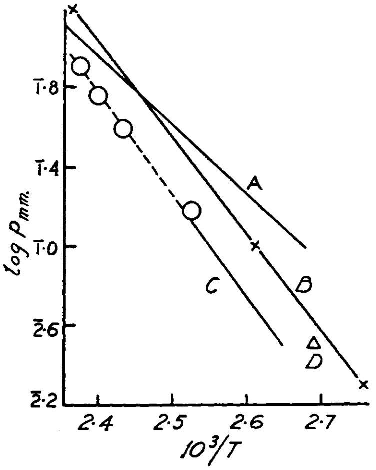
591. *Vapour Pressures and the Heats of Sublimation of Anthracene and of* 9 : 10-*Diphenylanthracene.*

By B. Stevens.

Vapour pressures and heats of sublimation of anthracene over the range 123—148°, and of 9 : 10-diphenylanthracene over the range 208—229° are determined by a fluorescence method. The values for anthracene are in good agreement with recent data, and when extrapolated to the melting point compare well with the value for the liquid at the same temperature obtained by previous workers.

During investigation of the fluorescence intensities, F, of anthracene and 9 : 10-diphenylanthracene as a function of concentration in the vapour phase, it was desirable to have reliable vapour-pressure data for these solids over the temperature ranges 120—217° (m. p.), and 200—248° (m. p.), respectively. No values seem to be available for the latter compound, whilst for anthracene the data of Niederschulte (Landolt–Börnstein, " Tabellen," Julius Springer, Berlin, 1912, 4th ed., p. 394), Mortimer and Murphy (*Ind. Eng. Chem.*, 1923, **15**, 1140), Mack (*J. Amer. Chem. Soc.*, 1925, **47**, 2473), Pringsheim (" Fluorescence and Phosphorescence," Interscience Publ., New York, 1949, p. 271), and Sears and Hopke (*J. Amer. Chem. Soc.*, 1949, **71**, 1732) are at variance or do not cover the desired temperature range (see Figure). The method described below is not as accurate as the latest determination by Sears and Hopke (*loc. cit.*), but it is capable of extending the pressure range used by these workers and is insensitive to traces of volatile impurity.



Vapour-pressure data of solid anthracene.
A, Niederschulte. *B*, Pringsheim. *C*, Sears and Hopke. *D*, Mack. ○ denote values obtained by the fluorescence method.

Experimental

Method.—A plot of log F of anthracene vapour at constant temperature against the reciprocal of the temperature of solid ($1/T$) in equilibrium with the vapour is linear up to a solid temperature of *ca.* 150° in the apparatus used, and affords a value for the heat of sublimation (L_s). If the amount of solid used is such that it is completely vaporised at a temperature (T_v) below 150°, then the plot is linear up to T_v, above which log F remains constant and a line of zero slope is obtained. The intercept of these lines gives $1/T_v$, at which temperature the vapour pressure may be calculated from the weight of solid taken and the temperature and volume of the cell. A similar plot for 9 : 10-diphenylanthracene is linear up to a solid temperature of *ca.* 230°, which, with 150° in the case of anthracene, imposes an upper limit on the temperature range over which the vapour pressures of these solids may be measured by this method with the degree of accuracy required.

Materials.—The anthracene was B.D.H. " Blue Fluorescence " quality, distilled twice from ethylene glycol and washed with hot water (Vogel, " Practical Organic Chemistry," Longmans Green, 1948, p. 826), and had m. p. 216·8—217·1°. 9 : 10-Diphenylanthracene was prepared according to Schlenk and Bergmann (*Annalen*, 1928, **463**, 148), and had m. p. 247—248°.

Procedure.—Pyrex tubes, *ca.* 7 cm. long and 1·4 cm. in internal diameter, containing small known quantities of anthracene in a lower limb *ca.* 5 cm. long and 0·6 cm. in internal diameter, were sealed in a vacuum and placed in a furnace at 200°. The lower limb rested in a hole in an aluminium block which could be electrically heated, thus controlling the temperature of solid anthracene; this temperature was recorded on a calibrated mercury thermometer resting in a second hole in the block. The vapour temperature was assumed to be that of the furnace which was controlled electrically to within 2°.

The small quantities of anthracene used were placed in the cells before evacuation in the form of benzene solutions of known strength and volume, and the solvent was evaporated by passage of a slow air current over the surface. This operation is responsible for the estimated experimental error of 5%.

The furnace was equipped with a window on to which the exciting radiation was directed by a half-silvered mirror, and from which the fluorescence intensities were measured. The light source, filters, and arrangement for measuring the fluorescence were otherwise as described by Metcalf and Bowen (*Proc. Roy. Soc.*, 1951, *A*, **206**, 437). The exciting radiation was cut off between readings to minimise any photo-reaction, and the observed fluorescence intensities were corrected for the light reflected from the surface of the cell.

Cell volumes were measured after the run by breaking off the tip and running in water from a standard burette.

Vapour pressures of 9 : 10-diphenylanthracene were measured in the same way, with a furnace temperature of 250°

Results.—The results for 9 : 10-diphenylanthracene obtained between 208° and 229° may be expressed as $\log P_{\text{mm.}} = 16{\cdot}058 - 8213/T$. The results for anthracene are plotted in the Figure. The mean percentage error in each case was 5%. The heats of sublimation are: anthracene 23·3 ± 0·5; 9 : 10-diphenylanthracene 37·5 ± 1·0 kcal./mole.

DISCUSSION

It is seen from the Figure that the vapour pressures obtained for anthracene lie on an extrapolation of Sears and Hopke's curve (*loc. cit.*), within the limits of experimental error. The value of L_s is also in excellent agreement with that of 23·4 kcal./mole obtained by these workers.

Mortimer and Murphy (*loc. cit.*), and Nelson and Senseman (*Ind. Eng. Chem.*, 1922, **14**, 58), measured the vapour pressures of liquid anthracene, and their results are in good agreement. The former workers give an expression for the vapour-pressure curve of solid anthracene derived from their extrapolated liquid vapour pressure at the melting point and a value of 13·1 kcal./mole for L_s obtained semi-empirically * (Mortimer, *J. Amer. Chem. Soc.*, 1922, **44**, 1429). Sears and Hopke (*loc. cit.*) use this expression to obtain a value of 0·353 mm. at 129° which they compare with their experimental value of 0·207 mm. at the same temperature. The divergence is not surprising in view of the fact that the L_s values of the two workers differ to a similar extent.

A more valid comparison can be made between an extrapolation to the melting point from Sears and Hopke's value for the solid vapour pressure and Mortimer and Murphy's value for the liquid at the same temperature. If the melting point of anthracene is taken as 217°, these values are 3·87 and 3·95 mm. respectively, which are in good agreement.

In view of the confirmation at higher pressures by the present work, and the agreement on extrapolation with data for liquid anthracene, it seems that the expression $\log p_{\text{mm.}} = 12{\cdot}002 - 5102/T$ obtained by Sears and Hopke from their data in the range 105—125° may be used in calculating the vapour pressures of anthracene up to its melting point, without serious error.

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* This value of L_s is calculated as the sum of the experimental heat of vaporisation of the liquid and the heat of fusion of the solid obtained empirically from $L_f = 12{\cdot}8 \times$ (m. p.).