

MOLECULAR WEIGHTS BY SURFACE TENSION WITHOUT USE OF BALANCE

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A routine physical chemistry experiment is the determination of surface tension of a liquid by the height it ascends into a capillary tube. By equating surface-tension force upward and gravitational force downward at the circle of contact between liquid surface and tube wall, it is deduced, for a small tube,

$$\text{rh}d\text{g}$$

that $\gamma = \frac{\text{rh}d\text{g}}{2}$, where γ is the sur-

face tension in dynes per cm., r the radius of the capillary in cm., d the density of the liquid in gms. per cc., g the acceleration of gravity in cm. per sec.², and h the height of capillary rise in cm.; h is usually measured by a scale attached to, or engraved on, the capillary, but sometimes by a cathetometer.

Instead of measuring h directly, a manometer filled with a liquid of known density may be used to create a pressure which depresses the capillary meniscus to its free-surface level. Water is a convenient manometric fluid. The pressure it creates may be applied positively to the top of the capillary or negatively to an otherwise air-tight vessel holding the sample liquid, at the capillary's bottom. The latter is preferable, as it minimizes contamination of the meniscus by water-vapor diffusion. The essential arrangement is shown in

figure 1. In either case, the pressure of h' cm. of water becomes $h'd'g$ dynes per sq. cm., d' being the density of water. This exerts a downward force of $\Pi r^2 h'd'g$ dynes on the capillary meniscus. If the meniscus be restrained from rising by this

force, γ equals $\frac{\text{rh}'d'g}{2}$. The new

equation for restrained rise is very like the old one for free rise, therefore: only h' , the "repressing head," replaces h , the "free rise," and d' , the density of water, replaces d , the density of the liquid being investigated.

Besides the convenience of applying the scale to the external manometer rather than the internal capillary, the manometric method has two other advantages: (1) the density of the unknown liquid need not be determined to get the surface tension; (2) the same cross section of tube is used in successive measurements, so that nonuniformity of diameter is not a source of error if surface tension only is sought.

It is not necessary to determine in advance the density of the unknown liquid, but this density may be found during the experiment's course. If the tube's bore is uniform and its length graduated, then γ may be expressed both as

$$\frac{rhg}{2} \text{ and } \frac{rh'd'g}{2}, \text{ whence } hd = h'd',$$

$$\text{or } d = \frac{h'}{h}d'. \text{ The principle is that}$$

of Hare's balancing columns. The accuracy suffers from the shortness of the columns involved, but this fact promotes economy of fluid.

The ability of this simple apparatus to give the surface tension and the density suggests the possibility of using Ramsay and Shield's modification of the Eötvös equation to determine the molecular weight of the liquid being studied. If this could be done with simple desk equipment, without recourse to the analytical balance which is usually remote from the fume-laden organic chemistry work space, it would be helpful in routine organic qualitative analysis. The equation reads:

$$\gamma (M/d)^{2/3} = 2.12(t_c - t - 6)$$

or

$$M = d \left[\frac{2.12}{\gamma} (t_c - t - 6) \right]^{3/2}$$

M being the required molecular weight, t_c and t , respectively, the centigrade critical temperature of the subject liquid and actual temperature of the experiment. Since, as an approximation, $t_c + 273 = 3/2 (t_b + 273)$ or $t_c = 3/2 t_b + 137$, t_b being the normal boiling point of the given liquid, a routine measurement of the boiling point should give the final requisite datum for a molecular weight determination. It would be advisable to combine the determination of the boiling point with the collection of a redistilled sample for the surface tension determination.

Although all the equations used in this study might be combined into one, this was not done for two reasons. In the first place, the resultant expression is unwieldy; second, it precludes checks on intermediate results, viz. density and surface tension.

A test setup was made, using a thermometer tube with the degree marks for a scale. Its uniformity was checked by moving a column of mercury through it, and noting the virtually constant number of degree-marks subtended by it as it progressed through the tube. The diameter of the bore was calculated from the length and weight of this column and from the density of mercury. A conversion factor was determined by measurement to enable the degree marks to be translated to centimeters. The side-necked test tube (fig. 1) was replaced by a wider test tube, through whose stopper passed the capillary, a thermometer, and the manometer connection. A T-tube was arranged between the manometer and this connection to permit quick atmospheric communication to the interior by removal of a pinch clamp, for determining h . The usual precautions of cleaning and rinsing the apparatus, especially the capillary, were observed; and of manipulating the meniscus (by the manometer) about the position of equilibrium. A light held behind the capillary was found most useful in following the movements of the meniscus. Our particular tube had a diameter of 0.01556 cm., and 0.1775 cm. per degree-mark. We considered this diameter about right; meniscus movements were annoyingly sluggish with much smaller

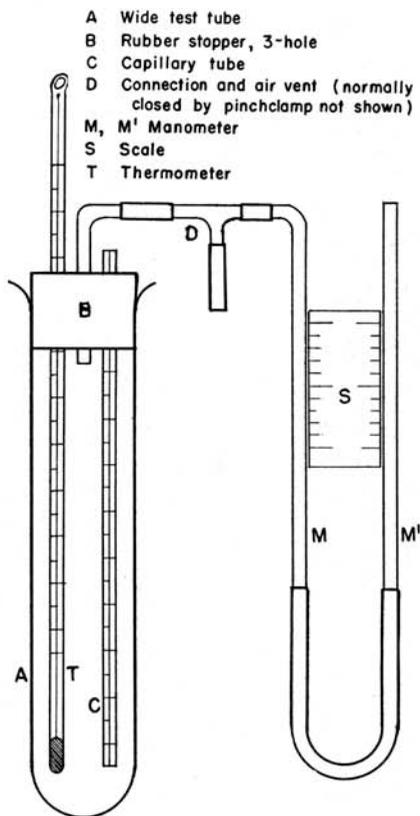


FIG. 1.—Apparatus for molecular-weight determination by Eötvös equation.

ones, but the rise was too low for accuracy with larger.

Here is the record of a typical experiment. Subject, acetone. Temperature, 27° C. Free rise, 41.3 degree-marks, or 7.33 cm. Repressing water head, 5.75 cm. Density found, 0.782 at 27° ; handbook, 0.792 at 20° C. Surface tension found, 21.8 dynes/cm.; handbook, 23.7 at 20° . Boiling point, 56° C; critical temperature found from it, 221° C.; handbook value, 235° C. Molecular weight by the Ramsay and Shields-Eötvös equation, 61.2; stoichiomet-

ric, 58.1; error, 5 percent. If literature values are taken for the density, surface tension, and boiling point, and the molecular weight calculated by the above equation, a molecular weight of 57.7 emerges, in error only 1 percent.

In table 1 are shown for several compounds the density, surface tension, and molecular weight; in parallel lines, for each substance, are given, first, values derived from the literature for each compound, and, second, those derived by student experimentation in our apparatus. It may be deduced from this table that large systematic errors may be expected in this determination, and that most of the error springs from the equation rather than from the apparatus used.

Considering that the manometric surface-tension method gave values of the molecular weight not extremely discrepant from those derivable from published data, we next inquired into the limiting accuracy of the method based only on the literature values of the densities, surface tensions, and boiling points, of a large number of typical simple organic compounds. The results are shown in table 2, in which the compounds are grouped functionally. It appears that considerable errors may be expected in very many cases.

The loosest approximation in the calculation is the formula connecting the absolute critical and boiling temperatures by a factor of $3/2$. To see if this was the main offense against accuracy in the proceedings, the percentage error in this calculation of the critical temperature was checked against that in the molecu-

TABLE 1.—TYPICAL PRECISION OF THE METHOD

L: taken from literature; CL, Calculated from literature values
 E: found by our experiments; CE, calculated from our expt. values

Compound	Density	Surf. tens.	Mol. wt.	% Error
Acetone.....	0.792 L	23.7 L	57.7 CL	-1
	0.782 E	21.8 E	61.2 CE	+5
Benzyl alcohol.....	1.050 L	39.7 L	109.8 CL	+2
	1.045 E	35.7 E	128.5 CE	+16
Carbon tetrachloride.....	1.595 L	26.7 L	121.0 CL	-21
	1.560 E	25.3 E	125.0 CE	-19
Acetic acid.....	1.049 L	27.6 L	103.8 CL	+73
	1.005 E	25.6 E	113.5 CE	+87
Nitrobenzene.....	1.199 L	43.4 L	113.8 CL	-8
	1.235 E	43.2 E	116.5 CE	-5
Ether (Ethyl).....	0.714 L	17.0 L	65.5 CL	-11
	0.705 E	16.15 E	67.3 CE	-9
Carbon disulfide.....	1.263 L	31.4 L	53.1 CL	-30
	1.285 E	31.3 E	51.6 CE	-32
Aniline.....	1.022 L	42.6 L	86.0 CL	-8
	1.185 E	42.3 E	98.2 CE	+5
Chloroform.....	1.498 L	27.1 L	94.2 CL	-21
	1.490 E	26.0 E	95.2 CE	-20

lar weight for some random cases. The results are shown in table 3. From this, it may be inferred that this approximation is not the sole source of error; that it often is not the major one; and that sometimes its error cancels other errors in the calculation.

In nine cases, the largest error found in the temperature approximation was 16-20 percent, for the

compounds chloroform-methylene chloride, ethyl bromide. The error was positive for isovaleric acid and phenetole, negative for all the others. It was less than 5 percent for acetic acid, phenetole, toluene, and aniline.

Returning to a consideration of the overall percentage errors in the molecular weights shown in the final columns of table 2, the need for the

TABLE 2.

Compound	Formula	Boiling Point °C	Density	Surface Tension + Temp °C	Molecular Weight	Cal. Molecular Weight	% Error
<i>Acids</i>							
Acetic	CH_3COOH	118.1	1.049 ²⁰	27.6 ²⁰	60.1	103.8	+ 73
Isovaleric	$(\text{CH}_3)_2\text{CHCH}_2\text{COOH}$	176.7	0.937 ²⁵	25.3 ²⁰	102.1	166.0	+ 63
Caprylic	$\text{CH}_3(\text{CH}_2)_6\text{COOH}$	238.	0.910 ²⁵	28.8 ¹⁸	144.2	184.5	+ 28
Heptylic	$\text{CH}_3(\text{CH}_2)_5\text{COOH}$	224.	0.913 ²⁵	28.3 ²⁰	130.2	175.8	+ 35
Undecylenic	$\text{CH}_3\text{CH}(\text{CH}_2)_9\text{COOH}$	295.	0.908 ²⁵	30.6 ²⁵	184.3	214.	+ 16
<i>Alcohols</i>							
Methyl	CH_3OH	65.6	0.793 ²⁰	22.6 ²⁰	32.0	68.3	+ 113
Ethyl	$\text{CH}_3\text{CH}_2\text{OH}$	78.5	0.789 ²⁰	22.3 ²⁰	46.1	80.4	+ 74
Cyclohexanol	$\text{C}_6\text{H}_{11}\text{OH}$	161.5	0.962 ²⁰	34.2 ¹⁶	100.2	100.4	0
n-Octyl	$\text{CH}_3(\text{CH}_2)_7\text{CH}_2\text{OH}$	195.	0.825 ²⁰	27.5 ²⁰	130.2	143.5	+ 10
2-Octanol	$\text{CH}_3\text{CH}(\text{OH})(\text{CH}_2)_6\text{CH}_3$	179.	0.819	26.5 ²⁰	130.2	137.0	+ 5
Benzyl	$\text{C}_6\text{H}_5\text{CH}_2\text{OH}$	205.	1.050 ¹⁵	39.7 ²⁵	108.1	109.8	+ 2
<i>Ethers</i>							
Ethyl	$\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$	34.6	0.714 ²⁰	17.0 ²⁰	74.1	65.5	- 11
Anisole	$\text{C}_6\text{H}_5\text{OCH}_3$	155.	0.995 ²⁰	35.2 ²⁰	108.1	93.8	- 13
Phenetole	$\text{C}_6\text{H}_5\text{OC}_2\text{H}_5$	172.	0.967 ²⁰	32.7 ²⁰	122.2	113.5	- 7
<i>Ketones</i>							
Acetone	CH_3COCH_3	56.5	0.792 ²⁰	23.7 ²⁰	58.1	57.7	- 1
Methyl propyl	$\text{CH}_3\text{CO}(\text{CH}_2)_2\text{CH}_3$	101.7	0.812 ¹⁵	24.2 ²⁰	86.1	90.0	+ 5
Ethyl propyl	$\text{C}_2\text{H}_5\text{CO}(\text{CH}_2)_2\text{CH}_3$	124.	0.813 ²⁰	25.4 ²⁰	100.2	99.8	0
Methyl butyl	$\text{CH}_3\text{CO}(\text{CH}_2)_3\text{CH}_3$	127.2	0.830 ²⁰	25.5 ²⁰	100.2	103.9	+ 4
Methyl hexyl	$\text{CH}_3\text{CO C}_6\text{H}_{13}$	173.5	0.818	26.8 ²⁰	128.2	130.5	+ 2
<i>Hydrocarbons + Halogen Derivs.</i>							
Trimethylethylene	$(\text{CH}_3)_2\text{C}=\text{CHCH}_3$	38.4	0.668 ¹⁵	17.3 ²⁰	70.1	62.0	- 11
Isopentane	$(\text{CH}_3)_2\text{CHCH}_2\text{CH}_3$	28.	0.621 ¹⁹	13.8 ²⁰	72.2	70.8	- 2
Cyclohexane	C_6H_{12}	81.4	0.779 ²⁰	25.3 ²⁰	84.2	66.0	- 21
n-hexane	$\text{CH}_3(\text{CH}_2)_4\text{CH}_3$	69.0	0.660 ²⁰	18.4 ²⁰	86.2	80.8	- 6
n-octane	$\text{CH}_3(\text{CH}_2)_6\text{CH}_3$	126.	0.704	21.8 ²⁰	114.2	110.5	- 3
Bisooxyl	$(\text{CH}_3)_2\text{C}(\text{CH}_2)_2\text{CH}(\text{CH}_3)_2$	159.7	0.748 ²⁰	22.2 ²⁰	142.3	144.5	+ 2
Benzene	C_6H_6	80.1	0.879 ²⁰	28.9 ²⁰	78.1	61.2	- 22
Toluene	$\text{C}_6\text{H}_5\text{CH}_3$	110.8	0.866 ²⁰	28.4 ²⁰	92.1	81.4	- 12
Styrene	$\text{C}_6\text{H}_5\text{CH}=\text{CH}_2$	146.	0.907 ²⁰	32.1 ¹⁹	104.1	92.5	- 11
Ethyl benzene	$\text{C}_6\text{H}_5\text{C}_2\text{H}_5$	136.2	0.867 ²⁰	29.6 ²⁵	106.2	94.0	- 11
O-xylene	$\text{C}_6\text{H}_4(\text{CH}_3)_2$	144.	0.874 ²⁰	29.9 ²⁰	106.2	97.2	- 8
P-xylene	$\text{C}_6\text{H}_4(\text{CH}_3)_2$	138.5	0.861 ²⁰	28.3 ²⁰	106.2	100.0	- 6
Mesitylene	$\text{C}_6\text{H}_3(\text{CH}_3)_3$	164.6	0.863 ²⁰	28.5 ²⁰	120.2	118.5	- 1
P-cumene	$\text{CH}_3\text{C}_6\text{H}_4\text{CH}(\text{CH}_3)_2$	176.	0.857 ²⁰	28.1 ¹⁹	134.2	129.0	- 4
C tetrachloride	CCl_4	76.7	1.595 ²⁰	26.7 ²⁰	153.8	121.0	- 21
Chloroform	CHCl_3	61.3	1.498 ¹⁵	27.1 ²⁰	119.4	94.2	- 21

Compound	Formula	Boiling Point °C	Density	Surface Tension + Temp C	Molecular Weight	Cal Molecular Weight	% Error
<i>Hydrocarbons + Halogen Derivs:</i>							
Bromoform	CHBr ₃	149.5	2.890 ²⁷	41.5 ²⁰	252.8	206.	- 19
Methylene chloride	CH ₂ Cl ₂	40.1	1.336	26.5 ²⁰	84.9	67.3	- 21
ethylene tetrachloride	CCl ₂ :CCl ₂	121.2	1.631 ²⁷	31.7 ²⁰	165.8	139.5	- 16
Ethyl bromide	CH ₃ CH ₂ Br	38.0	1.430 ²⁷	24.2 ²⁰	109.0	80.5	- 27
Ethyl iodide	CH ₃ CH ₂ I	72.2	1.933 ²⁷	29.9 ¹⁶	156.0	120.5	- 23
1,2-Dibromo propane	CH ₂ Br-CHBr-CH ₂ Br	220.	2.436 ²³	45.4 ²⁰	280.8	228.	- 19
Isobutyl chloride	(CH ₃) ₂ CHCH ₂ Cl	68.9	0.875	21.9 ²⁰	92.6	82.8	- 11
tert butyl chloride	(CH ₃) ₃ CCl	51-2	0.847 ²⁷	19.6 ²⁰	92.6	77.6	- 16
Iso amyl chloride	(CH ₃) ₂ CH(CH ₂) ₂ Cl	98.9	0.893	23.5 ²⁰	106.6	100.0	- 6
Bromo benzene	C ₆ H ₅ Br	155-6	1.499 ²⁷	36.3 ²⁰	157.0	135.5	- 14
Chloro benzene	C ₆ H ₅ Cl	132.	1.107 ²⁷	33.1 ²⁰	112.6	97.0	- 14
Iodo benzene	C ₆ H ₅ I	188.6	1.832 ²⁷	39.7 ²⁰	204.0	176.5	- 13
o-Bromo naphthalene	C ₁₀ H ₇ Br	281.1	1.488 ²⁷	44.6 ²⁰	207.1	189.0	- 9
o-Chloro naphthalene	C ₁₀ H ₇ Cl	263.	1.194 ²⁷	41.8 ²⁰	162.6	154.2	- 5
<i>Nitro compounds:</i>							
Nitro benzene	C ₆ H ₅ NO ₂	211.	1.199 ²⁷	43.4 ²⁰	123.1	113.8	- 8
o-Nitro toluene	NO ₂ C ₆ H ₄ CH ₃	222.	1.163 ²⁷	41.5 ²⁰	137.1	125.0	- 9
m-Nitro toluene	NO ₂ C ₆ H ₄ CH ₃	231.	1.157 ²⁷	41.0	137.1	132.8	- 3
Nitro methane	CH ₃ NO ₂	101.	1.130 ²⁷	36.8 ²⁰	61.0	65.8	+ 8
<i>Amines and Nitriles:</i>							
Aniline	C ₆ H ₅ NH ₂	184.4	1.022 ²⁷	42.6 ²⁰	93.1	86.0	- 8
Diisobutylamine	[(CH ₃) ₂ CHCH ₂] ₂ NH	139-40	0.745 ²⁷	22.0 ²⁰	129.2	126.0	- 2
Dipropylamine	[CH ₂ CH ₂ CH ₂] ₂ NH	110.7	0.738 ²⁷	22.5 ²⁰	101.2	98.3	- 3
Butyronitrile	CH ₃ CH ₂ CH ₂ CN	118.	0.796 ¹⁵	28.1 ²⁰	69.1	80.0	+ 16
Isovaleronitrile	(CH ₃) ₂ CHCH ₂ CN	129.3	0.802	26.0 ²⁰	83.1	99.1	+ 19
<i>Esters:</i>							
Diethyl phthalate	C ₆ H ₄ (COOC ₂ H ₅) ₂	296.	1.123 ²⁵	37.3 ^{20.5}	222.2	199.6	- 10
Ethyl nonanoate	CH ₃ (CH ₂) ₇ COOC ₂ H ₅	228.	0.866 ²⁷	28.0 ²⁰	186.3	174.0	- 7
Eth. hydrocinnamate	C ₆ H ₅ (CH ₂) ₂ COOC ₂ H ₅	249.	1.015 ²⁷	35.1 ^{20.5}	178.2	161.0	- 10
Ethyl cinnamate	C ₆ H ₅ CH=CHCOOC ₂ H ₅	271.	1.049	38.4 ^{19.5}	176.2	160.4	- 9
Ethyl caproate	CH ₃ (CH ₂) ₄ COOC ₂ H ₅	168.	0.871 ²⁷	25.8 ²⁰	144.2	141.0	- 2
Ethyl iso valerate	(CH ₃) ₂ CHCH ₂ COOC ₂ H ₅	135.	0.866 ²⁷	23.7 ²⁰	130.2	129.0	- 1
<i>Miscellaneous:</i>							
Carbon disulfide	CS ₂	46.3	1.263 ²⁷	31.4 ²⁰	76.1	53.1	- 30
Ethane thiol	C ₂ H ₅ SH	34.7	0.840	21.8 ²⁰	62.1	53.0	- 15
Phenyl isothiocyanate	C ₆ H ₅ NCS	218.	1.135 ²⁷	41.4 ²⁰	135.2	120.0	- 11
Chloro acetone	CH ₃ COCH ₂ Cl	119.	1.15	35.3 ²⁰	92.5	83.0	- 10
1,1-Dichloro acetone	CH ₃ COCHCl ₂	120.	1.234 ¹⁵	31.9 ²⁰	127.0	104.5	- 18

TABLE 3.—CRITICAL TEMPERATURE VS. MOLECULAR WT. ERRORS

Substance	Acetic acid	isoValeric acid	Anisole	Phenetole	Toluene	Aniline
% Error:						
t_c	-2	+10	0	+5	-6	-3
M	+73	+63	-13	-7	-12	-8

following restrictive rules upon the use of the modified Eötvös equation seems evident:

(1) The proposed method should not be used until the functional class of the compound has been found.

(2) It should not be applied to acids.

(3) It should not be applied to alcohols boiling at less than 100° C.

(4) For other substances included in table 2, values within 10 percent of correct for the molecular weight may be expected if the Eötvös values be corrected by the following percentages: (a) for alcohols, -10; (b) for ketones, 0; (c) for hydrocarbons, +10; (d) for nitro compounds, +5; (e) for

amines +5; (f) for nitriles, -15; (g) for esters, +5; (h) for other compounds, numbers depending on studies of more examples.

The determination of the molecular weight of a selected unknown by this method has been used as an assigned experiment in the physical chemistry course at Monmouth College.

Calculation of the approximate parachor $P = (M/d)\gamma^{1/4}$ could be done by the proposed apparatus without the use of the balance if the molecular weight were already known.

BIBLIOGRAPHY

GLASSTONE, Text-Book of Physical Chemistry. Van Nostrand, 1940, pp. 473-487.