196. *The Vapour Pressure of Phthalic Anhydride.*

By D. A. Crooks and (Miss) F. M. Feetham.

The vapour pressure of phthalic anhydride has been measured over the temperature range 30—143°. The latent heat of fusion calculated from the results has been checked by direct calorimetry. The results are compared with published data.

In the course of work requiring a knowledge of the vapour pressure of solid phthalic anhydride at temperatures below 60°, various anomalies were discovered in the available data for the vapour pressure of solid and liquid phthalic anhydride.

Unpublished German data are quoted (Landolt–Börnstein, " Tabellen," Erg. IIb, 1309) for the vapour pressure of solid phthalic anhydride in the temperature range 20—130°. The latent heat of sublimation at the m. p., calculated from these data by the Clapeyron–Clausius equation, is 96·5 cals./g. Two sets of measurements of the vapour pressure of liquid phthalic anhydride have been published. From measurements by Monroe (*J. Ind. Eng. Chem.*, 1919, **11**, 1116; 1920, **12**, 969), the calculated latent heat of vaporisation of liquid phthalic anhydride at the m. p. is 87·3 cals./g. From earlier measurements by Ramsay and Young (*Phil. Trans.*, 1886, *A*, **177**, 103) the latent heat of vaporisation is calculated to be 100·4 cals./g., which exceeds the calculated heat of sublimation. The difference between the heat of sublimation and the heat of vaporisation calculated from Monroe's data is only 9·2 cals./g., whereas Monroe calculates the heat of fusion to be 37·02 cals./g. from the cryoscopic constant.

Further discrepancies are found between the vapour pressures of the solid and liquid phthalic anhydride obtained by extrapolating the above data to the m. p. In view of these differences, the vapour pressure of phthalic anhydride was measured at temperatures from 30° to 143°, and the latent heat of fusion was checked by direct calorimetry.

Two methods were used to measure the vapour pressure. From 30° to 60°, the indirect method of Menzies (*J. Amer. Chem. Soc.*, 1920, **42**, 2218) was used; from 90° to 143° the vapour pressure was large enough to be measured directly on a mercury manometer.

The vapour pressures so determined can be related to the absolute temperature T by the following equations :

$$\text{For solid phthalic anhydride, } \log_{10}P = 12{\cdot}249 \pm 0{\cdot}005 - (4632 \pm 18)/T.$$

$$\text{For liquid phthalic anhydride, } \log_{10}P = 9{\cdot}209 \pm 0{\cdot}002 - (3410 \pm 44)/T.$$

Hence, from the Clapeyron–Clausius equation, the latent heat of sublimation is calculated to be $143{\cdot}0_5 \pm 0{\cdot}5_6$ cals./g., and the latent heat of vaporisation to be $105{\cdot}3_1 \pm 1{\cdot}3_6$ cals./g., giving by difference $37{\cdot}7_4 \pm 1{\cdot}4_7$ cals./g. for the latent heat of fusion. Direct calorimetric measurement gave 37·5 ± 0·8 cals./g. for the latter, in good agreement with Monroe's indirect determination from the cryoscopic constant and with the value calculated from the vapour-pressure measurements reported below.

The four sets of results are compared in the figure.

Experimental.

The sample of phthalic anhydride used had been purified by repeated sublimation; m. p. 130·2°.

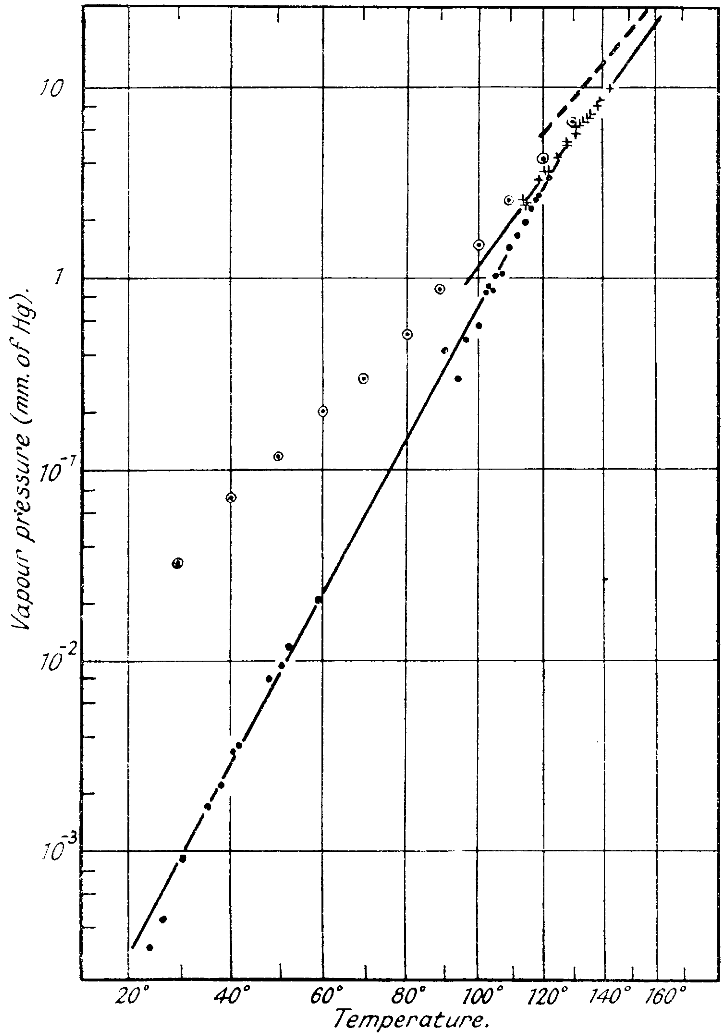
Vapour-pressure Determinations.—(a) For temperatures between 30° and 60°, Menzies's method was used, in which the vapour displaces permanent gas from a vessel of known volume at the temperature at which the vapour pressure is to be measured into another volume, including a McLeod gauge, at a constant temperature. The vapour is prevented from diffusing from one vessel to the other by a cold trap. Then if v is the volume of the vessel containing vapour at pressure P and gas at pressure $(P_1 - P)$ at temperature T, and if V is the volume of the second vessel containing only gas at pressure P_1 and temperature T_R, then

$$P = (P_1 - P_0)VT/vT_R + P_1 - P_0T/T_0$$

where P_0 is the pressure of gas in the apparatus at some temperature T_0, low enough for the vapour pressure to be negligible.

The results of measurements with phthalic anhydride are given in Table I. The ratio of volumes in the apparatus used was 0·480 and T_R was constant throughout at 290° K. In the final column of Table I, the values of $\log_{10}P$ calculated from the equation $\log_{10}P = 12{\cdot}249 - 4632/T$ are given (P in mm. of mercury) for comparison with the observed values.

(b) For temperatures between 90° and 145°, the vapour pressure was measured directly on a mercury manometer completely immersed in a thermostat so that the vapour pressure of mercury and the effects of surface tension were



—— *Present measurements.*
○ ○ *Data from Landolt and Börnstein's tables.*
– – – *Extrapolated from data by Monroe.*

TABLE I.

Vapour pressure of solid phthalic anhydride.

T, ° K.	10^3P_1.	$10^3(P_1 - P_0)\,\frac{TV}{T_Rv}$.	$10^3P_0\,\frac{T}{T_0}$.	10^3P.	$\log_{10} P$.	$\log_{10} P$ (calc.).
264·0	$54{\cdot}2_9$	—	—	—	—	—
303·3	$60{\cdot}2_8$	$3{\cdot}0_1$	$62{\cdot}3_6$	$0{\cdot}9_3$	$\bar{4}{\cdot}968$	$\bar{4}{\cdot}977$
313·6	$63{\cdot}2_0$	$4{\cdot}6_2$	$64{\cdot}4_8$	$3{\cdot}3_4$	$\bar{3}{\cdot}524$	$\bar{3}{\cdot}479$
248·1	$52{\cdot}3_2$	—	—	—	—	—
274·7	$56{\cdot}3_8$	$1{\cdot}8_6$	$57{\cdot}9_3$	$0{\cdot}3_1$	$\bar{4}{\cdot}491$	$\bar{5}{\cdot}387$
299·7	$59{\cdot}9_0$	$3{\cdot}7_6$	$63{\cdot}2_1$	$0{\cdot}4_5$	$\bar{4}{\cdot}643$	$\bar{4}{\cdot}794$
308·3	$61{\cdot}9_1$	$4{\cdot}8_6$	$65{\cdot}0_2$	$1{\cdot}7_5$	$\bar{3}{\cdot}243$	$\bar{3}{\cdot}225$
314·6	$63{\cdot}8_2$	$6{\cdot}1_0$	$66{\cdot}3_5$	$3{\cdot}5_7$	$\bar{3}{\cdot}553$	$\bar{3}{\cdot}526$
323·6	$68{\cdot}8_9$	$8{\cdot}8_8$	$68{\cdot}2_5$	$9{\cdot}5_2$	$\bar{3}{\cdot}979$	$\bar{3}{\cdot}936$
260·9	$72{\cdot}3_8$	—	—	—	—	—
304·6	$80{\cdot}6_4$	$4{\cdot}1_6$	$84{\cdot}5_0$	$0{\cdot}3_0$	$\bar{4}{\cdot}477$	$\bar{3}{\cdot}042$
311·0	$83{\cdot}0_4$	$5{\cdot}4_8$	$86{\cdot}2_8$	$2{\cdot}2_4$	$\bar{3}{\cdot}350$	$\bar{3}{\cdot}355$
320·9	$88{\cdot}4_9$	$8{\cdot}5_6$	$89{\cdot}0_2$	$8{\cdot}0_2$	$\bar{3}{\cdot}904$	$\bar{3}{\cdot}815$
325·6	$91{\cdot}6_9$	$10{\cdot}4_1$	$90{\cdot}3_3$	$11{\cdot}7_7$	$\bar{2}{\cdot}071$	$\bar{2}{\cdot}023$
332·1	$98{\cdot}4_2$	$14{\cdot}3_1$	$92{\cdot}1_3$	$20{\cdot}6_0$	$\bar{2}{\cdot}314$	$\bar{2}{\cdot}301$

identical in both limbs. The results of three series of measurements are given in Table II in the order in which they were made. On reducing the temperature below the m. p., super-cooling occurred down to about 114°.

TABLE II.

Vapour pressure of phthalic anhydride.

Temp.	*P.*	State.	Temp.	*P.*	State.	Temp.	*P.*	State.
135·1°	6·99	Liquid	103·6°	0·90	Solid	103·6°	0·87	Solid
128·4	5·16	Supercooled	111·9	1·72	,,	116·2	2·38	,,
121:1	3·62	,,	118·5	2·71	,,	91·1	0·42	,,
115·2	2·55	,,	130·9	6·13	Liquid	109·3	1·46	,,
104·0	0·82	Solid	135·5	7·27	,,	117·9	2·63	,,
95·0	0·30	,,	143·2	9·88	,,	132·4	6·37	Liquid
			138·4	8·03	,,	139·6	8·53	,,
			133·6	6·51	,,	130·7	5·69	,,
			128·1	5·01	Supercooled	124·9	4·30	Supercooled
			121·8	3·61	,,	119·2	3·29	,,
			114·7	2·44	,,	114·1	2·63	,,
			107·7	1·05	Solid	105·8	1·02	Solid
			100·6	0·56	,,	97·5	0·48	,,
						114·8	2·00	,,
						122·1	3·39	,,

Latent Heat of Fusion.—The latent heat of fusion was measured directly in order to check the value calculated from the vapour pressures. About 10 g. of phthalic anhydride, sealed into a glass tube, were warmed to a known temperature and then rapidly plunged into a calorimeter containing about 180 g. of water. The resulting rise in temperature was measured on a mercury thermometer and suitable cooling corrections were made. In this way, the latent heat of fusion and the specific heat of liquid and solid phthalic anhydride were determined. Three determinations of the latent heat of fusion gave 36·9, 38·4, and 37·2 cals./g. severally.

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