} + (10.883 \pm 0.304) \quad 404 \leq T/\mathrm{K} \leq 440 \quad (3)$$

From eqns. (2) and (3), the average enthalpy of sublimation, $\Delta H^{\circ}_{\mathrm{sub}}$ at the intermediate temperature 367 K and the enthalpy of vaporization at the mean temperature, 422 K were calculated by the second law method.

$$\Delta H^{0}_{\mathrm{sub}}\,(\text{phthalic anhydride, 367 K})/\mathrm{kJ\ mole^{-1}} = 84.4 \pm 1.2 \qquad (4)$$

and

$$\Delta H^{0}_{\mathrm{V}}\,(\text{phthalic anhydride, liq. 422 K})/\mathrm{kJ\ mole^{-1}} = 63.9 \pm 2.5 \qquad (5)$$

The difference between the expressions (4) and (5) yielded a value of $\Delta H^{\circ}_{\mathrm{f}} = 20.5 \pm 3.6$ kJ mole^{-1} at 405.5 K.

The melting temperature of 405.5 ± 2.0 K calculated from the measured temperature dependence of the vapour pressures of solid and the liquid phthalic anhydride is in good agreement with the directly measured melting temperature of 404.0 ± 0.5 K.

Beech and Lintonbon[3] reported a $\Delta H^{\circ}_{\mathrm{sub}}$ value of 81.0 ± 1.0 kJ mole^{-1} based on their DSC measurement which, considering the difference in the two methods, is in good agreement with the $\Delta H^{\circ}_{\mathrm{sub}}$ of 84.4 ± 1.2 kcal mole^{-1} calculated from the present investigations. The second law enthalpy of sublimation and enthalpy of evaporation [eqns. (4) and (5)] calculated from the present investigation, are in good agreement with those reported by Crooks and Feetham[4], viz, $\Delta H^{\circ}_{\mathrm{sub}}/\mathrm{kJ\ mole^{-1}} = 88.6 \pm 1.2$ and $\Delta H^{\circ}_{\mathrm{v}}/\mathrm{kJ\ mole^{-1}} = 65.3 \pm 0.8$ compared with our data of $\Delta H^{\circ}_{\mathrm{sub}}/\mathrm{kJ}$ $\mathrm{mole^{-1}} = 84.4 \pm 1.2$ and $\Delta H^{\circ}_{\mathrm{v}}/\mathrm{kJ\ mole^{-1}} = 63.9 \pm 2.5$.

But the agreement in the vapour pressures between the two sets of measurements is not equally good (Fig. 3). At all temperatures, the vapour pressures reported by Crooks and Feetham[4] based on their tensimetric technique are higher than the present data. The possibility of non-equilibrium conditions in the transpiration experiments has been eliminated by measuring the vapour transfer at flow rates of argon in the plateau region only. As the available experimental details of Crooks and Feetham[4] are insufficient, no explanation could be offered for this discrepancy.

As an additional internal consistency check of the present vapour pressure measurement, the enthalpy of fusion of phthalic anhydride was measured directly using the Perkin-Elmer differential scanning calorimeter (DSC-1B). From the measured heat effects, a value of 22.1 ± 3.5 kJ mole^{-1} was calculated as the enthalpy of fusion at 404.5 K compared with $\Delta H^{\circ}_{\mathrm{f}} = 20.5 \pm 3.5$ kJ mole^{-1} evaluated from the vapour pressure data. This good agreement renders additional support to the accuracy of the present vapour pressure data of phthalic anhydride.

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