[CONTRIBUTION FROM THE PHYSICAL CHEMISTRY LABORATORY OF THE UNIVERSITY OF WISCONSIN]

MOLECULAR WEIGHTS OF SATURATED VAPORS BY THE EFFUSION METHOD

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The application of the method of effusion in measuring the molecular weights of gases has been carefully studied by a number of investigators[1] since Graham first announced it. The success of the procedure depends upon accurate time and pressure measurements and upon the selection of an orifice of dimensions which reduce viscosity effects to a minimum. Under such circumstances molecular weights having an accuracy of 1% for gases of rather different properties are attainable.

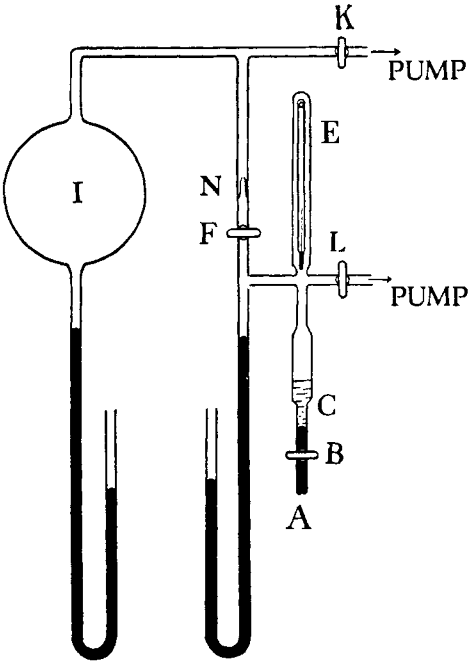

Fig. 1.

It seemed desirable to devise a rapid method of estimating the molecular weight of organic vapors if certain obvious difficulties could be overcome. The final all-glass apparatus which satisfactorily accomplishes this purpose was constructed as shown in Fig. 1.

The operations consist simply in evacuating the whole apparatus with a Hyvac pump, then admitting liquid into the vessel at B. The stopcock is then opened and the time taken with a stopwatch for the pressure in the receiving chamber to rise to some predetermined pressure. The same operations are repeated with air, care being taken to adjust stopcock B so that the pressure of air remains constantly equal to the vapor pressure of the liquid whose molecular weight is to be determined. The following data were obtained using purified *iso*propyl alcohol: time for air, 140 seconds; time for *iso*propyl alcohol, 202 seconds. Then the molecular weight of *iso*propyl alcohol = $(202/140)^2$ 28.8 = 60. The

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[1] Bunsen, "Gasometry," p. 198; J. N. Edwards, "Technologic Papers of the Bureau of Standards," No. 94.

whole determination can be conducted in less than a half-hour and involves no weighings. The apparatus is simple, involves no washing and can be permanently attached to the wall. The method can be applied to gases and to all vapors with vapor pressures greater than that of water without using a cathetometer. This range of course can be extended to lower vapor pressures by making more accurate pressure measurements or by raising the temperature.

If the pressure in the receiving chamber is permitted each time to rise to one-half the vapor pressure (pressure on side containing liquid) exactly the same calculation as was used to compare it with air can be used to intercompare liquids of different vapor pressures without the calibration run. In Table I this method has been styled Method 2 to distinguish it from the procedure in which the time for each vapor is compared directly with the time for air called Method 1. Thus it took 227 seconds for benzene to build up a pressure equal to half its vapor pressure while it took 317 seconds for carbon tetrachloride. Assuming a molecular weight of benzene of 78 we have for carbon tetrachloride $(317/227)^2\ 78 = 152$. The advantage of Method No. 2 is the elimination of the comparison run with air effectually cutting the time of a determination in two. The disadvantage is that the vapor pressure must be accurately measured and exactly one-half the vapor pressure (or some other convenient fraction) be taken as the pressure rise in the receiving chamber. If a large number of determinations are to be made, undoubtedly the second method, using a cathetometer or mounted telescope, is most satisfactory. Under such circumstances successive determinations can be made in about fifteen minutes.

The following times obtained for air to reach a pressure in the receiving chamber of one-half the constant pressure maintained on the sending side show this time to be independent of the sending pressure.

Pressure in cm..................	73.35	57.35	44.00	24.80
Time of half press. incr., sec.......	163.0	164.3	163.3	165.5

The independence of time of this "half pressure increase" follows from kinetic theory. Equation (318) of Jeans, "The Dynamical Theory of Gases," may be slightly modified to give

$$dn = \frac{(p_0 - p)}{\sqrt{2\pi MRT}} A dt = \frac{V_r dp}{RT}$$

where dn is the number of moles effusing through an orifice of A square centimeters per dt seconds; $p_0 - p$ is the vapor pressure minus the pressure in the receiving chamber, that is, the effective pressure; M is the molecular weight; R is the gas constant in ergs per degree; T is the absolute temperature and V_r is the volume of the receiving chamber.

Whence

$$\mathrm{d}t = \frac{V_r}{A}\sqrt{\frac{2\pi M}{RT}}\,\frac{\mathrm{d}p}{p_0 - p}\cdot$$

and

$$t = 2.303\,\frac{V_r}{A}\sqrt{\frac{2\pi M}{RT}}\,\log\frac{p_0}{p_0 - p} = \frac{V_r}{A}\,6.37 \times 10^{-4}\sqrt{\frac{M}{T}}\,\log\frac{p_0}{p_0 - p}$$

For $p = p_0/2$, we have

$$M = T\,t_0^2\left(\frac{A}{V_r}\right)^2 1572^2\left(\frac{1}{0.310}\right)^2$$

From this it is seen that the time for the pressure in the receiving chamber to reach one-half the sending pressure (or any other fraction) is independent of the sending pressure. The formulas for the preceding calculations of molecular weights follow immediately from the deduction above, since when the temperature T is constant, $M = Kt_0^2$. The cross sectional area of the orifice was calculated by taking $V_r = 2656$ cc.; $T = 296°$; $t_0 = 164$; whence A was found to equal 0.00097 sq. cm. or 0.097 sq. mm.

Orifices of platinum were found unsatisfactory, presumably because of flaps which changed the sizes of the openings. Glass orifices considerably smaller in cross section introduced errors due to viscosity. One orifice prepared by sending a large spark through the glass gave satisfactory results for the molecular diameter of hydrogen assuming viscous flow but entirely unsatisfactory results for its molecular weight using the relationship above. Apparently the leak was through a large number of small cracks.

The orifice shown in Fig. 1 at N was made by blowing a thin round bulb on 6 mm. glass tubing. A hot glass rod was then used to pull a small capillary out from the bulb which was then broken off flush with the bulb surface, giving an opening of 0.1 sq. mm., approximately. With an orifice of this size the receiving chamber should have a volume of about two and one-half liters to give a convenient time of efflux.

Certain details of operation seem necessary for the success of a determination. After evacuating the system, F and K are closed and a weighing bottle containing mercury and the liquid is placed at A and mercury drawn up until it reaches the stopcock B. The apparatus is re-evacuated, L being then closed. The weighing bottle is then lowered slightly and B opened until sufficient liquid is drawn into the apparatus. The weighing bottle is raised, mercury again being drawn up until any liquid in the neighborhood of the stopcock B has been displaced. In this way there was no difficulty in keeping a stopcock, lubricated with ordinary stopcock grease, from leaking with any organic liquids. Using either a pinch clamp on rubber tubing or a stopcock lubricated with phosphorus pentoxide proved unsatisfactory.

After introducing the liquid the stopcock F was turned at the same time a stop watch was started. The vapor pressure was kept at the desired pressure by occasionally warming the liquid C with the hand. When air is being run it can be kept very accurately at the desired pressure by occasionally partially closing A with the finger.

Some typical results are given below.

In addition to these experiments Mr. P. B. Tuttle made determinations on a number of substances not listed here, obtaining satisfactory results. The vapor from the constant boiling mixture of hydrochloric acid at 73.8

TABLE I

Vapor	Mol. wt.	Mol. wt., Method 1	Mol. wt., Method 2
CH_3OH	32	32.8	32[a]
C_2H_5OH	46	46.2, 46.9	45.4
C_6H_6	78	77.6	77.3
CCl_4	154	....	152
H_2O	18	16.8, 18.4	18.54
$(CH_3)_2CHOH$	60	56.2, 60	...
$CHCl_3$	119	116.5	...

[a] Assumed in determining constant.

cm. pressure gave a molecular weight of 22, showing the absence of association.

It has been customary to explain the high specific heat of saturated (wet) steam by assuming it to be due to the presence of large molecular aggregates.[2] Such aggregates might be due to a mechanical suspension of water or to associated molecules. The values obtained for saturated water vapor at room temperature give no indication of association. This seems consistent with results obtained by others using different methods.

The investigation of any supposedly associated vapors should yield interesting results. The simultaneous determination of successive vapor pressures and molecular weights of mixtures of organic liquids as the mixed vapors pass through the orifice N should be of value in analysis.

Summary

A method for the rapid determination of molecular weights of saturated vapors has been outlined. No appreciable association of saturated water vapor, of the vapor from constant boiling hydrochloric acid nor of organic vapors was observed.

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[2] Lewis, "A System of Physical Chemistry," Longmans, Green and Co., New York, **1916**, Vol. III, p. 8; Jeans, "The Dynamical Theory of Gases," Cambridge University Press, Cambridge, England, **1916**, p. 265.