A METHOD OF DETERMINING OF MOLECULAR WEIGHT OF ORGANIC SUBSTANCES IN SMALL QUANTITIES BY MEANS OF FREEZING POINT DEPRESSION.

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The molecular weight of minute quantities of valuable organic material can be determined by one of the two methods described recently by K. Rast[1] and F. Pregl.[2] The Pregl's method is an improved modification of the ordinary ebullioscopic method using a Beckmann's thermometer, and the Rast's is amazingly simple, using camphor as solvent and an ordinary apparatus for the determination of melting point as the means of measurement. Though both are quite excellent, the utility of the former is diminished by the difficulty in the performance of experiments and that of the latter is limited not only by the small choice of available solvents, but also often by the instability of the substance to be investigated at such a high temperature as the melting point of camphor.

It seemed to us that in spite of some investigators' examinations, the thermo-junction[3] and the Beckmann's thermometer[4] had no practical use for the micro-cryoscopic purpose, and that the electric resistance thermometer which was constructed with silver wire[5] by Mr. T. Ikebe in the Institute of Physical and Chemical Rasearch showed such an excellence in the determination of the temperature of small quantities of liquid that we were induced to attempt molecular weight determinations of organic substances in small quantities by the depression of freezing point.

(1) *Ber.*, **55** (1922), 1051 and 3727.
(2) "Die Quantitative Org. Mikroanalyse," 1923.
(3) Y. Yamaguchi, *J. Tokyo Chem. Soc.*, **37** (1916), 727.
(4) Drucker, *Biol. Zentralblatt.*, **33** (1913), 99.
(5) Silver wire was prefered to platinum one because the latter is expensive.

By means of the apparatus, which is shown in the following figures, a molecular weight determination was carried out by introduction of 4 to 8 mg. of substance into about 1 c.c. of solvent. It gave quite satisfactory results without disadvantages already mentioned.

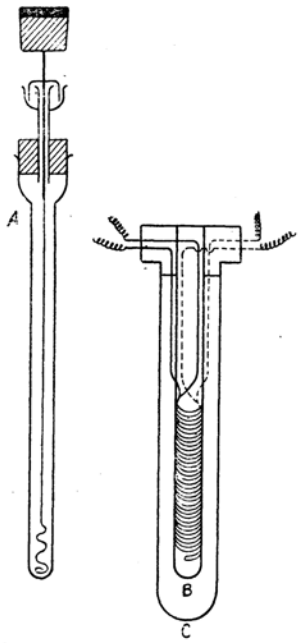

Fig. 1. ($\frac{1}{2}$ of actual size.)

It consists of an inner tube A which serves to freeze the solvent and is provided with a stirrer of platinum wire connected to a small glass rod. A is nicely fitted to the thin walled glass tube B which is coiled arround with silver wire of about 2 meters long and 0.11 m. in diameter, and is fixed in the air-jacketing tube C with a frame of ebonite. C is held in a Dewar's vessel containing the freezing mixture whose temperature depends upon the solvent.

For the measurement of resistance, the Müller type bridge of Leed and Northrup Co. was used, and as the resistance of the thermometer B changes with temperature practically in accordance with the formula $R_t = R_0(1+at)$, R_0 and R_t being resistances in ohms of the silver wire at 0° and $t°$ respectively, the change of its resistance per 1° was at first determined by two observations at 0°, the ice-water temperature, and at 8°.813, the room temperature, as follows:

$$R_0 = 1.2471, \qquad R_{8.813} = 1.2956$$

$$\frac{R_{8.813} - R_0}{8.813} = \frac{1.2956 - 1.2471}{8.813} = 0.0055$$

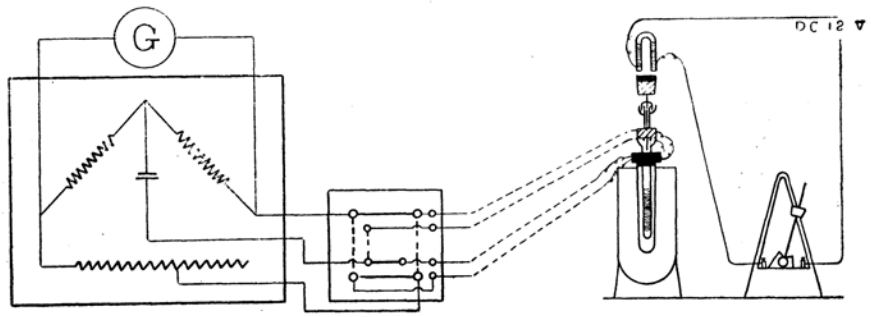

Fig. 2.

Now as much solvent was weighed in the tube A as its volume was enough to cover the whole length of the silver wire coil of the tube B. While agitating the solution with the stirrer of platinum wire which moves up and

down by the action of a small electro-magnet and a iron piece, the resistance was observed.

The thermometer changed its resistance gradually and passed a maximum and a minimum point just like the reading in the Beckmann's thermometer. The maximum point was naturally taken as the resistance at the freezing point of the solvent.

A was then removed, the solvent was again melted and the solid substance previously weighed in a small glass tube (about 20 mm. long and 1.5 mm. in diameter) opened in both ends was introduced. When the dissolution was complete, the readings of the new value of the resistance were taken as before.

Thus the depression of freezing point Δt was easily calculated as follows:

$$\frac{R_t - R_n}{0.0055} = \Delta t,$$

where R_t = resistance at the freezing point of the solvent, R_n = resistance at the freezing point of the solution, and the molecular weight of the substance was found from the usual formula. The results obtained with benzene, nitrobenzene and ethylene bromide as solvents are as follows.

(A). Benzene as solvent.

Molecular depression = 50.0 M = Molecular weight.

1. Acetanilide, 0.00404 gr. in 0.734 gr. of benzene.
   $R_t = 1.26961$. $R_n = 1.26848$. $\Delta t = 0.°206$
   Calc. $M = 135$. Found $M = 134$.
2. Naphthalene, 0.00705 gr. in 0.761 gr. of benzene.
   $R_t = 1.26937$. $R_n = 1.26742$. $\Delta t = 0.°360$.
   Calc. $M = 128$. Found $M = 127$;
3. Picric acid, 0.00820 gr. in 0.691 gr. of benzene.
   $R_t = 1.26892$. $R_n = 1.26747$. $\Delta t = 0°.264$
   Calc. $M = 229$. Found $M = 225$.
4. Phthalic anhydride, 0.00536 gr. in 0.666 gr. of benzene.
   $R_t = 1.26980$. $R_n = 1.26831$. $\Delta t = 0°.271$.
   Calc. $M = 148$. Found $M = 148$.

(B) Nitrobenzene as solvent.

Molecular depression = 70.0.

1. Acetanilide, 0.464 gr. in 0.884 gr. of nitrobenzene.
   $R_t = 1.27126$. $R_n = 1.126973$. $\Delta t = 0°.278$.
   Calc. $M = 135$. Found $M = 132$.
2. Naphthalene, 0.00720 gr. in 0.878 gr. of nitrobeneze.
   $R_t = 1.27140$. $R_n = 1.26890$. $\Delta t = 0°.454$.
   Calc. $M = 128$. Found $M = 126$.

(C). Ethylene bromide as solvent.

Molecular depression = 118.0.

As the second apparatus which was used was a little larger than the first one and, moreover, the specific gravity of ethylene bromide was comparatively large (2 18), a somewhat large quantities of the solvent had to be taken. The change of resistance per 1° of the thermometer was 0.01507.

1. Acetanilide, 0.00958 gr. in 2.972 gr. of solvent.
   $R_t = 4.03145$. $R_n = 4.02736$. $\Delta t = 0°.272$
   Calc. $M = 135$. Found $M = 140$.
2. Naphthlene, 0.01795 gr. in 2.850 gr. of solvent.
   $R_t = 4.03159$. $R_n = 4.02273$. $\Delta t = 0°.595$
   Calc. $M = 128$. Found $M = 126$.
3. Diphenyl, 0.01180 gr. in 3.031 gr. of solvent.
   $R_t = 4.03091$. $R_n = 4.02650$. $\Delta t = 0°.293$
   Calc. $M = 154$. Found $M = 158$.

We wish to express our deepest obligation to Mr. T. Ikebe for his kindness in constructing the apparatus for us and also our best thanks to Dr. N. Watanabe and Mr. S. Sugimoto, in the Department of Commerce and Industry, for his kindness in placing the resistance bridge to our disposal.

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