

**131.** *The Determination of the Vapour Densities of Indigo and Other Organic Compounds by Means of a Spoon Gauge.*

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The application of the spoon gauge to the determination of the molecular weights of volatile organic compounds is described. The molecular weights of indigo, phthalimide, and of the polymeride of phthalonitrile are recorded.

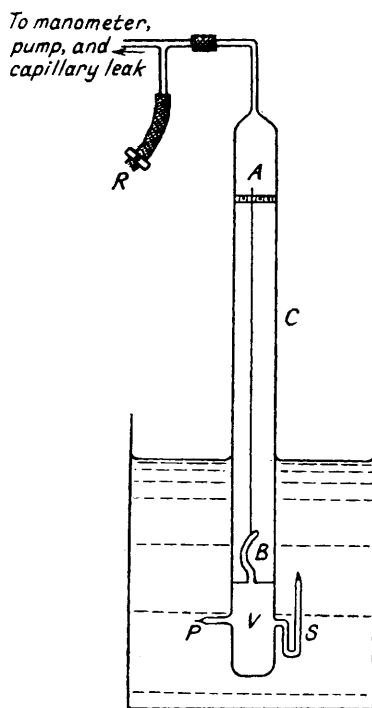
SOME years ago we attempted the direct measurement of the vapour densities of stable organic compounds at high temperatures in connexion with an investigation of the molecular weights of various phthalocyanines. For this purpose an apparatus embodying a spoon gauge was utilised, such as has been used for certain inorganic substances (see, *e.g.*,

Jackson, J., 1910, 99, 1066; Smits, J., 1924, 125, 2554) but not previously, as far as we are aware, for organic compounds. In this apparatus a measurement is made of the pressure exerted by a known weight of the substance under investigation when completely volatilised and occupying a known volume. The advantages of the method are (1) that it requires only small amounts of material (10—50 mg.), and (2) that it can be used at temperatures (200—400°) which may be inconvenient for the usual vapour-density methods. Hence it is particularly useful for more complex molecules. Its application is, of course, limited to thermally stable substances.

The molecular weight of indigo at 430° was found to be  $257 \pm 9$ , in agreement with the monomeric formula (*M*, 262). The vapour of phthalimide was monomeric over the range 295—340°. The polymeride of phthalonitrile of m. p. 296° (Linstead and Lowe, J, 1934, 1025) was found to be trimeric, from measurements at 420—430°. This suggests strongly that it is tricyanocyaphenine.

This very stable substance may be crystallised from hot concentrated nitric acid without decomposition, but on long standing with this reagent it undergoes fission to phthalimide.

An attempt to determine the vapour density of copper phthalocyanine failed, as the spring began to bend under its own weight at about 500°. After 30 minutes at this temperature the copper phthalocyanine was recovered unchanged. No pressure was developed, showing that no decomposition or sublimation occurs at this temperature (compare Dent and Linstead, J., 1934, 1027).



#### EXPERIMENTAL.

The apparatus is shown in the figure. A convenient weight of the substance was weighed into the side arm *S*, which was then sealed. The apparatus, made of Pyrex glass, was then evacuated, the side tube *P* being open and connected to *R* by pressure tubing. During this process as much as possible of the lower chamber *V* was heated, care being taken to avoid volatilising the substance in *S*. The tubing between *P* and *R* was then closed with a pinchcock, and *P* was sealed off. The apparatus was then immersed in an insulated and mechanically-stirred bath of fused nitrates to the level indicated, and the pointer *A* on the glass spring *B* was kept at zero by altering the pressure in the upper chamber *C*; this was connected to a manometer, to a large reservoir, and to a three-way tap, joined to a pump and a capillary for the admission of air. When the substance had completely volatilised and the vapour obeyed Charles's

law, the pressure in *C* and the temperature were measured, the latter by means of a direct-reading platinum-resistance thermometer. The volume of *V* was measured after the experiment by filling it with water and weighing. The main source of error lies in the measurement of pressure when the substance is so unstable that fairly low pressures have to be used. The springs used in our experiments responded to pressure differences of about 1 mm.

*Results.—Phthalimide.* Weight: 62.0 mg. Volume: 39.4 c.c.

Temp., κ. ....	478°	533°	543°	568°	583°	603°	613°	603°	593°
Pressure, mm. ...	61	199	259	373	384	399	405	399	390
$T/p$ .....	7.8	2.7	2.1	1.52	1.515	1.51	1.51	1.51	1.515
<i>M</i> .....	—	—	—	148	147.5	—	147	—	—

Mean *M* = 147.5 between 295 and 340° (Calc. for  $C_8H_5O_2N$ : *M*, 147).

*Indigo.* Weight: 14.3 mg. Volume: 51.5 c.c.

Temp., κ. ....	648°	668°	688°	703°	688°	658°
Pressure, mm. ....	13	26	44	47	46	36
$T/p$ .....	49	25.7	15.6	15.0	15.0	18.3
<i>M</i> .....	—	—	—	257	—	—

The estimated error in this measurement is  $\pm 3.5\%$ , mainly from a possible error of 2% in the reading of the pressure. Hence  $M = 257 \pm 9$  (Calc. for  $C_{11}H_{10}O_2N_2$ :  $M$ , 262).

*Phthalonitrile polymeride.* Trial experiments showed that the polymeride was undecomposed during 5—10 minutes at 400—450°, but began to char on longer heating. Preliminary readings of pressure were therefore made after 1-minute immersions in the bath, preheated to the required temperature, an excess of the solid being used. The vapour pressures then exerted were 36—37 mm. at 420°, 42 mm. at 425°, and 49 mm. at 430°. For the final readings a quantity of the solid was taken which exerted less than these pressures when fully volatilised.

Weight: 11.7 mg. Volume: 47.7 c.c. At 691° K. the pressure was 24 mm.; and was unchanged at 703° K. The estimated error is 6.25%, mainly from a possible error of 4% in the reading of pressure. Mean  $M = 396 \pm 25$  [Calc. for  $(C_8H_4N_2)_3$ :  $M$ , 384].

At 430°, but not noticeably at 420°, the trimeride was observed in two different apparatus to pass through the thin glass spring *B* into the cool part of the upper chamber *C*. The sublimate was the pure polymeride, m. p. 296°. The most likely explanation seems to be the development of a pin-hole or crack at 430°. The apparatus could, however, be kept at this temperature with a constant deflexion of the pointer when there was a 20 mm. difference in pressure between the upper and lower chambers. This shows that, whatever the cause of the migration of material, it cannot affect the measurements of pressure.

The trimeride (5 g.) was dissolved in concentrated nitric acid (70 c.c.) at 100°, and kept for 2 days at room temperature. It was then diluted with 200 c.c. of water and kept for a further 3 days. An excellent yield of crystalline phthalimide (m. p. 229°, 4.25 g.) was obtained.

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