DETERMINATION OF MOLECULAR WEIGHTS IN THE VAPOR STATE FROM VAPOR PRESSURE AND EVAPORATION DATA

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ABSTRACT

If one determines at the same temperature the vapor pressure of a substance and the amount of it required to saturate, by aspiration, a measured volume of an indifferent gas, the molecular weight of the substance in the gaseous state is calculable. By employing a reference substance of known molecular weight the measurement of the volume of aspirated gas is unnecessary and the quantities measured have small temperature coefficients. A precision discussion of the method is given. It should be capable of a high degree of accuracy in many cases and is applicable at much lower temperatures than are the methods commonly employed.

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I. NOMENCLATURE

M, Molecular weight.
p, Vapor pressure.
B, Barometric pressure.
ΔP, Manometric pressure difference.
m, Mass in grams.
v, Volume.
R, Gas constant.
T, Temperature, ° K.
t, Temperature, ° C.
$\delta_x M$, Variation in M caused by a variation δx in any variable x.

II. PRINCIPLE OF THE METHOD

None of the methods commonly employed for determining the molecular weights of substances in the vapor state are applicable at temperatures at which the vapor pressure of the substance is small.

A method which is based upon determining, at the same temperature, the vapor pressure of the substance and the amount of it required to saturate, by aspiration, a known volume of an indifferent gas is applicable at low vapor pressures and offers possibilities of a degree of precision equal to or better than that attainable with the more commonly used methods. The method should be applicable even at temperatures at which the vapor pressure is not more than 0.1 mm Hg, if the temperature is within the working range of one of the types of sensitive low-pressure manometers.[1] The purpose of the present paper is to discuss the precision aspects of the method.

III. HISTORY OF THE METHOD

According to Wrewsky,[2] the method was first proposed and used by Horstmann.[3] More recently Wrewsky [2] has employed the method for investigating the dissociation of formic and acetic acids in the vapor state.

In the form in which the method was employed by these investigators, the molecular weight, M, is calculated from the perfect gas law

$$M=\frac{mRT}{pv}$$

where p is the vapor pressure and m the number of grams of the substance present in v liters of the saturated gas.

When used in this form, however, the method has two objectionable features.

1. A given percentage error in v produces the same percentage error in M, consequently in precision work v has to be very accurately determined. This may be done either by measuring the volume of the indifferent gas [4] or by absorbing and weighing the indifferent gas after condensing out of it the substance under investigation;[5] for example, CO_2 by absorption, H_2 by combustion and absorption of the H_2O, O_2 (or the O_2 content of air) by absorption with hot copper, etc. The accurate determination of v is therefore possible.

2. The second objectionable feature of the method arises from the large temperature coefficient of p, which necessitates very close regulation of temperature during both the vapor pressure determination and the frequently prolonged saturation determination.

The required precision in temperature control can be computed as follows:

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[1] For example, the Rayleigh tilting manometer sensitive to 0.0005 mm Hg up to $p=5$ mm. Rayleigh, Phil. Trans., **196**, p. 205: 1901; Scheel and Heuse, Z. Instrumentenk., **29**, p. 344; 1909.

[2] Wrewsky, Z. physik. Chem., **133**, p. 363; 1928.

[3] Horstmann, Ber. Deutsch. Chem. Ges, **3**, p. 78; 1870; **11**, p. 1287; 1878.

[4] Compare Wrewsky, Z. physik. Chem., **133**, pp. 360, 366, Table 4; 1928.

[5] See footnote 3.

It is obvious from the above equation that a fractional error, $\frac{\delta p}{p}$, in p will produce an equal fractional error, $\frac{\delta M}{M}$, in M. From the Clausius-Clapeyron equation

$$\frac{\delta_T M}{M}=\frac{\delta_T p}{p}=\frac{L}{RT^2}\delta T$$

where L is the latent heat of vaporization per mole.

It is obvious, therefore, that the two bath temperatures must be identical and constant within

$$\delta T=\frac{RT^2}{L}\frac{\delta_T M}{M} \text{ degrees}$$

if the fractional error in M arising from the temperature difference or fluctuation is not to exceed $\frac{\delta_T M}{M}$.

Illustrative example: Suppose the substance whose molecular weight is to be determined belongs to the class of liquids for which Trouton's ratio has the value

$$\frac{L}{T_B}=22$$

at the normal boiling point, T_B °K.

Combining this with the above equation gives

$$\delta T=\frac{T}{11T_B}\times T\times\frac{\delta_T M}{M}.$$

If now we assume that the error in M arising from the uncertainty $\delta T°$ in T is not to exceed $\frac{\delta_T M}{M}=0.001=0.1$ per cent and, if further, $\frac{T}{T_B}$ has the value $\frac{3}{5}$ and T the value 300° K., we find the limiting condition

$$\delta T \not> 0.016° \text{ C.}$$

Temperature control within this limit is difficult but possible. The necessity for such close regulation of temperature can, however, be avoided by employing a reference substance of known molecular weight, thus making the method practically independent of temperature fluctuations and at the same time eliminating the measurement of the volume of gas aspirated in the saturation determination.

IV. DESCRIPTION OF THE REFERENCE METHOD

This method is carried out as follows:

1. Place the substance, the molecular weight of which is to be determined, in a tube connected to a mercury manometer and evacuate until all air and other dissolved gases are removed.

2. Immerse the manometer in a bath and make an approximate determination of two points on the vapor pressure curve (for example, at $p=1$ mm and $p=10$ mm).

3. From available vapor pressure and boiling point data select a reference substance, the vapor pressure of which in the same temperature region is as near as possible to that of the substance under investigation and the molecular weight of which in the vapor state is known. Let the difference in the two vapor pressures, D_p, equal p_1-p_2, where D_p is a positive quantity. The two substances are now identified by the subscripts 1 and 2.

4. Determine in accordance with the following relations the temperature, t, at which the measurements are to be made. (These relations are derived below, p. 708.)

$$p_1 < \frac{\delta D_p}{\frac{\delta_{D_p} M}{M}}$$

$$p_2 < \frac{\delta p_2}{1+\left(\frac{\delta p_2}{p_1 \frac{\delta_{p_2} M}{M}}\right)\frac{\delta_{p_2} M}{M}}$$

where δD_p and δp_2 are the unavoidable errors in measuring D_p and p_2, and $\frac{\delta M}{M}$ the corresponding allowable fractional errors in M arising therefrom.

5. By means of a differential manometer and a manometer immersed in the same well-stirred bath, determine D_p and p_2 at the temperature t.

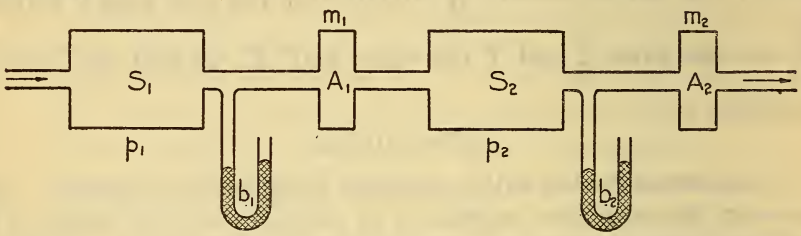

FIG. 1

S_1, S_2, saturators for saturating the gas stream with substances 1 and 2 whose vapor pressures are p_1 and p_2

A_1, A_2, condensers or absorbers for condensing substances 1 and 2, the condensates weighing m_1 and m_2 grams, respectively

b_1, b_2, open-arm manometers indicating the slight pressure differences ΔP_1 and ΔP_2 respectively

6. By means of two similar saturators immersed close together in a well-stirred bath, saturate a gas stream successively with the vapors of 1 and 2 and determine the mass, m, of each substance evaporated (for example, by the arrangement shown diagrammatically

in fig. 1). If these two masses are to be obtained by the weighing of condensers or absorbers of like size and shape, the operation of weighing should be conducted so as to give as accurately as possible the difference, $m_1 - m_2$. This could be conveniently accomplished by one weighing with the absorbers or condensers on opposite pans of the balance followed by a direct, and usually less accurate, weighing of one of the absorbers or condensers.

Accurate temperature control is not necessary in either experiment (5 and 6), but uniformity of temperature in the bath is essential in both cases.[6]

From the above data the molecular weight of either substance can be calculated, if that of the other is known.

The general technic of both of the operations involved is well established. Consequently, an experimental test of the method is not required. The special technic will depend upon the natures of the substances employed.

V. DERIVATIONS

$$M = \frac{mRT}{pv} \tag{1}$$

$$\frac{M_1}{M_2} = \frac{m_1 p_2 v_2}{m_2 p_1 v_1} \tag{2}$$

$$\frac{v_1}{v_2} = \frac{B - p_2 - \Delta P_2}{B - p_1 - \Delta P_1} \tag{3}$$

$$D_p = p_1 - p_2 \text{ and } \frac{p_1}{p_2} = 1 + \frac{D_p}{p_2} = 1 + R_p \tag{4}$$

$$\frac{v_1}{v_2} = 1 + \frac{\Delta P_1 - \Delta P_2 + D_p}{B - p_2 - D_p - \Delta P_1} = 1 + R_v \tag{5}$$

where R_v is small in comparison with unity. ΔP_1 and ΔP_2 can usually be made negligibly small.

$$m_1 - m_2 = D_m \tag{6}$$

$$\frac{m_1}{m_2} = 1 + \frac{D_m}{m_2} = 1 + R_m \tag{7}$$

Combining equations (2), (4), (5), and (7) gives finally

$$\frac{M_1}{M_2} = \frac{(1 + R_m)}{(1 + R_p)\ (1 + R_v)} \tag{8}$$

from which either M_1 or M_2 may be calculated in terms of quantities which are not sensitive to temperature.[7]

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[6] See below, p. 709.

[7] Compare the similar equation for determining vapor pressure differences, J. Am. Chem. Soc., 37, p. 311; 1915.

If the two substances employed are solid and (or) not soluble in each other at the temperature of the experiment, and if they do not react chemically with each other or interfere with the rapid attainment of vaporization equilibrium, and if, further, their mixture can be conveniently analyzed, then only one saturator and one absorber need be employed and R_v becomes equal to zero.

VI. PRECISION DISCUSSION

Inspection of equation (5) shows that errors in D_p and p_2 will produce in the factor $1+R_v$ an effect which is entirely negligible in comparison with that produced in the factor $1+R_p$ by these same errors. Consequently, since at most only two significant figures are required in a precision factor, R_v may, for purposes of precision computations, be taken as equal to zero; that is, $v_1=v_2=v$. On differentiation of equation (8) we obtain

$$\frac{\delta_{R_x} M}{M}=\frac{\delta R_x}{1+R_x} \tag{9}$$

in which M is either M_1 or M_2 and x is either m or p.

1. THE PRESSURE MEASUREMENTS

Putting

$$x=p \tag{10}$$

and combining with equation (4) gives

$$\frac{\delta M}{M}=\frac{p_2}{p_1}\delta\left(\frac{D_p}{p_2}\right) \tag{11}$$

For D_p as the variable this becomes

$$\frac{\delta_{D_p} M}{M}=\frac{\delta D_p}{p_1} \tag{12}$$

and for p_2

$$\frac{\delta_{p_2} M}{M}=\frac{D_p \delta p_2}{p_1 p_2}=\frac{(p_1-p_2)\delta p_2}{p_1 p_2} \tag{13}$$

Solutions of these equations determine minimum values for p_1 and p_2 as follows:

In each of these equations let $\frac{\delta M}{M}$ represent the maximum allowable fractional error in M_1. Then

$$p_1 \nless \frac{\delta D_p}{\frac{\delta_{D_p} M}{M}} \tag{14}$$

and

$$p_2 \nless \frac{\delta p_2}{\left(1+\frac{\delta p_2}{p_1 \frac{\delta_{p_2} M}{M}}\right)\frac{\delta_{p_2} M}{M}} \tag{15}$$

The minimum value which p_2 can have obviously occurs when p_1 has the value given by equation (14). If the errors in D_p and p_2 produce equal errors in M (that is, $\delta_{D_p} M = \delta_{p_2} M = \delta M$; principle of equal effects), then equations (14) and (15) give

$$p_2 < \frac{\delta p_2}{\left(1 + \frac{\delta p_2}{\delta D_p}\right)\frac{\delta M}{M}} \tag{16}$$

which is the smallest value p_2 can have under these conditions.

From equation (15) it is obvious that the largest minimum value for p_2 will occur when $\frac{\delta p_2}{p_1 \frac{\delta_{p_2} M}{M}}$ is negligible in comparison with unity and will be

$$p_2 < \delta p_2 \Big/ \frac{\delta_{p_2} M}{M} \tag{17}$$

2. TEMPERATURE CONTROL

The required precision in temperature control can be computed as follows:

From equation (9)

$$\frac{\delta_T M}{M} = \frac{\delta_T R_p}{1 + R_p} = \delta_T \log (1 + R_p) = \delta_T \log \frac{p_1}{p_2} = \delta_T \log p_1 - \delta_T \log p_2$$

From the Clausius-Clapeyron equation

$$\delta_T \log p_1 - \delta_T \log p_2 = \frac{L_1 - L_2}{RT^2} \delta T$$

Hence

$$\frac{\delta_T M}{M} = \frac{\Delta L}{RT^2} \delta T$$

The preliminary measurements (see p. 706) will ordinarily yield the necessary data for computing $\frac{\delta_T M}{M}$ in any specific case. It is obviously zero when ΔL is zero, that is, when the two vapor-pressure curves have the same slope at the temperature of the experiments.

Illustrative example: Suppose that both substances belong to the class of liquids for which Trouton's ratio has the value

$$\frac{L}{T_B} = 22$$

and that they differ in boiling point by Δt_B. It follows that $\Delta L = 22 \Delta t_B$ and if we assume that ΔL is independent of T, we have

$$\frac{\delta_T M}{M} = \frac{22 \Delta t_B}{RT^2} \delta T$$

For example, if $\Delta t_B = 10°$ C. and $T = 300°$ K. and if we impose the condition that $\frac{\delta_T M}{M}$ is not to exceed $0.001 = 0.1$ per cent, this gives

$$\delta T \ngtr 0.8° \text{ C.}$$

which may be compared with the analogous case when no reference substance is employed (see above, p. 709).

3. THE SATURATION MEASUREMENTS

Putting $x = m$ in equation (9) and proceeding as in 1 above we obtain an analogous set of relations as follows:

$$\frac{\delta_{Dm} M}{M} = \frac{\delta D_m}{m_1} \tag{18}$$

and

$$\frac{\delta_{m_2} M}{M} = \frac{D_m}{m_1} \frac{\delta m_2}{m_2} = \frac{(m_1 - m_2)\, \delta m_2}{m_1 m_2} \tag{19}$$

$$m_1 \nless \frac{\delta D_m}{\frac{\delta_{Dm} M}{M}} \tag{20}$$

$$m_2 \nless \frac{\delta m_2}{\left(1 + \frac{\delta m_2}{m_1 \frac{\delta_{m_2} M}{M}}\right) \frac{\delta_{m_2} M}{M}} \tag{21}$$

By combining relations (20) and (21) with equation (1) and solving for v, we obtain an expression giving a minimum value for v as follows:

$$v \nless \frac{RT}{M_1 p_1} \frac{\delta D_m}{\delta_{Dm} M/M} \nless \left(\frac{RT}{M_2 p_2} - \frac{RT}{M_1 p_1}\right) \frac{\delta m_2}{\delta_{m_2} M/M} \tag{22}$$

which may also be written

$$v \nless \frac{RT\left(\frac{M_2}{M_1}\right)}{p_1 M_2} \frac{\delta D_m}{\delta_{Dm} M/M} \nless \left(\frac{RT}{p_2 M_2} - \frac{RT\left(\frac{M_2}{M_1}\right)}{p_1 M_2}\right) \frac{\delta m_2}{\delta_{m_2} M/M} \tag{23}$$

For equal effects the second expression in (23) takes precedence over the first for all values of $\frac{M_2}{M_1}$ up to

$$\frac{M_2}{M_1} = \left(\frac{\delta m_2}{\delta D_m + \delta m_2}\right) \frac{p_1}{p_2} \tag{24}$$

or for the common case where $\delta D_m = \delta m_2$, the second expression will take precedence up to

$$\frac{M_2}{M_1} = \frac{1}{2} \frac{p_1}{p_2} \tag{25}$$

VII. ILLUSTRATIVE EXAMPLE

Suppose the substance whose molecular weight is to be determined has at 27° C. a vapor pressure of 10 mm and let us select naphthalene as the reference substance. Its vapor pressure at 27° is 9.57 mm. We have then

$$p_2 = 9.57 \text{ mm}$$
$$D_p = 0.430 \text{ mm}$$
$$M_2 = 128.06$$
$$M_1 = ?$$

Let us further assume that the permissible error in M_1 arising from the error in each measured factor is

$$\frac{\delta M_1}{M_1} = 0.001 = 0.1 \text{ per cent.}$$

From equation (12) we find the allowable error in D_p to be

$$\delta D_p = p_1 \frac{\delta M}{M} = 10.0 \times 0.001 = 0.01 \text{ mm}$$

Suppose that δD_m and δm_2 be taken as 0.0002 g each.

From relation (22) we find the minimum value for v to be

$$v_{\text{min.}} = \frac{0.08207 \times 300 \times 0.0002 \times 760}{10 \times 128.06 \times 0.001 \times M_1/M_2} = 2.92 \frac{M_2}{M_1} \text{ liters} \tag{26}$$

or

$$= 3.05 - 2.92 \frac{M_2}{M_1} \text{ liters} \tag{27}$$

The values of $v_{\text{min.}}$ as given by equations 26 (v_1) and 27 (v_2), respectively, are shown in the following table:

TABLE 1.—*Values of $v_{\text{min.}}$ for $\delta D_m = \delta m_2 = 0.0002$ g*

M_2/M_1	$\delta D_m = 0.0002$ g v_1	$\delta m_2 = 0.0002$ g v_2
0	0	3.05
.1	.292	2.66
$0.522 = \frac{1}{2}\frac{p_1}{p_2}$	1.53	1.53
1.0	2.92	.13
$1.045 = \frac{p_1}{p_2}$	3.05	0
$2.090 = \frac{2p_1}{p_2}$	6.10	3.05
5	14.6	11.6
10	29.2	26.9
100	292	289

Taking any value, v, larger than $v_{\text{min.}}$, we have (equation (1)) $m_2 = 0.65\ v$ g.

The allowable errors in p_2 and m_2 then become (equations (13) and (19)).

$$\delta p_2 = \frac{p_2 p_1}{D_p}\frac{\delta M_1}{M_1} = \frac{9.57 \times 10}{0.43} \times 0.001 = 0.22 \text{ mm}$$

$$\delta m_2 = \frac{m_2 m_1}{D_m}\frac{\delta M_1}{M_1} = \frac{v M_2 \dfrac{\delta M_1}{M_1}}{RT\left(\dfrac{1}{p_2} - \dfrac{M_2}{M_1} \times \dfrac{1}{p_1}\right)} = \frac{0.0068\ v \times 0.001}{\dfrac{1}{9.57} - \dfrac{1}{10}\dfrac{M_2}{M_1}}$$

TABLE 2.—*Values of δm_2 for $M_2 = 126$, $\frac{\delta m_2 M}{M} = 0.001$, $p_2 = 9.57$ and $p_1 = 10$ mm Hg*

$\frac{M_2}{M_1}$	δm_2 in milligrams		
	For $v = v$	For $v = 10$	For $v = 30$
0.0	0.065 v	0.65	2.0
.1	.072 v	.72	2.2
.5	.127 v	1.27	3.8
1.0	1.5 v	15	45
1.045 $\left(=\frac{p_1}{p_2}\right)$	∞	∞	∞
1.1	.123 v	1.23	3.7
2	.0712 v	.71	2.1
2.090 $\left(=\frac{2p_1}{p_2}\right)$	.065 v	.65	2.0
5	.0172 v	.17	.5
10	.0076 v	.076	.2

Suppose now that as a result of this preliminary survey we decide to impose the condition that $\delta D_m \nless 0.002$ g, since it will be much easier to attain this moderate degree of accuracy. Suppose further that a preliminary determination has yielded the information that $\frac{M_2}{M_1}$ = about 0.5. Equation (26) now gives $v_{\text{min.}}$ = about 15 liters. This value for v will, according to Table 2, require an accuracy in m_2 given by "δm_2 need not be less than 0.0018 g." It will suffice therefore if $v \nless 15$ liters. As regards the accuracy required in D_p and p_2, the values computed above are not difficult of attainment. Our final conclusions might therefore be somewhat as follows:

For $\frac{M_2}{M_1}$ = about 0.5; $p_1 = 10$ mm, $p_2 = 9.57$ mm, $D_p = 0.430$ mm, $M_2 = 128.06$, and $v = 15$ liters, the allowable errors in the measured quantities are

For p_2, 0.2 mm

For D_p, 0.01 mm

For m_2, 0.0018 g

For D_m, 0.002 g

The final precision in M will be

$$100\frac{\delta M}{M}=100\sqrt{4\times(0.001)^2}=0.2 \text{ per cent}$$

and the largest possible error in M will be

$$100\left(\frac{\delta M}{M}\right)_{\text{max.}}=0.4 \text{ per cent}$$

VIII. EFFECT OF ATMOSPHERIC PRESSURE

In the equations given above it has been tacitly assumed that D_p and p_2 as measured by the manometers are identical with the values which prevail during the saturation determination. This is not strictly true, since both values are functions of the external pressure and, in the case of liquids, are also functions of the solubilities of the gas used in the saturation measurements. In exact work small corrections may, therefore, be necessary to allow for these two effects. These corrections may be computed as follows:[8]

1. The pressure correction.

Increase the measured value of p_2 by Δp_2

$$\Delta p_2=\frac{p_2V_2}{RT}(B-\Delta P_2-p_2)$$

where V is the molal volume of the substance at $T°$ K. and in the state (liquid or solid) in which it exists at $T°$ and B mm.

Similarly *increase* the measured value of D_p by ΔD_p

$$\Delta D_p=(\text{approx.})\frac{B}{RT}[V_1D_p+p_2(V_1-V_2)]$$

2. The gas-solubility correction (for liquids only).

Decrease the measured value of p_2 by $\Delta' p_2$

$$\Delta' p_2=\frac{p_2V_2\ (B-\Delta P_2-p_2)}{RT}\left(1-\frac{1}{S_2}\right)$$

where S is the solubility of the gas in the liquid; that is, S = the ratio of the concentrations of the gas in the two phases, gas/liq.

Similarly *decrease* the measured value of D_p by

$$\Delta' D_p=\frac{p_1V_1(B-\Delta P_1-p_1)}{RT}\left(1-\frac{1}{S_1}\right)-\frac{p_2V_2(B-\Delta P_2-p_2)}{RT}\left(1-\frac{1}{S_2}\right)$$

In practically all cases the algebraic sum of these two corrections will be negligible.

WASHINGTON, August 7, 1928.

[8] Compare Washburn, Science, 51, p. 49; 1925.