What has been said of selenium oxychloride applies equally well to thionyl chloride, whose dielectric constant is 9.05,[20] and which is known to yield conducting solutions.[13] The conclusions of Riesenfeld and Feld[19] concerning the action of hydrogen sulfide on sulfur dioxide in water solution are that sulfur monoxide is the primary product, and that this polymerizes to yield (with water) polythionic acids. It is entirely possible that sulfur monoxide, produced in a water-free environment, such as in the electrolysis of a hypothetical thiono-acid in thionyl chloride solution, might be capable of independent existence.

Many more solvents suggest themselves as worthy of study. Whatever the results of investigation might be, they cannot fail to throw new and important light on the theory of electrolytic dissociation, and advance our knowledge of the theory of solution.

Summary

Based on a study of the analogy between reactions in water and in phosgene solution, a general theory of acids, bases and salts as related to a parent solvent has been outlined, and applications to other solvents have been suggested.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE OHIO STATE UNIVERSITY]

AVERAGE CROSS-SECTIONAL AREAS OF MOLECULES BY GASEOUS DIFFUSION METHODS

BY EDWARD MACK, JR.

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During the past few years our ideas regarding the sizes and shapes of typical organic and inorganic molecules have been greatly clarified by several interesting lines of work. The Hardy-Langmuir-Harkins treatment of oriented molecules in oil films has developed for us, especially in the hands of Langmuir,[1] and in the extension of his general method by Adam,[2] fairly definite ideas about the length and cross-section of long, slender molecules. Also, the inferences drawn by W. H. Bragg[3] about the sizes and shapes of molecules like naphthalene and anthracene from the X-ray examination of the crystals, and the deductions of W. L. Bragg[4] and Davey[5] regarding the distances separating the centers of atoms in

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[20] Schlundt, *J. Phys. Chem.*, **5**, 513 (1901).

[1] Langmuir, *Proc. Nat. Acad. Sci.*, **3**, 251 (1917); THIS JOURNAL, **39**, 1848 (1917), and other papers.

[2] Adam, *Proc. Roy. Soc.*, **103A**, 676, 687 (1923), and other papers.

[3] W. H. Bragg, *Proc. Phys. Soc.*, **34**, 33 (1921); **35**, 167 (1923); and W. H. and W. L. Bragg, "X-Ray Analysis and Crystal Structure," G. Bell and Sons, **1924**.

[4] W. L. Bragg, *Phil. Mag.*, **40**, 169 (1920).

[5] Davey, *Phys. Rev.*, **18**, 102 (1921); **22**, 211 (1923).

crystals, are all highly suggestive. Again, the extremely important measurements of the viscosities of gases by Rankine[6] and his co-workers have made it possible for them to calculate the average cross-sectional, or "collision" area (by using Chapman's equation) for a considerable number of gases and volatile liquids.

A knowledge of the *average cross-sectional area* may be of great help in drawing some very significant conclusions about the sizes, shapes and structures of molecules, and it has therefore seemed desirable to find a general method for determining the average cross-sectional areas of molecules of substances which are too slightly volatile to be amenable to the viscosity method. Much of our chemical interest centers in substances that are only slightly volatile.

Calculation of the average cross-sectional areas for the molecules of such substances may be made from their diffusion coefficients. In other words, the rate at which molecules A diffuse through a gas B as, for example, through air, depends not only on the absolute velocities of the molecules A and B, but also on the size, that is on the average cross-sectional area of both A and B. The larger the area of A, the more frequently will A molecules collide with B molecules, and consequently the greater will be the interference with the progress of A molecules through the gas. By *average cross-sectional area* is meant that area which, on the average, a diffusing molecule presents to collision or bombardment from all directions by the molecules of the gas through which it is moving.

As a matter of fact, the theory of gaseous diffusion has already been rather fully built up, and the equations which show the precise relationship between the diffusion coefficient and the average cross-sectional area have been derived through the work of Maxwell, Boltzmann, Stefan, Meyer, Langevin, Chapman, Jeans and others. Numerous diffusion coefficients have been measured and some average cross-sectional areas have been calculated and reported in the kinetic-theory literature. Most of these are for gases and very volatile liquids. That the diffusion values for collision areas do not agree closely with Rankine's viscosity values may be largely attributed to the fact that the experimental determinations of diffusion coefficients in most, if not in all cases, have been of a lower order of accuracy than Rankine's results.

It is the purpose of the present paper to describe a new and very simple method for determining diffusion coefficients, and to give the coefficients and the collision areas of such molecules as iodine, benzene, naphthalene, anthracene, toluene, octane, diphenyl, aniline and benzidine. After the description of the experimental method has been given, a comparison of the conclusions reached in this paper will be made with those of W. H.

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[6] Rankine, (a) *Proc. Phys. Soc.*, **33**, 362 (1921); (b) *Proc. Roy. Soc.*, **98A**, 360 (1921), and many other papers.

Bragg and of Huggins[7] regarding the sizes and shapes of benzene, naphthalene and anthracene; with those of Langmuir and of Müller and Shearer[8] regarding the structure of carbon chains; and with the speculations of Kauffler,[9] Cain and Micklethwait,[10] Adams, Bullock and Wilson,[11] and Adkins[12] as to whether diphenyl and benzidine have an extended or a collapsed structure.

Experimental Part

Diffusion coefficients were determined by measuring the rate of evaporation of the various substances through an air space.

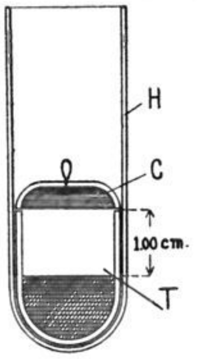

Fig. 1.

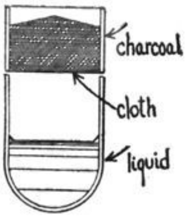

Fig. 2.

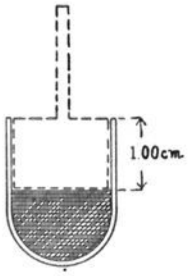

Fig. 3.

In the case of *solids*, a small brass (or glass) cup C, in Fig. 1, was filled with the melted substance. When this had solidified, the surface was rubbed with fine sand paper or emery paper until it was smooth and flush with the rim of the cup. It was then weighed in a small glass weighing bottle on a sensitive assay balance kept in a room at constant temperature (±0.1°). The actual weighings could be easily made to 0.000,01 g. After being weighed, the cup was placed, as shown in the figure, over the open end of a glass tube T containing powdered charcoal (80–100 mesh) in such a way that the substance could evaporate, diffuse through the air space and finally be absorbed by the charcoal at the bottom. This system was contained in a holder tube H which was closed with a rubber stopper and a stopcock, and was placed in a thermostat. On starting the diffusion, the barometer was read and the stopcock was closed.

In the case of *liquids*, a disk of blotting paper of proper size was pressed into the cup C, and then wet thoroughly with the liquid. An alternate method was to place the liquid in the lower end of the tube T, as in Fig. 2, with the charcoal above in a basket made by attaching a piece of silk cloth to the bottom of a glass tube of the same diameter as T.

The diffusion coefficients were calculated by means of the equation

$$g = D.A.t\,(d_1 - d_2)/l \tag{1}$$

where g is the loss in weight in grams of the evaporating substance, D is the diffusion coefficient, A is the circular area in sq. cm. of the air space, t is the time of the determination in seconds, d_1 is the density of the vapor in g. per cc. at the surface of the evaporat-

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[7] Huggins, This Journal, **44,** 1607 (1922); **45,** 264 (1923).

[8] Müller and Shearer, *J. Chem. Soc.*, **123,** 3156 (1923).

[9] Kauffler, *Ann.*, **351,** 156 (1907); *Ber.*, **46,** 3250 (1907).

[10] Cain and Micklethwait, *J. Chem. Soc.*, **105T,** 1437, 1442 (1914), and other papers.

[11] Adams, Bullock and Wilson, This Journal, **45,** 521 (1923).

[12] Adkins, *ibid.*, **46,** 1917 (1924).

ing substance, and d_1 is the vapor density at the other end of the air space, that is, at the charcoal surface. It was assumed that the charcoal, a very highly activated coconut charcoal (for which the author is indebted to Mr. O. L. Barneby, Columbus, Ohio) absorbs the vapor as fast as it reaches the charcoal surface. This assumption was amply justified by the data collected during the progress of the experiments; d_2 may then be set equal to zero. The length l of the air space was adjusted and measured by means of solid brass cylinders each provided with a handle (Fig. 3). These cylinders, which themselves had the desired lengths l, were used to press the powdered charcoal into a firm, compact layer having a flat surface. The length l was generally 1 cm. but in the case of some liquids it was made 6 or 8 cm. to prevent the vapor from approaching the charcoal too rapidly for complete absorption. A greater length also tends to diminish the error introduced by the liquid meniscus; however, it also increases the area of the glass wall on which the vapor may condense. It seems desirable, if the conditions will permit, to let l equal 1 cm.

The effect of gravity on the rate of diffusion is within the experimental error.

Diffusion Coefficient of Iodine

As an illustration of this method for the determination of diffusion coefficients, let us take the results for iodine.

The area A of the diffusion column was 1.50 ± 0.02 sq. cm., the length 1.00 ± 0.01 cm. In one-half hour at a temperature of 25° ± 0.01° and at an average barometric pressure of 739.1 mm. the cup lost 0.001,245 ± 0.000,015 g. This result is the average of six experiments. One sample of iodine was prepared according to the method of Foulk and Morris,[13] a method which has been shown to yield a product of very high purity, approaching the purity obtained by Baxter's method.[14] Another sample used was simply C. P., resublimed iodine. Both samples gave the same results within the stated limit of experimental error. Furthermore, the results were the same when soda lime was substituted for charcoal as the absorbing agent. It is difficult to believe that charcoal and soda lime both absorbed iodine vapor at the same rate, unless they were both absorbing *all of the iodine vapor as fast as it arrived.* Hence d_2 must be zero. To evaluate d_1 it is necessary to know the vapor pressure of iodine at 25°. The value of Baxter, Hickey and Holmes,[15] namely 0.305 mm., was taken. Substitution in Equation 1 gives 0.111 for the diffusion coefficient of iodine in air at 25° and 739.1 mm. At 760 mm. it would be 0.108.

Langmuir[16] has made a rough estimate of the value of the diffusion coefficient for iodine at 20° from the data of Morse on the rate of evaporation of small iodine spheres[17] in quiet air. He found 0.07 as a probable value. I have calculated from my data at 25° that at 20° the diffusion coefficient would be about 0.105. Very recently Mullaly and Jacques[18] have carried on an experiment in which they let iodine vapor and mercury vapor diffuse towards each other through nitrogen gas in a partially evacuated glass tube. Where the mercury and iodine meet, a band of the mercury iodides precipitates and appears on the glass. While it is hardly fair to extrapolate their results to atmospheric pressure (they were working at 10 mm. and lower), I have calculated from their data that the diffusion coefficient at 19.4° in nitrogen at 760 mm. would be 0.075, and

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[13] Foulk and Morris, THIS JOURNAL, **44**, 221 (1922), "Iodine 2," p. 223.

[14] Baxter, *ibid.*, **26**, 1579 (1904).

[15] Baxter, Hickey and Holmes, *ibid.*, **29**, 127 (1907).

[16] Langmuir, *Phys. Rev.*, **12**, 368 (1918).

[17] Morse, *Proc. Am. Acad. Arts Sci.*, **45**, 363 (1910).

[18] Mullaly and Jacques, *Phil. Mag.*, **48**, 1105 (1924).

at 25° in air 0.077, taking into account the fact that the average air molecule has a smaller cross section than a nitrogen molecule (Rankine's values). This value for the diffusion coefficient of iodine in air at 25° seems somewhat too small.

Calculation of Average Cross-Sectional Areas

The calculation of the cross-sectional areas of molecules from the diffusion coefficients may be made by means of the Stefan-Maxwell-Jeans equation.[19]

$$S^2 = \sqrt{\bar{c}_1^2 + \bar{c}_2^2}/3\pi Dn\,(1 + \alpha) \qquad (2)$$

Here, S is the average radius of the diffusing molecule plus the average radius of an air molecule; that is, S equals the distance from the center of a diffusing molecule to the center of an average air molecule when the two are in collision; $\bar{c}_1$ is the mean velocity of all the molecules of the diffusing vapor and $\bar{c}_2$ of all the air molecules; $\bar{c}$ is 0.921 C where $C = \sqrt{3RT/M}$; D is the diffusion coefficient and n the number of molecules in 1 cc. of the gas at the temperature of the experiment and at 760 mm. pressure, since all the present values of D have been reduced to standard pressure; α is a correction which must be made for the persistence of velocity due to the mass of the diffusing molecule which is greater than the mass of the average air molecule. The manner in which α depends on the ratio of the two masses has been fully set forth by Jeans, and the plot of this relationship given in Fig. 4 is made from Jeans' calculated values.

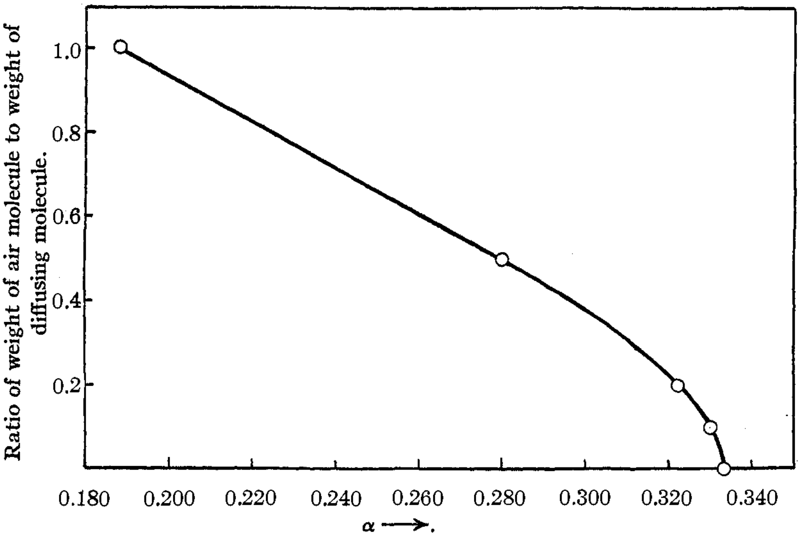

Fig. 4.

In using Equation 2 to obtain the radius of the diffusing molecule, the

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[19] Jeans, "The Dynamical Theory of Gases," Cambridge University Press, **1921**, p. 316.

radius of the average air molecule must be subtracted from S. The value 1.542×10^{-8} cm. was taken as the radius for an average air molecule. This value was made up from Rankine's latest data for the radii of nitrogen, oxygen, argon and water molecules, and from Leduc's values[20] for the volumetric composition of air. It was assumed that the air in the diffusion space was one-half saturated with water vapor, although by actual test there was no detectable difference between the values for the diffusion coefficient when the air was moist and when it was dry.

Using the value 0.108 for the diffusion coefficient of iodine and substituting in Equation 2, the average radius of the iodine molecule is found to be 2.29×10^{-8} cm. and its average cross-sectional area 16.5×10^{-16} sq. cm. Rankine found[6b] by his viscosity method 15.6×10^{-16} sq. cm. The agreement is certainly very good (a difference of less than 6%) especially since Rankine considers that his value may be in error by as much as

TABLE I

DIFFUSION DATA

1 Substance	2 Formula	3 Temp., °C.	4 Vapor press. Mm.	5 Rate of evapn. mg./sq. cm./hr. at l = 1 cm.	6 Diff. coeff. (760 mm.)	7 α	8 Av. radius in 10^{-8} cm.	9 Av. cross-sectional area in 10^{-16} sq. cm.	10 Av. cross-sectional area by shadow method (sq. cm.)
Iodine	I_2	25 ± 0.01	0.305	1.665 ± 1.2%	0.108	0.329	2.29	16.5	
Benzene	C_6H_6	42	(Winkelmann)		.100	.301	2.88	26.1	28.9
Benzene	C_6H_6	42	(Le Blanc and Wuppermann)		.102	.301	2.84	25.3	
Naphthalene	$C_{10}H_8$	25 ± 0.01	0.103	0.1588 ± 1.7%	.0611	.320	3.70	42.9	40.5
Anthracene	$C_{14}H_{10}$	99.2 ± 0.2	.033	.0679 ± 7%	.0783	.325	4.02	50.7	53.8
Methane	CH_4	(Rankine's value, viscosity method)				..	1.57	7.72	7.48
Toluene	$C_6H_5.CH_3$	25 ± 0.1	27.4	42.36 ± 3.6%	.0844	.309	3.01	28.5	31.5
n-Octane	C_8H_{18}	25 ± .1	17.1	2.906 ± 1.3%	.0602	.316	3.79	45.1	(I) 42.1, (II) 33.2
Ammonia	NH_3	(Rankine's value, viscosity method)				..	1.43	6.40	..
Aniline	$C_6H_5.NH_2$	25 ± .1	0.71	0.929 ± 7.5%	.0726	.310	3.41	36.6	..
Diphenyl	$C_6H_5.C_6H_5$	25 ± .01	.0085	.0188 ± 6%	.0727	.323	3.22	32.5	(I) 37.6, (II) 50.9
Benzidine	$H_2N.C_6H_4.C_6H_4.NH_2$	99 ± .1	.00143	.00355 ± 8.5%	.0555	.326	3.60	40.7	..

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[20] Leduc, *Compt. rend.*, **123**, 805 (1896).

several per cent. This agreement encourages the belief that the general method described in this paper is able to give reliable values for diffusion coefficients and also for average cross-sectional areas.

Table I presents the experimental data and the calculated values (Col. 9) for the collision areas of the various molecules.

The accuracy of the experimental values given in Col. 9 depends not only on the accuracy of the determination of the rate of evaporation (Col. 5) but also on the reliability of the vapor-pressure data (Col. 4) and on the reliability of Equation 2. It seems fair to claim an accuracy of 2–5% for the molecular areas of iodine and naphthalene, and of 5–15% for anthracene, toluene, octane, aniline, diphenyl and benzidine.

The meaning of the values in Col. 10 will be explained in the next section. Benzene is too volatile at 25° to lend itself readily to examination by the present method and it is to be hoped that Rankine and his co-workers will study benzene by the viscosity method. However, in Table I there are given the diffusion-coefficient values for benzene at 42°, found by Winkelmann[21] and by LeBlanc and Wuppermann.[22] The vapor pressures of naphthalene and toluene were taken from Barker,[23] and of octane from Woringer.[24] There appeared to be no vapor-pressure data for aniline at room temperature, and the value extrapolated to 25° from Kahlbaum's[25] data (43.1° and higher) seemed improbably low. An approximate determination was therefore made with the usual 4-bulb tensimeter, using paraffin oil as the manometer liquid, and the value 0.71 mm. (mercury) was found for 25° ± 0.1°. All of the other vapor pressures in Table I were determined by a modification of Knudsen's method described elsewhere.[26] The author is indebted to Dr. T. H. Swan of this Laboratory for the vapor-pressure determination for diphenyl and also for checking Barker's value for naphthalene, and to Mr. G. M. Karns for those of benzidine and anthracene. The value for anthracene at 99.2° is in good agreement with that of Niederschulte for 100°; namely, 0.04 mm.[27] Thanks are also due Mr. L. C. Swallen and Mr. H. B. Hass for assistance in the measurement of the diffusion coefficients of toluene, octane and diphenyl, and Mr. W. W. Mills for the preparation of the purified iodine.

Discussion of Results

No inferences about the shape of a molecule can be drawn from a knowledge of its average cross section alone. But if we build a model of the

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[21] Winkelmann, (a) Landolt-Bornstein, "Tabellen," Julius Springer, **1912**, 4th edition, p. 137.

[22] LeBlanc and Wuppermann, *Z. physik. Chem.*, **91**, 143 (1916).

[23] Barker, *ibid.*, **71**, 235 (1910).

[24] Woringer, *ibid.*, **34**, 257 (1900).

[25] Kahlbaum, *ibid.*, **26**, 603 (1898).

[26] Swan and Mack, THIS JOURNAL, **47**, 2112 (1925).

[27] Ref. 21 a, p. 394.

molecule based on chemical behavior or on X-ray examination, or on other types of evidence and, having made the model to scale, determine its average cross-section by some projection method, a close agreement between the diffusion value for the cross section and the model's cross section might reasonably be construed as excellent grounds for thinking the model a good one, especially if the extension of this procedure to a whole family or series of chemical compounds yielded consistent agreement.

The average cross-sectional area of a model would be the average area presented by the model when viewed from all directions or, what amounts to the same thing, the average area viewed from one direction when the model is turned through all possible positions. When a stationary model is viewed from a certain direction, let us say from the front, there are five other directions, or six directions in all, 90° apart, from which the model may be observed; namely, front, back, right, left, above and below. In the same way, there are 26 directions 45° apart, 114 directions 22.5° apart, etc. Obviously, the cross-sectional area as viewed from any one direction is the same as that from the exactly opposite direction as, for example, from the front and from the back. In order to obtain the average cross section of the model for directions 90° apart, only three observations are necessary; for directions 45° apart, 13 observations, for 22.5°, 57 observations, etc.

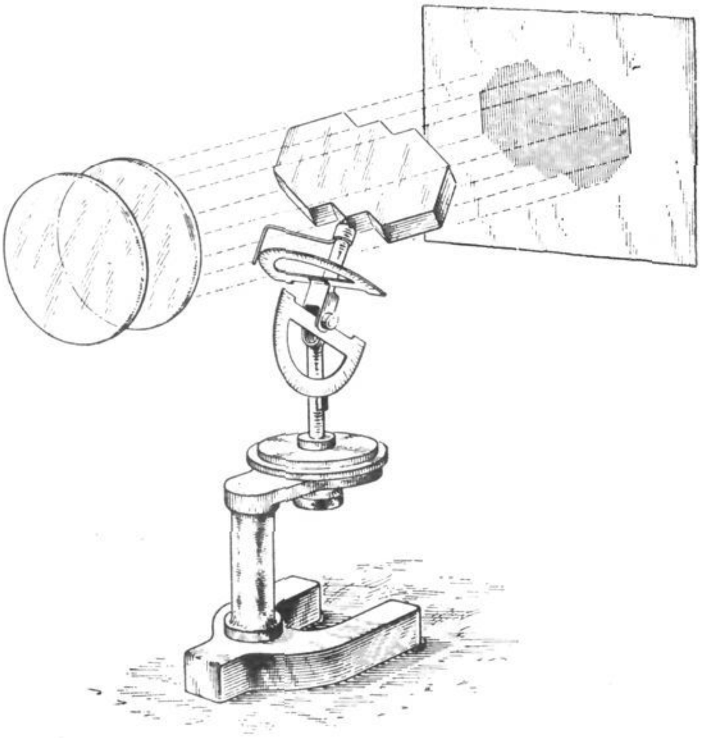

Fig. 5.

Models were constructed of beeswax and were mounted on the device shown in Fig. 5. Shadows of the model were thrown on a paper screen by a strong beam of parallel light coming from a stereopticon lantern and a suitable lens system. The model was easily brought successively into all of the desired positions by turning it through the required angle measured on the upper protractor of the figure and at the same time dipping the model through the required angle on the lower protractor. The outline of each shadow was traced with a pencil, and its area computed with a planimeter. *Since every position of the diffusing molecule is equally* probable, the average cross section of the model is found simply by adding up all the shadow areas and dividing the sum by the number of shadows. Each model was constructed to scale so that 1 cm. represented 1 Å. (10^{-8} cm.). Consequently, the value found for the model's average shadow area in sq. cm. would also represent the average cross section of the molecule itself in 10^{-16} sq. cm.

The question naturally arises as to how many shadow positions must be taken to obtain a fair average value. If the model were a sphere, one shadow would suffice, and of course the more nearly spherical in shape the model, the smaller would be the necessary number of shadows. Table II shows that even for as slender a model as that of anthracene, the average shadow area rapidly approaches an asymptotic value, as the number of positions increases.

TABLE II

THE RAPID APPROACH TO ASYMPTOTIC VALUE

No. of positions	3	13	57
Diff. in angle, deg.	90	45	22.5
Av. shadow area, sq. cm.	41.1	52.8	53.8

All of the shadow areas in Col. 10 of Table I are for 13 positions 45° apart, and they undoubtedly have values very close to those for an infinite number of positions.

Benzene, Naphthalene and Anthracene

The dimensions of the molecules of naphthalene and anthracene have been inferred by W. H. Bragg[3] from the X-ray examination of the crystals and from crystallographic data (axial ratios and angles, and the density) and the results have been found to be in good agreement with Bragg's hypothesis that 6-membered carbon-atom rings of approximately the same size and shape as those present in the diamond lattice also exist in the molecules of such aromatic compounds as benzene, naphthalene, anthracene, phenol, etc. Fig. 6 shows the suggested arrangement of the atoms in anthracene. (The carbon atoms might just as well be represented by tetrahedra as by spheres.) When the four carbon atoms on the right are removed and hydrogen atoms (the smaller spheres) attached to the two carbon atoms C and D, we obtain naphthalene. The diameter of the carbon atoms is approximately 1.50 Å., and the angles of the bonds holding together the carbon atoms and the carbon and hydrogen atoms are tetra-

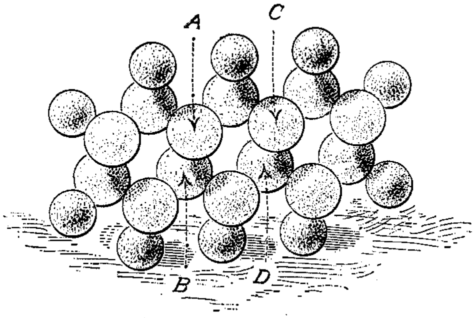

Fig. 6.—Anthracene.

hedral angles, 109°28′. Bragg's X-ray measurements show that the difference in length of the naphthalene and anthracene molecules is 2.5 Å., which is almost exactly the distance A——C across the 6-membered ring of the diamond lattice. By subtracting the over-all length (9.00 Å.) of the carbon rings in anthracene from Bragg's experimental value for the length (11.18 Å.) of the whole molecule, and dividing by 2 we obtain the length of the space occupied by the hydrogen atoms at each end. This is 1.09 Å. in anthracene and also in naphthalene. If we take into account the angle at which the hydrogen atoms are attached to the carbon atoms, we find that the effective diameter of the hydrogen atoms is 1.35 Å., or the distance from the center of a carbon atom to the outermost surface of the attached hydrogen atom is 0.75 + 1.35 or 2.10 Å.

In preparing the skeletal model shown in Fig. 6 for examination by the shadow method for determination of its average cross section we are perhaps justified in making a solid model of it by enclosing it with plane bounding surfaces tangent to the hydrogen atoms, as shown in Fig. 7. The justification for this procedure is that the molecule itself possesses a certain field of force, molecular domain, or co-volume, into which molecules of air cannot penetrate (during the diffusion of anthracene molecules through air). The solid models of anthracene and naphthalene, shown in Figs. 7 and 8, have been made up from Bragg's values, letting 1 cm. equal 1 Å. The sharp edges and corners, and the re-entrant angles certainly have very little, if any significance. But since we have no means of knowing in just what manner the field of force is rounded off, we may adopt the models as shown as the best approximations which can be made for the present. It should be pointed out that the depth of the skeletal structures for naphthalene and anthracene (about 2 Å.) is not as great as the depth of the solid models, in which we have used approximately Bragg's value for the depth, 3.02 Å., which is the depth deduced for the molecules as they are packed together face to face in the crystal solid. Of course,

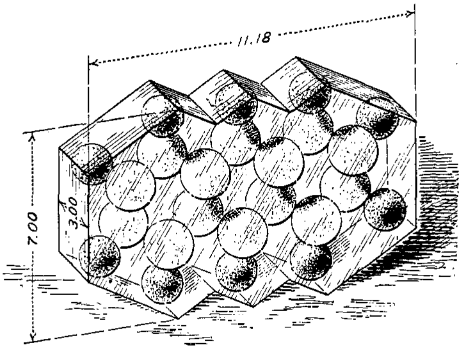

Fig. 7.—Anthracene.

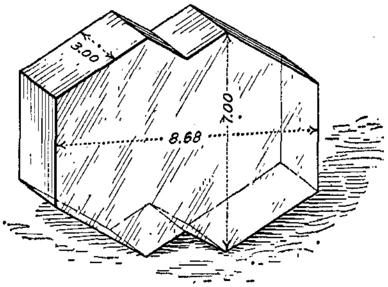

Fig. 8.—Naphthalene.

it does not follow necessarily that the molecules will exhibit the same size to kinetic-diffusion tests that they do to X-ray examination; in fact it has already been shown by workers in this field that viscosity values for the radii of molecules of neon, argon, krypton and xenon are distinctly different from the X-ray values.

In the present case, however, the agreement between the experimentally determined cross sections for both naphthalene and anthracene, namely, 42.9 and 50.7 × 10^{-16} sq. cm., and the average shadow areas of the Bragg models, 40.5 and 53.8 sq. cm., is remarkably close (Col. 10, Table I).

Fig. 9 represents the model for benzene, which is also made by attaching hydrogen atoms of effective diameter 1.35 Å. to the diamond carbon ring. The resulting dimensions are slightly different from those suggested by Bragg based on X-ray examination of solid benzene. But the shadow area is practically the same for both models. The agreement between the shadow area 28.9 and the experimental value for the cross section 25.3 is fair. But it is probable that the value 25.3 obtained from the diffusion coefficient of LeBlanc and Wuppermann (which seems more reliable than that of Winkelmann) is too high, due to the errors inherent in the diffusion method employed.

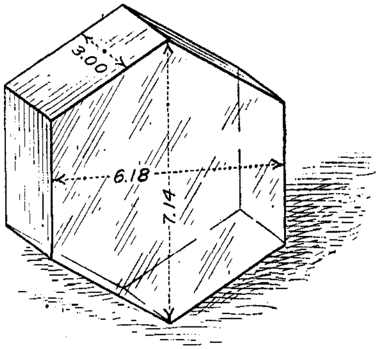

Fig. 9.—Benzene.

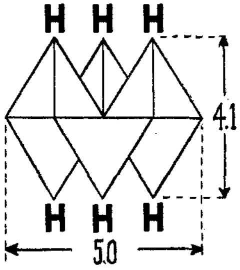

Fig. 10.—Huggins' model for benzene.

The value found by Adam[2] for the cross-sectional area (23.8 × 10^{-16} sq. cm.) of the benzene group *tipped up on end* in an oriented molecule of an oil film, and viewed from above, is in substantial agreement with the model of Fig. 9.

Huggins[7] has also proposed models for benzene and other aromatic molecules, which seem to fit very well some of the crystallographic data (axial ratios and angles, and the density). Fig. 10 shows the model for benzene. Since in Huggins' suggested arrangement of the molecules in the crystal lattice of benzene the vertical distance, between centers, from one molecule to the next one above it is 7.86 Å., we might fairly consider

7.86 Å. as the height of the molecule, or at least as the height of its molecular domain. This means that the hydrogen atoms would have an effective diameter of about 1.9 Å. and that the average cross section of the model would be about 30 sq. cm., for naphthalene about 45.5, and for anthracene about 59.5. These values are too large to fit the diffusion data. This is not necessarily a serious objection to Huggins' theory of the lattice structure of the crystals of aromatic compounds since, as has already been said, there is no good reason for expecting molecules to exhibit exactly the same shape and volume when they are individual gas molecules that they do when parts of a solid crystal.

When we construct a model of the gaseous benzene molecule by taking Huggins' 6-membered carbon ring and attaching hydrogen atoms of effective diameter 1.35 Å., as in the Bragg model, the average cross section becomes about 24.0 sq. cm. In the same way, for naphthalene it would be about 35.5 and for anthracene about 51.0.

Methane and Toluene

If we assume that the effective diameters of the carbon atom and the four hydrogen atoms in the methane molecule are the same that they are in naphthalene and anthracene, the model for methane is that shown in Fig. 11. The average shadow area for this model is 7.48 sq. cm., which agrees quite well with Rankine's value for the molecule itself, 7.72 × 10^{-16} sq. cm., found by the viscosity method.

The toluene model, which need not be shown, was simply made from the models of benzene and methane, and gave an average shadow area of 31.5 sq. cm.; it shows the same order of agreement with the experimental value as does that of benzene. Since the methyl group is attached to the phenyl group by a single bond, it is no doubt free to rotate around the axis of the bond to some equilibrium position with respect to the phenyl group, and while we do not know what this position is, it is true that the shadow area for any other position would not be appreciably different from that which was determined.

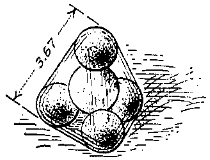

Fig. 11.—Methane.

Octane

Langmuir has shown through his oil-film experiments that the carbon atoms in aliphatic chain compounds are arranged in a zigzag fashion. Müller and Shearer[8] have confirmed his conclusions by X-ray examination. They have further concluded that the character of the zigzag arrangement may differ in different cases. For example, in the ester octyl-palmitate, represented in Fig. 12, Müller and Shearer interpret their X-ray data as showing that the alcohol end of the molecule (the part below the carboxyl group in the figure) has its carbon atoms arranged in the manner depicted in the drawing, and that the carbon atoms of the acid part of the molecule are connected together in an entirely different way, as shown. All of the angles between the bonds holding the carbon atoms together are in both cases tetrahedral angles, approximately 109°.

It would be very interesting to determine what the type of arrangement is in the *n*-octane molecule. Two beeswax models were made, one on the assumption that the carbon atoms are arranged as in the upper part of Fig. 12, the other as in the lower part. Hydrogen atoms, of the same diameter as in methane, were attached to each carbon atom. Each hydrogen atom in the long rows of the figure is directly above, and conceals a hydrogen atom lying below it on a line perpendicular to the plane of the paper. Viewed from the end, the lower octane model has a rectangular cross section 3.86 cm. wide and 3.67 cm. deep, with the corners rounded to correspond to the curvature of the hydrogen atoms. The ends taper like those of a pyramid. The length from tip to tip is 12.21 cm. The upper octane is obviously much shorter, only 10.7; it is 4.10 wide, and its depth (perpendicular to the plane of the paper) is the same as for the lower octane, and also the same as the length of the edge of the methane molecule, namely, 3.67 cm. The average shadow area for the smaller model is 33.2 sq. cm., for the larger 42.1. The latter is in good agreement with the experimental diffusion value 45.1 × 10^{-16} sq. cm., and hence the diffusion evidence is strongly in favor of the same zigzag arrangement for octane as found by Müller and Shearer for the alcohol part of the ester molecule.

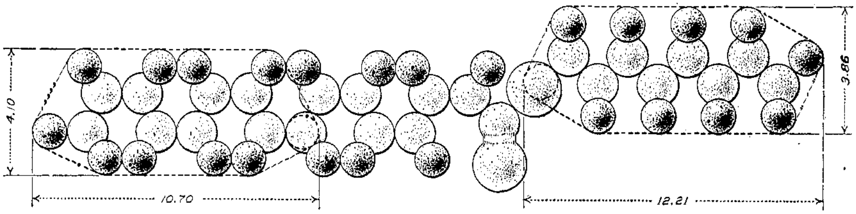

Fig. 12.

Huggins' theory would lead to no different structure for aliphatic carbon chains than that presented here.

Diphenyl

A considerable quantity of chemical evidence[9,10,11,12] has been brought forward to support the view that diphenyl does not have an extended structure, such as shown in Fig. 13, but that one phenyl group is bent back on the other one to give a folded or collapsed structure. This information about the structure of diphenyl was brought to the author's attention by Dr. Homer Adkins of the University of Wisconsin, who suggested that it might be worth while to study diphenyl. The extended model of Fig.

13 gave an average shadow area of 50.9 sq. cm. The collapsed model of Fig. 14 was constructed by pushing together two phenyl groups, face to face, until the carbon atoms touched. This produced a depth of 5.0 cm. for the model. The end of the molecule at which the two groups are linked together, the "hinge" end, was rounded off, as shown in the figure, because of the detachment of the two hydrogen atoms. The average shadow area of this collapsed model is 37.6 sq. cm., in fairly good agreement with the experimental result 32.5×10^{-16} sq. cm., quite possibly within the experimental error and certainly in much better agreement than in the case of the extended form.

There are several other positions, intermediate between those of Figs. 13 and 14, which the two phenyl groups might take with respect to each other, assuming always tetrahedral bonding and free rotation, about the bond connecting the two phenyl groups, to a most stable position. But the value for none of these would check as well with the diffusion value as does that of the model of Fig. 14. Regardless, however, of whether or not the model of Fig. 14 is a fair representation of the real structure of diphenyl, the diffusion value for the average cross section of diphenyl, 32.5×10^{-16} sq. cm., is so slightly larger than that for benzene, 25.3×10^{-16} sq. cm., that some sort of a highly collapsed structure for diphenyl is clearly indicated.

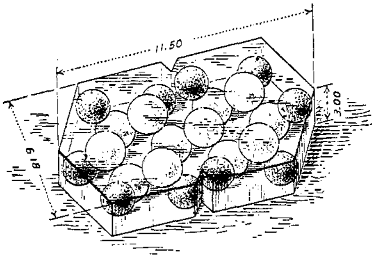

Fig. 13.—Diphenyl, extended.

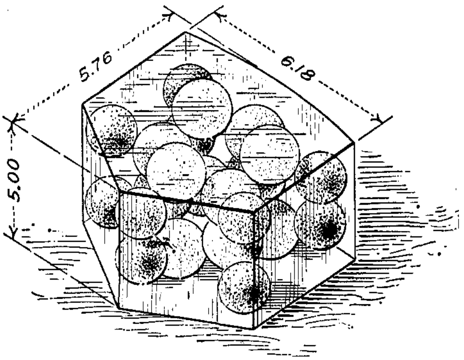

Fig. 14.—Diphenyl, collapsed.

When two of Huggins' models for benzene are combined to give diphenyl (with hydrogen atoms of diameter 1.9) the extended molecule has an average cross section of about 55 sq. cm., and the most highly collapsed form is not much smaller, about 53 sq. cm. Even with hydrogen atoms of diameter as small as 1.35, the extended and collapsed models have average cross-sectional areas of about 45 and 43 sq. cm., respectively. Furthermore, it seems doubtful whether, with the Huggins' model, the extreme carbon atoms of the two phenyl groups could be brought closely enough together in the collapsed form to satisfy the demands of the chemical evidence regarding the nature of the bridging which occurs between these two positions, each *para* to the hinge corner of the rings.

Ammonia, Aniline and Benzidine

There seems to be hardly enough information about the size of the nitrogen atom, and the distance between the centers of atoms of nitrogen and hydrogen and of nitrogen and carbon chemically combined, to permit the construction of models of ammonia, aniline and benzidine. It is best for the present, at least, merely to point out that the experimental values for the average cross sections listed in Table I, Col. 9 (the ammonia value is Rankine's) are of the right order of magnitude. The small cross section of benzidine suggests the conclusion that it, too, like diphenyl, possesses a highly collapsed structure.

There are some chemical reasons for believing that the nitro analog of benzidine, that is, *p*-dinitro-diphenyl has an *extended* structure. We are at present engaged in testing this hypothesis by the diffusion method. Work is also in progress on the molecules of di- and triphenylamine, di-, tri- and tetraphenylmethane, fumaric and maleic acids, two diphenic acids and other compounds.

Summary

1. A new and simple method for the determination of the diffusion coefficients of volatile substances is described.

2. From the diffusion coefficients the average cross-sectional areas of the molecules of iodine, benzene, naphthalene, anthracene, toluene diphenyl, aniline and benzidine are calculated by the Stefan-Maxwell-Jeans equation.

3. The cross sections of molecules so determined are compared with the average cross sections of the molecules of benzene, naphthalene and anthracene proposed by Bragg from X-ray analysis. Models of Bragg's molecules have been constructed of wax, to scale, and the average cross sections determined by a shadow-projection method. The agreement is very good. Values determined from Huggins' models do not agree with the diffusion values quite so well.

4. It is shown that the carbon atoms in the chain of the *n*-octane molecule are probably arranged in the same zigzag manner as found by X-ray examination by Müller and Shearer for the alcohol part of ester molecules. The diffusion method confirms the conclusion, based on chemical evidence, that diphenyl and benzidine have a collapsed structure.

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