ON THE APPLICATION OF GRAPHIC METHODS IN CERTAIN CHEMICAL STUDIES.

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The graphic methods so generally applied in the different branches of science possess the great advantage of representing physically to the eye laws deduced from the observation of certain phenomena or metaphysical conceptions, laws generally expressed by complicated equations of which the solution would involve impracticable calculations. In a general manner, the more complicated and difficult of conception by our mind is a physical law, the higher is the degree of the equation or empirical formula which embodies it. When applied to the study of the laws of gravitation for instance, to quote a well known example, this graphic method furnishes curves from which can be at once calculated by measurements on a diagram, the principal data of a given question. Transported to the domain of chemistry the method is found very useful for the solution of many problems.

The curve of solubility of certain salts of which the solubility varies with the temperature furnishes at once the amount of such salts in solution in water at different temperatures.

When saline solutions are used for certain specific purposes similar curves constructed from actual observations of the densities of different saturations or the degree they show with a given areometer, can give readily the amount of the salt to be dissolved in a certain amount of water to obtain the density required, or vice versa.

If we pass from these simple examples to curves representing certain conceptions of the intimate constitution of matter, the use of graphic methods proves equally advantageous.

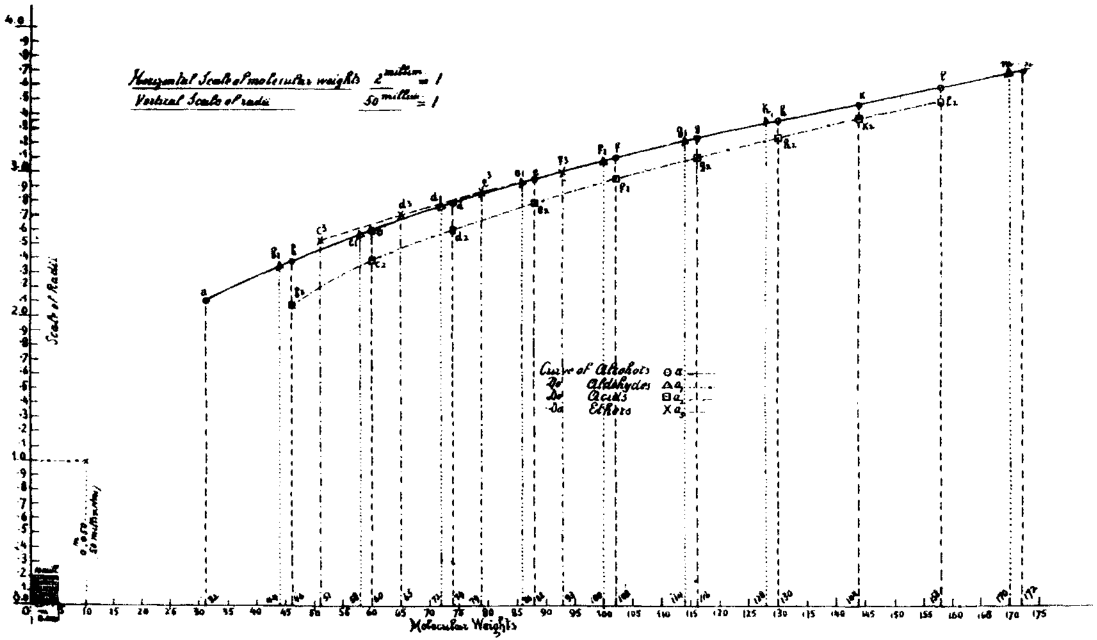
A curve reproducing the results of certain observations may and will often present "breaks" or solutions of continuity, and a consideration of these missing parts may prove the means of discovering the probable properties of an unknown compound, which, graphically, would find its place at such a point. We may mention as an example the well known curve of Mendelejeff, embodying a classification of the elements. Without entering into a discussion of the question if this curve does really or not represent a natural classification of the elements, it is well known that by the consideration of some missing points of the curve, it has been possible for Mendelejeff to foresee that the "gap" observed at certain points would have to be filled by an element which, by its position between certain others of which the properties were known ought to possess certain characters of atomic weight, specific gravity, and even chemical affinities which the subsequent discovery of such an element has emphatically confirmed. In other cases these curves may serve as affording a corroboration, a control, of certain assertions generally admitted, and even if useful only to that extent, they would be very valuable. We have thought that in this line of investigation it might prove interesting to submit the results of some personal researches.

If the molecular weight W of a compound be divided by its specific gravity D, the quotient expresses the molecular volume of the compound

$$V = \frac{W}{D}$$

and this ratio of the molecular weight to the specific gravity can be easily computed in each particular case.

Of the nature of the atoms we do not know much, we are not in this respect any more advanced than the Greek philosophers were twenty centuries ago, we have no definite ideas of their shape, we do not know if their number is limited. We admit that under certain circumstances they can assume an individuality and form molecules which we consider as the smallest conceivable parts of matter which can pass into or out of combination ; we admit also, that these molecules affect the spherical form, from which it can be inferred that a compound constituted by such molecules separated by intermolecular spaces will affect also a spherical form.


Horizontal Scale of molecular weights 2 millim = 1
Vertical Scale of radii 50 millim = 1
Curve of Alcohols ○ a
Do Aldehydes △ a1
Do Acids ⊡ a2
Do Ethers × a3
Scale of Radii
Molecular Weights
a 0.250 50 millimetres
a
b
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b2
c
c1
c2
c3
d
d1
d2
d3
e
e1
f
f1
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The graphic consideration of these molecular volumes for certain class of compounds give rise to interesting deductions. If, for instance, we consider the primary alcohols and their derivates, aldehydes, acids, ethers, we know that, in each series of these compounds, the molecular weights proceed by regular and equal increments by the addition to the preceding term of the series of the molecular weight of the radicle which heads it. If we carry then on a horizontal line, taken as the axis of abcissae and at a proper scale, these equal increments from an assumed point O, and applying to each compound the proper molecular weight W, represented by a corresponding abcissa, we erect at each point, thus determined in the axis AX of abcissae, a perpendicular; by carrying on these ordinates the lengths measured at the same or any other scale assumed, for clearness of diagram, which represent the calculated molecular volumes V in each case and joining the points by a continuous curve we will obtain a curve which will be the graphical representation of the law by which, so to speak, we pass from one compound to the other. If it happens that certain of these compounds be unknown, the curve at the corresponding point (or the ordinate) will present a "gap," but the general curvature assumed will allow us to trace it, with a sufficient approximation, by joining the points corresponding to the term or terms of the series preceding and following the missing compound or compounds and we shall be able, by actual measurements of the missing ordinates thus supplied, to foresee very closely the physical characters of the missing term.

These molecular volumes being generally represented by numbers rather large may render the construction of the diagram on a scale sufficiently large rather difficult. They can be advantageously replaced by such quantities, proportional to them, as can be readily calculated, the volumes being known, for instance, the corresponding radii of the spheres which represent the molecular volumes.

We have then

$$\frac{W}{D} = V = \frac{4\pi}{3} R_3$$

and

$$R = \sqrt[3]{\frac{V}{4.1888}}$$

We have calculated such radii for the primary alcohols, their ethers, aldehydes and acids for the compounds of which the molecular weights W and specific gravities D are given below, calculating and tabulating first the molecular volumes from which the corresponding radii were deduced, and for each series or group of compounds we have constructed the special corresponding curve by carrying, as explained above, as abcissae the respective molecular weights in each case and as ordinates at each point thus determined on the line of abcissae the calculated radii of the spheres corresponding to the different molecular volumes.

ALCOHOL.

	W	D	$V=\frac{W}{D}$	$R=\sqrt[3]{\frac{V}{4.1888}}$
CH_4O	32	0.8098	39.5159	2.112
C_2H_6O	46	0.812	56.6502	2.382
C_3H_8O	60	.820	73.170	2.593
$C_4H_{10}O$	74	.824	89.805	2.778
$C_5H_{12}O$	88	.83	106.204	2.939
$C_6H_{14}O$	102	.8312	122.7141	3.082
$C_7H_{16}O$	116	.838	138.4248	3 209
$C_8H_{18}O$	130	.8375	155.2238	3.333
$C_9H_{20}O$	144	.8415	171.1229	3.444
$C_{10}H_{22}O$	158	.8389	188.3418	3.555
$C_{11}H_{24}O$	172	.8268	208.0430	3.675

ALDEHYDES.

CH_2O Gas.				
C_2H_4O	44	.807	54.5229	2.351
C_3H_6O	58	.83	69.8795	2.555
C_4H_8O	72	.834	86.3309	2.741
$C_5H_{10}O$	86	.822	104.6228	2.923
$C_6H_{12}O$	100	.842	118.7648	3.057
$C_7H_{14}O$	114	.827	137.8476	3.204
$C_8H_{16}O$	128	0.82	156.0975	3.340
$C_9H_{18}O$?				
$C_{10}H_{20}O$?				
$C_{11}H_{22}O$	170	.85	200.00	3.627

ACIDS.

CH_2O_2	46	1.245	36.9477	2.066
$C_2H_4O_2$	60	1.0701	56.0695	2.374
$C_3H_6O_2$	74	1.0154	72.8776	2.591
$C_4H_8O_2$	88	0.9746	90.2934	2.783
$C_5H_{10}O_2$	102	.9562	106.6722	2.941
$C_6H_{12}O_2$	116	.9446	122.8033	3.083
$C_7H_{14}O_2$	130	.935	139.0374	3.213
$C_8H_{16}O_2$	144	.9139	157.5664	3.350
$C_9H_{18}O_2$	158	.9082	173.9704	3.463

ETHERS.

$CH_3O\frac{1}{2}$ Gas.				
$C^2H_5O\frac{1}{2}$	37	.735	50.3401	2.290
$C_3H_7O\frac{1}{2}$	51	.763	66.8414	2.517
$C_4H_9O\frac{1}{2}$	65	.784	82.9081	2.704
$C_5H_{11}O\frac{1}{2}$	79	.799	98.8735	2.846
$C_6H_{13}O\frac{1}{2}$	93	.862	107.8886	2.953

The specific gravities are for the temperature of 0°C. and have been obtained from Prof. Clarke's "The Constants of Nature." Instead of writing the formulæ of the ethers $\left.\begin{matrix}CnH_2n+1\\CnH_2n+1\end{matrix}\right\rangle O$ their molecule has been halved so as to obtain volumes comparable with the volumes given by the alcohols, aldehydes and acids, and this has been done only as a matter of convenience in calculation, bearing in mind, however, that the formulæ represents only half a molecule which, according to present chemical theories, cannot exist.

In the series of the aldehydes we have omitted the methylic aldehyde which is a gas, beginning the curve only at the next liquid compound. The aldehydes $C_9H_{18}O$, $C_{10}H_{20}O$ are unknown at these points, the curve is supplied from the general radius of curvature it assumes. The interpolated curves would furnish at once very approximately the corresponding ordinates, and by measuring these ordinates on the scale the radii of the spheres, representing the molecular volumes could be obtained. From these radii the molecular volumes could be readily calculated, and as the abcissae corresponding to the measured ordinates are known and furnish the molecular weights, the specific gravity $D=\frac{W}{V}$ could be obtained. The properties of these unknown aldehydes could be also inferred from the fact of their falling between two of which the properties have been already ascertained. In the same manner the curve might serve as control for results already obtained; any important deviation from the general curvature at some point corresponding to a new compound, which might have been furnished by an ordinate calculated as explained, would justify a revision of the results accepted for this compound, of its specific gravity for example.

An inspection of the diagram in which all the curves have been plotted on the same scale show how closely the alcohol and aldehyde curves especially and even that furnished by the ethers follow each other; practically they cover each other and give one and the same curve if we consider how large the vertical scale has been taken in proportion to the horizontal one; in this diagram it is twenty-five times as large and any discrepancy shows itself much magnified. The curve of the acids is decidedly different and falls below the others, but keeping in mind always the large vertical scale adopted it follows still closely the other in general curvature though apparently nearing them as it recedes from the origin.

This rapid examination of one particular class of compounds may serve to show the utility of graphic methods in pointing the way to the discovery of some errors in the determination of certain properties of a compound or in calling the attention on certain anomalies made apparent, so to speak, in a physical manner.

In pursuing this line of investigation in a summary manner, if we compare together the elements taken in the gaseous state under a condensation of 2 volumes and calculate the radii of their molecular volumes as explained above we obtain a curve which demonstrates graphically the known fact that under these condition the elements occupy in space the same volume.

$O_2=R\ 1.904$

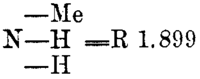
$H_2=R\ 1.902$

$N_2=R\ 1.902$

$$
\begin{aligned}
&Cl_2 = R\ 1.908\\
&Br_2 = R\ 1.903\\
&I_2 = R\ 1.909\\
&S_2 = R\ 1.902
\end{aligned}
$$

If we calculate in the same manner the radii of the spheres representing the molecular volumes of gaseous compounds, we find

$$
\begin{aligned}
&NH_3 = R\ 1.900 \text{ 2 volumes}\\
&H_2O = R\ 1.904\\
&CO_2 = R\ 1.900\\
&SO_2 = R\ 1.898\\
&SO_3 = R\ 1.904\\
&CO = R\ 1.904\\
&AsH_3 = R\ 1.904\\
&PH_3 = R\ 1.899\\
&2\ (CH_3) = R\ 1.904\\
&2\ (C_2H_5) = R\ 1.891\\
&CS_2 = R\ 1.900
\end{aligned}
$$



$$N\begin{cases}-Me\\-H\\-H\end{cases} = R\ 1.899$$

All these numbers are practically equal, and, in fact, the differences observed are so small that they might be due to errors of observation. The curve which will represent these molecular volumes, as given by their radii, is, in fact, a straight line parallel to the axis of abcissae at a distance of 1.90, all the ordinates being equal.

With this constant radius equal to 1.90, we can calculate the hypothetical specific gravity in the gaseous state of bodies that we cannot volatilize, carbon, for example.

The formula

$$\frac{4\pi}{3} R^3 = V$$

gives

$$1.9^3 = 6.859 \times 4.1888 = 28.7309$$

and

$$\frac{W}{V}=D$$

$$\frac{24}{28.7309}=0.835$$

Büchner gives the number 0.8316.

There are, however, some exceptions.

Mercury, taken as equal to two volumes of vapor, will give 2.392 for the number corresponding to its radius; but if we reduce the two volumes to one, we will have

$$Hg''=R\ 1.898$$

For phosphorus and arsenic the nearest numbers to the constant 1.90 are obtained with

$$P_4=R\ 1.895$$
$$As_4=R\ 1.890$$

Therefore as 1 atom of mercury occupies the same volume as 2 atoms of hydrogen, the atom of mercury is twice the bulk of an atom of hydrogen and the atom of phosphorus and of arsenic in the vapor state occupies only one-half the bulk of an atom of hydrogen.

Since this paper has been read before our Society, I have found a very able and very interesting communication from Mr. A. J. Rossi in the "Iron Age." In this paper Mr. Rossi, in adapting the use of a graphic method, shows that, knowing the analysis of an iron ore, a lime stone and the amount and composition of the ash contained in the fuel to be employed, the charges of a blast furnace corresponding to a certain grade of iron and consequently to a slag of a given composition and fusibility can be obtained without calculation.

CONSTRUCTION OF THE DIAGRAM.

The use of profile paper ruled to the millimeter is very convenient for such diagrams.

We have carried the molecular weights on the line of abcissae at a scale of two millimeters for one of molecular weight and the paper being divided to the millimeter we could even estimate a fractional number very closely.

The vertical scale has been taken equal to twenty-five times the horizontal scale, fifty millimeter vertical representing a radius of 1, five millimeter a radius of 0.1 and every millimeter a radius of 0.02. As we can accurately estimate one-half of the smallest division of the paper we see that the radius can be read exactly to the second decimal. To render the construction of each curve easier to understand we have plotted the ordinates or radii of all the points determined in distinct lines down to the line of abcissae, marking at the foot of each ordinate the abcissae or molecular weight which correspond to it in the tables.