216. *Phthalocyanines. Part V. The Molecular Weight of Magnesium Phthalocyanine.*

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DETERMINATION of the molecular weights of phthalocyanines enables an independent estimate to be made of the number of C_8 units in the molecule. The magnesium compound (dihydrate) was selected for examination, as its solubility is greater than that of other phthalocyanines. It did not dissolve sufficiently in molten naphthalene, benzophenone, thymol, or camphor to furnish accurate cryoscopic determinations; even when the delicate thermometer described below was used, the experimental error was comparable with the observed depressions. 4-Chloroquinoline dissolved rather more of the compound and had a convenient melting point, but was unsuitable on account of its hygroscopic nature and great tendency to supercool.

The ebullioscopic method has the advantage that stronger solutions can be made, but even so, 100 parts of boiling naphthalene dissolve only about 0·4 part of magnesium phthalocyanine and the maximum possible elevation of the boiling point is about 0·04°, and quinoline proved to be an unsuitable solvent. A very delicate platinum resistance thermometer was therefore constructed for use in conjunction with the ordinary apparatus of Beckmann (*Z. physikal. Chem.*, 1908, **63**, 187). The molecular weights obtained at different concentrations were 550, 565, 538; mean, 551 (calc. for $C_{32}H_{20}O_2N_8Mg$, 572). The molecule therefore contains one atom of magnesium and four C_8 units.

The apparatus could not be used for determing the molecular weight of phthalocyanine itself for the remarkable reason that the metal of the heating coil attacked phthalocyanine with the formation of metallic derivatives. A platinum heater could not be constructed.

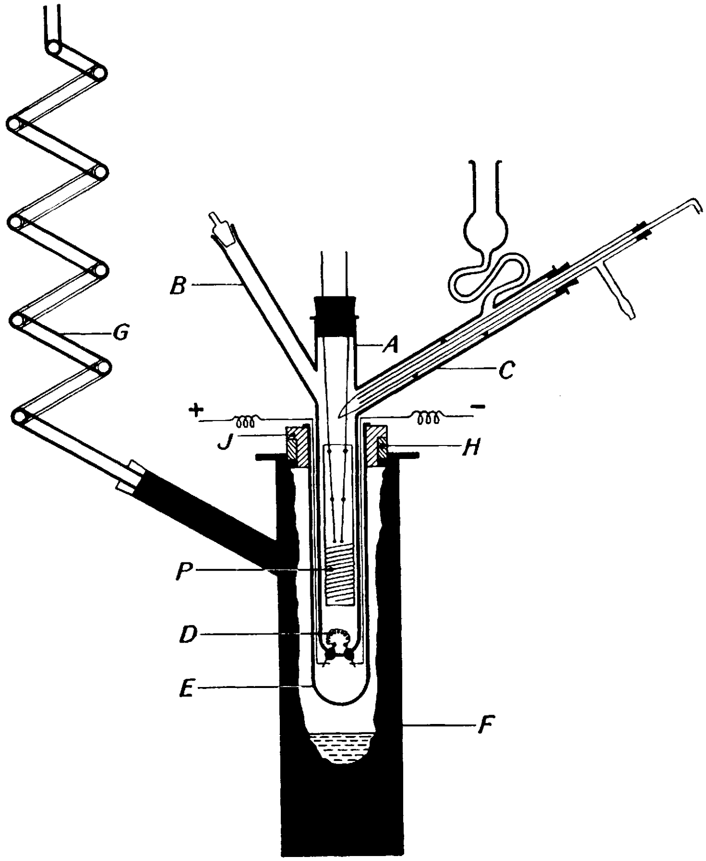
EXPERIMENTAL.

Apparatus.—The platinum resistance thermometer, P, was made from 48 cm. of platinum wire, 1/500″ in diameter, wound on a former of thin mica. The leads were of silver wire, the end effect of these being compensated by the incorporation of one turn of the same wire on a similar former. The measurement of resistance was carried out by means of a standard Callendar–Griffiths bridge. Owing to the exceptionally high " fundamental interval " of the thermometer (7·629 ohms) it was necessary to insert an additional standard resistance in the compensator arm of the bridge for measurements at the b. p. of naphthalene in order to bring the balance point of the bridge on to the bridge wire. The results in the table are therefore differential.

The thermometer was mounted by means of a moulded asbestos stopper in the inner tube A, of Pyrex glass, which was fitted with two side arms, B for the introduction of the solute and C for the condenser and drying tube. Most of the heat necessary to keep the solvent in A boiling was provided by an outer jacket containing the vapour of boiling naphthalene, and the additional heat by a resistance, D, totally immersed in the solvent. This was composed of 20 cm. of nichrome wire (No. 30 S.W.G.) wound in the form of a spiral and " spot-welded " to two small pieces of nickel foil. These were welded to two tungsten electrodes, which were sealed through the walls of A. Two silver wires, welded to the exterior ends of the electrodes, were led out of the apparatus through the annular space between A and E. The heating coil, which had a resistance of 2·4 ohms, was in series with a source of current (20 volts), a rheostat, and an ammeter. A current of 1—2 amps. was used. The tube A was contained in a glass jacket E, held in a copper can, F (10″ × 3″), with a " silver-soldered " side arm leading to a condenser G. The top of the can was flanged and a brass ring H, 2″ in diameter, was let into the brass flange plate. Mounted on this was a turned Bakelite stopper, J, which carried the jacket E and closed the vessel. The can was filled to about $\frac{1}{4}$ capacity with naphthalene, which was boiled by means of a burner.

The thermometer was calibrated in the usual manner in ice and in water boiling under 775·6 mm. (this pressure was read on a brass scale at 17°, whence the corrected b. p. is 100·52°). Resistance at 0° = 1002·36 cm. of bridge wire; at 100·52° = 1765·26 cm. Hence 1 mm. of bridge wire = 0·0132°. The sensitivity was 0·2 mm. or about 0·0026°.

Solvent.—The use of quinoline was abandoned, as the boiling point of carefully purified material (regenerated from well-crystallised dichromate and stored in an evacuated desiccator over phosphoric oxide) was found to fluctuate. Recrystallised and dried naphthalene showed no such variation. The temperature at which this material boiled was independent of the current supplied through the coil D.



Boiling-point apparatus for use with platinum-resistance thermometer

Procedure.—100·0 G. of pure naphthalene were introduced into A, the naphthalene in the outer can was boiled, and a current of about 1 amp. was passed through the heating coil D. The boiling point was then determined by taking bridge-readings at gradually increasing values of current until a steady and reproducible maximum was obtained (see Table). Some difficulty was experienced at first owing to the extreme sensitivity of the thermometer, for when the liquid was boiled vigorously by means of a fairly large current in the heating coil, superheated bubbles passing over the thermometer caused continuous oscillation of the galvanometer spot. This was corrected as follows. The commutator in the bridge circuit was arranged so that a deflection of the galvanometer spot to the right meant that the contact had to be moved to the right. Oscillations due to superheating were then entirely to the right and the null-point was taken when there was the slightest deflection to the left. This was readily determined during gentle ebullition, but when the stream of bubbles was rapid, frequent depressions of the bridge contact were necessary and 6—7 minutes were required to obtain a trustworthy reading.

A weighed quantity of magnesium phthalocyanine was then added, the mixture boiled for some time to ensure solution, and readings were taken in exactly the same manner and as quickly as possible to avoid a variation in the barometric pressure. The sets of readings *b* and *c* in the Table followed immediately those of *a*; and *e* followed *d*.

TABLE.

(*a*) Pure naphthalene.

Current in heating coil (amps.)	1·3	1·4	1·5	1·6	1·65	1·7	1·75	1·80
Bridge reading (cm.)	1276·72	1278·55	1278·92	1280·41	1280·42	1280·43	1280·42	1280·42

(*b*) 0·2489 G. of magnesium phthalocyanine in 100 g. of naphthalene.

Current	1·5	1·6	1·65	1·7	1·8	1·85
Bridge reading	1280·18	1280·24	1280·32	1280·61	1280·62	1280·62

(*c*) 0·3513 G. of magnesium phthalocyanine in 100 g. of naphthalene.

Current	1·5	1·6	1·7	1·75
Bridge reading	1280·64	1280·74	1280·69	1280·70

(*d*) Pure naphthalene.

Current	0·89	1·0	1·1	1·2	1·25	1·3
Bridge reading	1276·02	1283·02	1285·92	1286·42	1286·52	1286·58
Current	1·35	1·4	1·45	1·5	1·6	1·7
Bridge reading	1286·80	1286·85	1286·85	1286·85	1286·85	1286·85

(*e*) 0·3913 G. of magnesium phthalocyanine in 100 g. of naphthalene.

Current	1·0	1·1	1·2	1·25	1·3	1·35
Bridge reading	1285·92	1286·32	1286·72	1286·87	1287·11	1287·17
Current	1·4	1·45	1·5	1·55	1·6	
Bridge reading	1287·17	1287·17	1287·17	1287·17	1287·17	

These figures give the following values for the molecular weight, the molecular constant for naphthalene being taken as 58·0 (*Z. physikal. Chem.*, 1914, **89**, 111):

Expt.	Concn., g./100 g.	Δt (mm. wire).	Mol. wt.
b	0·2498	2·0	550
c	0·3513	2·8	565
e	0·3913	3·2	538

A series of determinations carried out at a concentration of about 0·6% gave unsatisfactory results and traces of undissolved solid could be seen in the boiling naphthalene.

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