

TABLE I
 DATA AND CALCULATED VALUES

Wt. % of NaCl	$t \dots 10$		30	40	Σxy	d_{25}	$\alpha \times 10^4$	
	$x \dots -3$	-1					Calcd.	Graph.
1	0.0	17.3	44.6	79.9	267.0	1.0041	2.659	2.64
2	.0	19.6	48.5	84.9	283.6	1.0111	2.805	2.82
4	.0	24.0	55.9	94.3	314.8	1.0253	3.070	3.09
6	.0	28.1	62.7	103.0	343.6	1.0396	3.305	3.34
8	.0	31.8	68.8	110.9	369.7	1.0541	3.507	3.56
10	.0	35.1	74.3	118.1	393.5	1.0688	3.682	3.66
12	.0	38.0	79.3	124.7	415.4	1.0837	3.833	3.83
14	.0	40.6	84.0	130.9	436.1	1.0987	3.969	3.92
16	.0	43.5	88.5	136.8	455.4	1.1140	4.088	4.05
18	.0	45.3	92.8	142.5	475.0	1.1295	4.205	4.18

Average deviation from curve $\approx 0.018 \approx 0.05$

Summary

In conclusion, a simplified method of calculating tangents from the theory of least squares has been presented. By choosing equally spaced positive and negative values of the independent variable and making the y -axis pass through the point at which the tangent is desired, $dy/dx = \Sigma xy / \Sigma x^2$. Tangents may thus be calculated more rapidly and precisely than by graphical means. The method may be applied in many other cases beside that used as an illustration.

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

THE COLLISION AREAS AND SHAPES OF CARBON CHAIN MOLECULES IN THE GASEOUS STATE: NORMAL-HEPTANE, NORMAL-OCTANE, NORMAL-NONANE

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In a chapter on "The Effects of Molecular Dissymmetry on Properties of Matter," Langmuir presents¹ plausible reasons, based on surface energy considerations, for believing that a molecule such as palmitic acid, when isolated in the gas phase or in solution, has its carbon chain coiled up into an approximately spherical form rather than fully extended as a straight chain. Du Noüy concludes that the chain of the giant protein molecules is, in certain situations, folded up² into a parallelepiped or prism-like form, and Hauser³ recently interprets the x-ray diffraction patterns, obtained when rubber is stretched and unstretched, as meaning that the

¹ Alexander, "Colloid Chemistry," The Chemical Catalog Co., New York, 1926, Vol. I, pp. 525-546.

² Du Noüy, *J. Biol. Chem.*, **64**, 595 (1925).

³ Hauser, *Ind. Eng. Chem.*, **21**, 249 (1929).

rubber molecule is coiled up in a helix before stretching and becomes pulled out during the stretching process. Indeed these views all bear a resemblance to Frankland's suggestion many years ago that a carbon chain may be coiled into a helix—a suggestion borne out by the work of Pickard and Kenyon on the dependence of rotatory power on chemical constitution.⁴ The present investigation was undertaken to determine whether the molecules of normal heptane, octane and nonane, in the gas phase, are extended or coiled up or what their shapes are.

The method employed involves a calculation of the collision area of the molecule from gaseous viscosity measurements, and then, in an attempt to obtain a definite idea of the average molecular shape, a comparison of the numerical value of this collision area with the numerical value of the average cross-sectional area of a *model of the molecule made to scale*. For the purpose of estimating such model areas a shadow-graphic scheme was suggested and applied in a previous paper.⁵ That scheme, with some modification, serves satisfactorily in the present investigation. In the meantime, also, the data regarding the sizes of atomic domains, and the distances between atomic centers, and the general background of information needed to construct good models, have been greatly improved.

The details of the model area technique will be given later in this paper after the experimental procedure and the gaseous viscosity data have been presented.

Experimental Procedure

We have made use of the form of apparatus set up by Lowry and Nasini,⁶ which in turn closely resembles that employed by Rankine and Smith.⁷ Figure 1 shows the arrangements. The glass parts were all made of Pyrex glass. The vapor of the volatile liquid (which itself was stored in the reservoir tube R_1) was allowed to transpire through the capillary tube C from a region of higher temperature T_1 to a region of lower temperature T_2 , and the viscosity was calculated in the usual way from the time of transpiration, the dimensions of the capillary, and the pressure head of the transpiring vapor.

The liquid, *e. g.*, heptane, was boiled out to remove dissolved gases, and then in a small sealed tube, A, which was completely filled with the liquid to avoid the presence of air, was introduced into the apparatus in the chamber B. The whole system was thoroughly exhausted through a connection at P with a mercury vapor diffusion pump, and sealed at P. The tube A was then broken by allowing the slug of iron I, encased in glass and magnetically controlled, to fall. The liquid was distilled into the reservoir R_1 , which was cooled by pouring some ether over it. During the process of breaking the glass container A and the subsequent distillation of the liquid into R_1 , the glass trap D prevented the entrance of small pieces of broken glass into the capillary. The system was sealed off at S_1 and S_2 , and the accessory loading tubes (drawn in the figure with dotted lines) removed.

⁴ Pickard and Kenyon, *J. Chem. Soc.*, **103**, 1923 (1913).

⁵ Mack, *THIS JOURNAL*, **47**, 2468 (1925).

⁶ Lowry and Nasini, *Proc. Roy. Soc. (London)*, **A123**, 686 (1929); Nasini, 692, 704.

⁷ Rankine, *ibid.*, **A88**, 575 (1913); Smith, *ibid.*, **A106**, 83 (1924).

During a run the water thermostat T_1 was automatically controlled at a convenient temperature, within 0.01° , and the temperature of T_2 was maintained at 0° with crushed ice. The rate at which transpiration occurred was followed by measuring the rate of travel of the liquid meniscus down the small tube R_1 . This tube was carefully calibrated and was mounted over a milk-white porcelain scale. The position of the meniscus was observed through the glass front of the thermostat, with a reading microscope, and interpolations between scale divisions made with a filar micrometer. From the volume of the escaped liquid, and its density, the mass transpired in a given time was calculated. The densities of heptane, octane and nonane at the thermostat temperatures were calculated from the following general empirical formula, where t_s is 0° , t is the temperature at which the density is sought and d_s is the density at 0° .

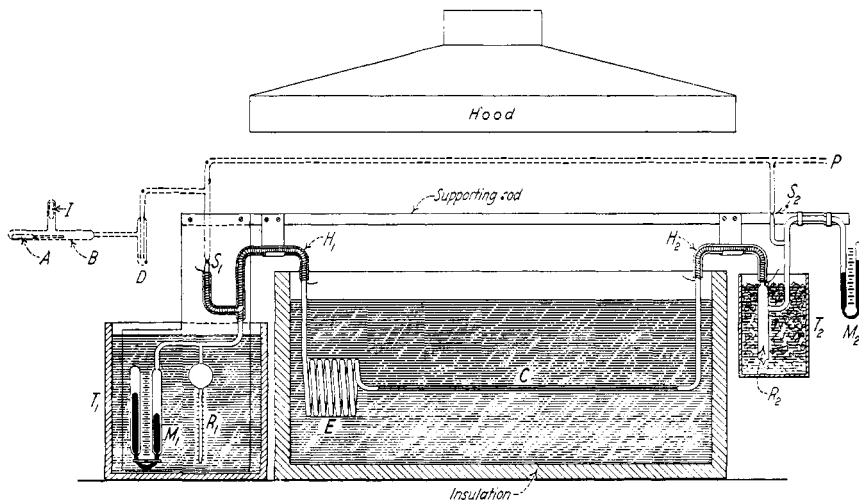


Fig. 1.

$$\text{Density}^8 = [d_s + 10^{-3}\alpha(t - t_s) + 10^{-6}\beta(t - t_s) + 10^{-9}\gamma(t - t_s)^3] \pm 10^{-4}\Delta$$

For *n*-heptane: $d_s = 0.70048$; $\alpha = -0.8476$; $\beta = 0.1880$; $\gamma = -5.23$

For *n*-octane: $d_s = 0.71848$; $\alpha = -0.8239$; $\beta = 0.4459$; $\gamma = -5.293$

For *n*-nonane: $d_s = 0.7333$; $\alpha = -0.75$; $\beta = -0.455$

The two portions, H_1 and H_2 , of the system which project above the temperature-controlled baths were heated electrically to prevent condensation of the vapor in them. The capillary tube C was supported in a large thermostatically controlled ($\pm 0.5^\circ$) and well-stirred tank of tempering oil, with arrangements for heating the oil electrically to temperatures of 100, 150, 200 and 250° . The fumes from the hot oil were carried away by the hood which hung over the apparatus. The glass coil E gave the transpiring vapor a chance to attain the temperature of the oil-bath before reaching the capillary. The driving pressure and the condensing pressure were both observed with reading microscopes on the scales of the mercury manometers M_1 and M_2 , respectively. In general the driving pressure was somewhat lower and the condensing pressure somewhat higher than the true vapor pressures.

The capillary C was selected from a stock of small Pyrex capillary tubes. The

⁸ "International Critical Tables," The McGraw-Hill Book Co., Inc., New York, 1929, Vol. III, pp. 29-30.

uniformity of bore was carefully tested at 5-cm. intervals by measuring the length of a mercury thread with a comparator, and then a section of very uniform bore was cut out of the much longer piece for use. The capillary, when sealed into the apparatus, had a length of 52.2 cm. measured on a standard brass scale, and an average radius of 0.01449 cm.

After a transpiration, the liquid which collected in the condenser R_2 could, of course, be returned to R_1 by reverse distillation, for further runs.

With this apparatus we were able to obtain most satisfactorily reproducible results. We checked Lowry and Nasini's⁶ viscosity results for toluene very closely. Ordinarily it was possible to check transpiration times over a period of two to three hours to within ten or twelve seconds and, in the case of nonane, two transpirations of 105 minutes each checked within two seconds.

The exceptionally pure samples of *n*-heptane, *n*-octane and *n*-nonane, with corrected boiling points, respectively of 98.38, 125.59, and 150.71°, were very kindly supplied to us by Mr. Thomas Midgley, Jr.

Viscosity Data.—The viscosity, η , of the vapor was calculated from the experimental data by means of the equation,

$$\eta = \frac{\pi r^4 (p_1^2 - p_2^2) t}{16 l p_0 m} \cdot \frac{T_0}{T_1} \cdot d$$

where r and l are the radius and length of the capillary, p_1 and p_2 the driving and condensing pressures, p_0 is normal pressure (76 cm.), m is the mass transpired in time t , T_0 is 273° absolute and T_1 the absolute temperature of the capillary, and d is the density of the vapor at N. T. P.

Corrections for expansion of the Pyrex capillary tube with rising temperature are small enough to be neglected, as are also the kinetic energy corrections. The correction for slip, however, is appreciable and was made. This was done with the equation

$$\eta \text{ (corrected)} = \eta (1 + 4 \zeta / r)$$

where r is the radius of the capillary, and ζ , the coefficient of slip, is given by the equation

$$\zeta = 1.70 \eta \sqrt{3RT/M} / (p_1 + p_2)$$

Reynolds' criterion was applied to determine whether the experimental conditions of transpiration had been correctly chosen to insure viscous flow and not to allow turbulent flow. This criterion, expressed in the form

$$r d v / \eta < 1000$$

demands that the left-hand side be less than about 1000. Here r is the radius (in cm.) of the capillary, d is the density (in g./cc.) of the vapor, v is the velocity of efflux of vapor (cc./sec./sq. cm. of capillary cross section) and η is the viscosity (g./cm./sec.). In all of the measurements reported here, this term is considerably less than 1000. For example, in the case of heptane at 100°, the most rapid transpiration, it has a value of about 29.

In Table I are listed the viscosity data, including the viscosities corrected for slip (in the last column).

TABLE I
 VISCOSITY DATA FOR HEPTANE, OCTANE AND NONANE

	Temp. (°C.) of capillary	p_1 , cm.	p_2 , cm.	Rate of transpira- tion, g./hr.	$\eta \times 10^{-4}$	η (corrected) $\times 10^{-4}$
<i>n</i> -Heptane	100.4 ^a	6.33	2.10	0.1721	0.711	0.717
	150.5	6.39	2.18	.1356	.803	.811
	202.2	6.52	2.18	.1115	.910	.922
	251.6	6.60	2.34	.09331	.994	1.08
<i>n</i> -Octane	100.4	3.04	0.800	.05054	.664	0.675
	150.6	3.04	.800	.03996	.740	.750
	202.2	3.035	.830	.03154	.828	.848
	250.9	3.05	.845	.02645	.903	.928
<i>n</i> -Nonane	100.3	2.29	.401	.03593	.620	.633
	150.3	2.29	.478	.02830	.685	.702
	202.1	2.29	.500	.02271	.760	.781
	250.8	2.282	.555	.01858	.824	.851

^a Temperatures were read on thermometers, corrected for stem emergence, and standardized against Bureau of Standards thermometers.

Sutherland Constants.—The Sutherland equation

$$\eta = \frac{k \cdot T^{3/2}}{C + T}$$

was employed to obtain the Sutherland constant C . The different values of $T^{3/2}/\eta$ at the different temperatures, T , were plotted against T , and the straight line was extrapolated to obtain the negative intercept on the temperature axis. The values of these intercepts, which are the Sutherland constants, were as follows: *n*-heptane, $C = 445$; *n*-octane, $C = 337$; *n*-nonane, $C = 276$.

The Sutherland constants, obtained in this way, are necessarily approximate values only, because of the very considerable extrapolation involved. They represent, however, the best obtainable values under present circumstances and, in view of the fact that the data points lie almost exactly on a straight line, the Sutherland constants are probably not very much different from the true values.

In this connection, an empirical equation, $C = 1.47 T_b$, has been suggested,⁹ to predict the Sutherland constant from the boiling point on the absolute scale. Titani,¹⁰ who has carried out a large number of measurements of the viscosities of organic vapors, compares his results for the Sutherland constants of ethane, propane, butane and a number of other substances, with the values predicted empirically from the boiling points. The agreement is not particularly good. Arnold¹¹ uses the Vogel equa-

⁹ Vogel, *Ann. Physik*, **43**, 1235 (1914).

¹⁰ Titani, *Bull. Chem. Soc. Japan*, **4**, 277 (1929); **5**, 98 (1930).

¹¹ Arnold, *Ind. Eng. Chem.*, **22**, 1091 (1930).

tion to obtain Sutherland constants, and then by a further treatment of these, calculates diffusion coefficients.

While this empirical relationship may serve a useful purpose in arriving at rough estimates of Sutherland constants for certain kinds of molecules, particularly small molecules, it can hardly be universally valid. One would expect it to break down entirely in the case of even moderately large and complicated molecules. During the boiling process, the forces which come into play to prevent the escape of a molecule from the liquid are active, undoubtedly, over practically the whole surface of the molecule, or at least over a large fraction of the surface. In the encounter of two *gaseous* molecules, if the molecules are small, it is possible that a large part of the van der Waals field of force of each molecule becomes involved in the act of attraction, when the two molecules approach closely. But, on the other hand, as the molecules become larger and increasingly complicated, so that the spacial arrangement of atoms and groups of atoms interferes appreciably with close approach of the effective centers of the two molecules, in increasing measure will smaller and smaller portions of the whole molecular surface be involved in the collision. Since the Sutherland constant is a measure of the attractive force during collision, it is therefore to be expected that the Sutherland constants may decrease, through a series of larger and larger molecules, while at the same time the boiling points are increasing.

Thus the present values for Sutherland constants for *n*-heptane, *n*-octane and *n*-nonane have just been given as 445, 337, 276, respectively; the values calculated from the boiling points by Vogel's equation are 546, 586, 613. The empirically calculated values for benzene and toluene are 372 and 564, whereas Lowry and Nasini⁶ report experimental values of 380 and 370; and we would predict that the Sutherland constants for ethyl-, propyl-, butylbenzene, etc., will be found to be successively smaller, in spite of the increasing boiling points.

Collision Areas.—The collision areas of the heptane, octane and nonane molecules were calculated with Chapman's¹² equation

$$\bar{A} = \frac{0.0868 (1 + \epsilon_\alpha) d_0 \bar{V}}{n\eta [1 + (C/T)]}$$

where \bar{A} is the collision area of the molecule considered as an attracting, elastic sphere; d_0 is the density of the vapor at standard conditions; \bar{V} is the average velocity of the molecules at temperature T ; n is the number of molecules per cc. at standard conditions; η is the viscosity of the vapor at temperature T ; C is Sutherland's constant; $(1 + \epsilon_\alpha)$ is a correcting term, but in the present cases differs from unity by less than 1%, and hence is not applied.

¹² Chapman. *Trans. Roy. Soc. London*, **A216**, 347 (1916).

The results of the calculation of the collision areas, expressed in square Ångström units, are: *n*-heptane, 26.7; *n*-octane, 34.9; *n*-nonane, 42.5. Rankine and Smith have obtained the value 7.72 for methane;¹³ and Titani¹⁰ gives the values 10.63, for ethane, 13.5 for propane, 16.1 for *n*-butane, and 17.0 for isobutane. These collision areas, calculated from the Chapman equation, are independent of temperature, and may be false to the extent to which the Sutherland model does not hold; and may be in error because the Chapman equation is strictly applicable only to spherical molecules, such for example as the rare gas atoms. It has not yet been possible to develop an equation for an assembly of molecules with other than spherical symmetry. It does seem likely, however, that non-spherical molecules, if approaching one another with an equal degree of probability from all directions, and if oriented with respect to one another in a purely chance fashion, would behave on the average effectively as spheres. At any rate the collision areas just listed are of the proper order of magnitude and are very self-consistent.

Method for Obtaining Model Areas.—In a paper,¹⁴ soon to be published, where the hydrogen atom size is discussed, it is pointed out that the average methane molecule, although of tetrahedral structure, is probably spinning rapidly enough to present itself as a sphere of revolution in molecular encounters in the gaseous state. We can, therefore, calculate its *effective radius* from Rankine and Smith's value of 7.72 sq. Å. for the average cross-sectional area. The result is 1.57 Å. Further, since the distance between the carbon nucleus and the nucleus of a hydrogen atom bonded chemically to the carbon as in methane, is calculated¹⁴ to be about 1.08 Å., the atomic domain, or electron bulge beyond the hydrogen nucleus, under the conditions of gaseous molecule bombardment, is therefore 0.49 Å., or about 0.50 Å. With these dimensions in mind, and with the assumption of tetrahedral carbon bonds, we may proceed to build models of the longer carbon chain molecules. These models, of course, represent the sizes of molecules in collision. Between collisions the atomic domains of the hydrogen atoms around the outer surface of the molecules may enlarge considerably. But the impact of encounter may be thought of as virtually compressing these domains, and the outer surface envelope of the model corresponds to the surface of a molecule when battered in by collision.

Figure 2 (a) gives the model of ethane with an end view at (b). The distance between the nuclei of the two carbon atoms is taken as 1.54 Å. That the methyl groups would be spinning about the *x-x* axis rapidly enough to make the ethane molecule effectively a cylinder of revolution can be shown by the same reasoning employed in the case of methane.¹⁴

¹³ Rankine and Smith, *Phil. Mag.*, **42**, 615 (1921).

¹⁴ Mack, *THIS JOURNAL*, "The Spacing of Non-polar Molecules in Crystal Lattices."

The molecule would also be spinning end over end about the y - y axis and the z - z axis (the latter perpendicular to the plane of the paper in (a)). Such end over end spins are to be expected from the partition of energy among the different active degrees of freedom as indicated by the value of the ratio of specific heats, 1.21. However, because of the relatively considerably smaller frequencies of the end over end rotations, the ethane molecule would probably present itself in molecular encounters only partially as a sphere and much more nearly only as a cylinder of revolution, with a length of about 3.25 \AA ., and a radius of about 1.52 \AA ., and with the end edges rounded off to the hydrogen atom domain curvature, as shown in Fig. 2 (a). At least, the molecule may now be treated as a cylinder, rather than as a sphere, for the purpose of illustrating the shadow-graphic method of estimating the average cross-sectional area.

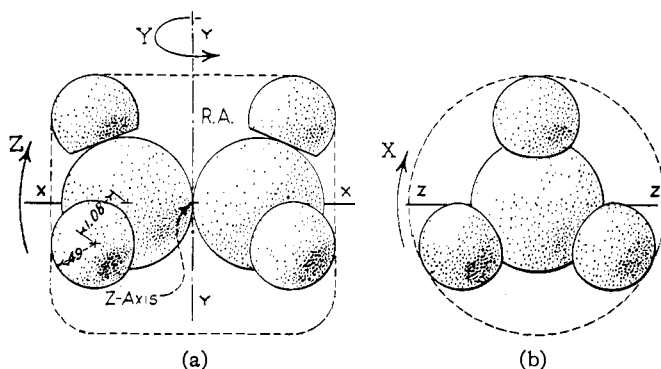


Fig. 2.

Such a cylindrical molecule of ethane would, in the gaseous state, be continuously bumped by neighboring molecules which drive in upon it from all directions. All directions of approach may be supposed to be equally probable. The target area which the molecule presents to this bombardment would therefore be the average of all its cross-sectional areas viewed from all directions. Similarly, every molecule which approaches will have the opportunity, because of its chaotic spin, of orientation in any possible position, at the instant of impact; or at least this will be true if there are no forces acting to swing the axes of the two colliding molecules into certain definite positions with respect to one another (Keesom orientation). On the assumption that there are no orientating forces of this sort the target area of a bombarding molecule would also be its average cross-sectional area viewed from all directions.

The counterpart of this with the model would be the average of all the cross-sectional areas of the model when viewed from all positions. Conceivably such an average could be obtained by integration of the cross-

sectional area of the model turned through the proper angles. But such an integration for most of the ordinary molecules would, as Rankine¹⁵ has pointed out, be exceedingly difficult and laborious. Another method, very simple and satisfactory enough for the purpose in view, is the shadow-graphic method, already mentioned. A model is made to scale (one inch for an Ångström unit is found to give a very convenient model size), and mounted on a support provided with two protractor circles and arranged so that the model can be brought into any orientation by dipping and turning motions. The cross-sectional area of the model in any particular position is obtained by throwing a shadow of it, with parallel light, onto a paper screen, and measuring the area of the shadow in square inches with a planimeter.

Naturally it would be impossible to take enough shadow areas to correspond with all of the infinitely large number of positions around the model from which it could be viewed. Fortunately, only a few positions are necessary, about a dozen equally spaced as to angle, around the model. It can be shown that as the number of positions increases, the average shadow area very rapidly approaches an asymptotic value.

For example, let us take the case of ethane. Imagine that the model of Fig. 2 (a) is placed in a polar axis of a regular octahedron. If we view the model along the axes of the octahedron, *i. e.*, from positions 90° apart, there are six cross-sectional areas, namely, those viewed from above, from below, from right, from left, from in front and from behind. Pairs of shadows taken from opposite ends of polar axes are exactly alike; and we need take only three shadows, therefore, to obtain the average cross-sectional area with respect to approach positions 90° apart. These three shadow areas are 9.5, 9.5 and 7.4 sq. inches; the average is 8.8.

Now let us place the ethane model in one of the axes, a_1 (Fig. 3), of an icosahedron, the polyhedron having the largest number of regular faces that can be inscribed in a sphere. We may now view the model from the twelve summits of the icosahedron, from positions 63°26' apart; and here again the two areas obtained from opposite ends of the same polar axis are of course identical. We need, therefore, to take six shadows, one along the line a_1 and five along the lines a_2 , as shown in Fig. 3. All of the a_2 shadows are identical for a cylindrical model such as ethane. The average of these six shadows is 10.0 sq. inches.

Again, let us view the model from the twenty positions, 41°50' apart,

¹⁵ Rankine, *Trans. Faraday Soc.*, 17, Part 3, 1 (1922); *Proc. Phys. Soc. (London)*, 33, Part 5, 362 (1921).

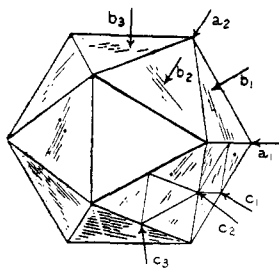


Fig. 3.

corresponding to the centers of the twenty flat equilateral triangular faces of the icosahedron, namely, along b_1 , b_2 and b_3 , etc., of Fig. 3, with the long axis of the ethane cylinder placed along b_2 . The average of the ten required shadows is 10.1 sq. inches.

Finally, if the equilateral triangle faces of the icosahedron are all divided up into four smaller triangles, with an edge length equal to one-half the original edge, and the model is viewed from all of the thirty edge-midpoints, as well as from the twelve summits of the icosahedron, we view the model from forty-two positions which are almost, although not exactly equally spaced as to angle. The north pole distances (N. P. D.) and longitudes of the positions from which the twenty-one required shadows are taken are as follows: one shadow from the north pole, along the line a_1 ; five shadows from points c_1 , N. P. D., $31^\circ 45'$, long. 0, 72, 144, 216 and 288° ; five shadows from points c_2 , N. P. D., $58^\circ 17'$, long. 36, 108, 180, 252 and 324° ; five shadows from points a_2 , N. P. D., $63^\circ 26'$, long. 0, 72, 144, 216 and 288° ; five shadows from points c_3 , N. P. D. 90° , long. 18, 90, 162, 234 and 306° .¹⁶ The average of the twenty-one shadows is 10.1 sq. inches.

It is evident from a cylinder such as the ethane model that the average cross-sectional area very rapidly approaches an asymptotic value, and that for most purposes the average shadow taken from six positions, *i. e.*, from the poles of an icosahedron, would be sufficiently close to the asymptotic value. Later, in connection with octane it will be shown that even with a much more elongated cylinder, departing much more than ethane does from spherical form, the six-shadow average is satisfactory.

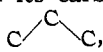
From this model of the ethane molecule, and from the shadow-graphic estimation of its average cross-sectional area, a collision area of 10.1 sq. Å. is predicted for the gaseous ethane molecule. It is further to be noted that in measuring the area of the shadows of the ethane molecule, and also of the other models in general, the reëntrant angle as shown at R. A. in Fig. 2 (a) is neglected; that is, the surface envelope of the model is drawn straight across from hydrogen atom to hydrogen atom. The justification of this procedure is two-fold; in the first place, the space included in such a reëntrant angle is far too narrow to permit the passage or entrance of a bombarding molecule, or even any appreciable portion of it; in the second place, the size of the hydrogen atom domain is really a great deal larger than that shown in Fig. 2. It is pounded down to the given size by molecular impact, and it seems reasonable to suppose that in such elastic encounters the atomic domain of the hydrogen, fluid-like, is flattened out and is squeezed into neighboring crevices corresponding to reëntrant angles.

¹⁶ For a list of these angular positions see "The Collected Mathematical Papers" of Arthur Cayley, Cambridge University Press, 1896, Vol. X, pp. 270-273.

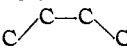
If, on the other hand, the end over end rotations of the ethane molecule were rapid enough to cause the molecule to behave effectively as a sphere of revolution in molecular encounters, we would expect a collision area of 12.6 sq. Å., taking as a radius the distance from the center of the molecule out to the periphery of a hydrogen atom of domain radius 0.50 Å. The fact that Titani's experimental value for ethane, 10.6 sq. Å., lies between the area values predicted from the two shapes, 10.1 from the cylinder and 12.6 from the sphere, but resembles much more nearly that of the cylinder, justifies the expectation that the molecule will behave effectively as a cylinder, and only partially and to a very limited degree as a sphere. This expectation also finds support in an argument based on the probable frequencies of the end over end spins of the ethane molecule, as may be shown from the following considerations.

From the equi-partition principle it follows that E , the energy of spin of the ethane molecule, *e. g.*, about the z - z axis of Fig. 2, is given by the equation, $E = \frac{1}{2} kT$, where k is the Boltzmann constant and T the absolute temperature. At 25°, E equals about 2.04×10^{-14} ergs. The frequency of spin, ν , may then be calculated from the relationship, $\nu = \sqrt{2E/I}/2\pi$, where I , the moment of inertia of rotation about the z - z axis, can readily be shown to be about 36.2×10^{-40} . The calculated frequency is about 53.3×10^{10} rotations per second, which means that the time for one complete rotation is about 18.7×10^{-13} seconds, and for rotation through, let us say 120°, about 6.2×10^{-13} seconds. Since both molecules which partake in the collision are spinning, we may cut this time to 3.1×10^{-13} seconds. But during this time interval, the approaching molecule will travel, on the average, a distance of a little more than 1.5 Å., as calculated from the equation $u = \sqrt{3kT/m}$. Even keeping in mind the fact that there is a simultaneous spin about the y - y axis (as well as the z - z axis which is here being considered), it yet seems very likely that the approaching molecule will be able to penetrate deeply into the spherical envelope in regions where the hydrogen atoms do not happen to be at the instant of impact. Thus we reach the probable conclusion that the end over end spins are relatively so slow that they fail to guard the spherical envelope against invasion, and hence the molecule falls short by a considerable margin of being able to present itself as a sphere of revolution.

Propane, Butane and Isobutane.—The cross-sectional areas of the models of propane, butane and isobutane are obtained by the same sort of treatment as that just described for ethane.

In propane, with its carbon atoms assumed to be linked together at tetrahedral angles, , the frequencies of spin about the long axis of the molecule and of the end over end spins, are considerably too small to make the molecule effective either as a cylinder or as a sphere of revo-

lution, although the two end methyl groups are undoubtedly spinning rapidly enough about the bond which connects them to the middle carbon atom to present themselves as rings of revolution. The average shadow area (twelve positions) for such a propane model, with hydrogen atoms of domain radius 0.50 and with the methyl groups in the form of rings, is 13.0 sq. inches.

Similarly, butane, , gives an average shadow area of 14.5 sq. inches. Isobutane, with three spinning methyl groups connected to the fourth carbon, averages 17.0 sq. inches.

These shadow areas, together with Titani's collision area results (Titani gives them as diameters) are collected in Table II. In the last column, for the sake of comparison, the cross-sectional areas of the very improbable spheres of revolutions are given.

TABLE II
COMPARISON OF COLLISION AREAS WITH MODEL AREAS

		Collision area, sq. Å.	Average shadow area of model, sq. inches	Average cross-sectional area of sphere of revolution
Methane	CH ₄	7.72	7.72	7.72
Ethane	C ₂ H ₆	10.63	10.1	12.6
Propane	C ₃ H ₈	13.53	13.0	22.7
Butane	C ₄ H ₁₀	16.11	14.5	27.7
Isobutane	C ₄ H ₁₀	17.05	17.0	22.4

In the case of methane, the size of the hydrogen atom domain is, of course, chosen to make the model cross-sectional area agree exactly with Rankine and Smith's collision area, 7.72 sq. Å. The divergencies between the other collision area values and the corresponding shadow values are in part attributable to the fact that the hydrogen atom domain probably increases slightly with the ascent of the homologous series, as will be explained later (and no account has been taken of this effect in the shadow areas presented in Table II); and also in part to the fact, already mentioned in the case of propane, that no allowance whatever has been made for the effect of the spins, except for the end methyl groups, and undoubtedly the effect would be to enlarge the shadow areas in some measure.

Inspection of the table shows, however, in spite of our neglect of these second order effects, that agreement between the two columns for ethane, propane, butane and isobutane is quite good; sufficiently good, in fact, to make this whole scheme of model construction and shadow-graphic treatment of the average area a very plausible procedure. On the basis of this foundation of justification, we may now proceed to a consideration of the probable shapes of the molecules of longer carbon atom chains.

n-Heptane, *n*-Octane, *n*-Nonane.—In the discussion of the molecules of heptane, octane and nonane, only octane will be considered in detail,

in the interests of brevity, since the other two are treated in precisely the same manner. The results for all three are listed below in Table III.

If a normal octane molecule in the gaseous state exists in the most extended possible form, it would have the shape shown in Fig. 4, with all the carbon valencies at tetrahedral angles. The frequency of spin of such a molecule about its long axis would be rapid enough compared with the relatively slow translatory motion of a heavy approaching molecule, to present the bombarded molecule as a cylinder of revolution. The end over end spins would be much too slow to prevent invasion; in fact deep penetration into the spherical envelope would be expected. It is justifiable, then, to treat such a hypothetical gaseous molecule as being effectively a cylinder and to proceed to an estimation of its average cross-sectional area by the shadow-graphic method.

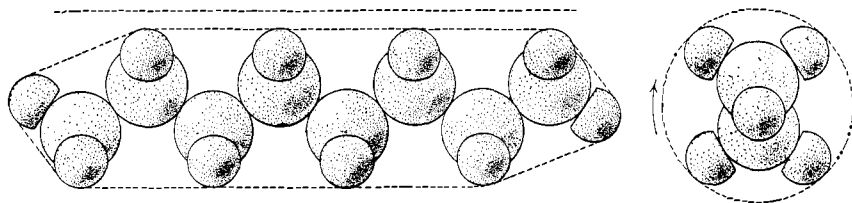


Fig. 4.

Before this can be done, however, there is another very important matter to be taken into consideration. In the case of the collision of two methane molecules it is probably true that not more than one hydrogen atom on each molecule is on the average involved in the impact, or takes part in the act of repulsion which ultimately forces the two molecules apart, and which also determines the depth to which the molecular surface envelopes are compressed. But as we go up the series from ethane to nonane, finding an increasing number of hydrogen atoms per molecule and in general a decreasing velocity of molecular spin, we would expect a larger and larger number of hydrogen atoms to be involved in the impact. Judging from the manner in which hydrogen atoms are studded over the surface of an octane molecule, we might expect about four atoms, on the average, to partake in the collision. Since the average force of impact for all of these molecules, in spite of their different masses, is the same (at the same temperature), naturally the extent to which the hydrogen atom domain is battered in will not be as great where several atoms receive the impact as it will where one atom unaided bears the brunt of the same blow. Or to put the matter possibly more correctly, a set of several dipoles (hydrogen atoms) driven against another set of several will not approach as closely as one dipole driven with the same force against a single dipole.

If we assume that the repulsion between two such approaching hydrogen atoms is developed entirely by the two nuclei, $+\dots+$, the repulsive force would be inversely proportional to s^2 , where s is the distance between the two positive charges. If, on the other hand, we assume that the repulsive force is due to the mutual interaction of two dipoles, $+-\dots-+$, with the full electronic charge active, none of it shielded out, the force would be inversely proportional to s^4 . Actually the situation is probably somewhere between these two, since undoubtedly part of the electron density in the hydrogen atom domain is to be found surrounding the positive nucleus on all sides. Perhaps the best approximation that can be made here is to assume a third power law of repulsion. If this is done s , the distance of closest approach of the two hydrogen nuclei, would be about $2 \times 0.49 \text{ \AA.} \times \sqrt[3]{4}$, when four hydrogen atoms on each colliding molecule take part in the act of impact. This distance is 1.55 \AA. , and means that the radius of the hydrogen atom domain in octane would be about 0.78 \AA. , as compared to 0.49 \AA. in methane. With a fourth power law the domain radius¹⁷ would be about 0.70 \AA. The effective size of the hydrogen atom domain undoubtedly increases somewhat regularly in the ascent of the homologous series. For this reason, the model areas in the previously given Table II are all, with the exception of methane, a little too small.

Let us return now to the shadow area of the octane model (most extended and with hydrogen domain radius of 0.78). The average shadows at the various numbers of equal angle positions from which a model can be viewed are given here again to prove how rapidly the asymptotic average is approached even for such an extended form as this octane cylinder.

Number of positions	6	12	20	42
Average shadow area (sq. inches)	38.7	39.95	39.9	39.95

Thus the extended octane model yields a shadow area of about 40.0. This is too large to represent the octane molecule. The calculated collision area of the molecule from the viscosity data is 34.9 sq. \AA. The actual molecule is therefore not extended, but exists in a smaller, more collapsed form.

The most highly compact helix into which the octane model chain can be wound, by rotating the carbon atoms on the bonds which connect them, but without changing the tetrahedral angles, is practically a sphere, shown in Fig. 5, and gives an average shadow area (when the outside surface of

¹⁷ The authors recognize that this estimation of the hydrogen domain size is quite inadequate. Eventually, no doubt, a precise calculation can be made when the wave function in the system C-H is known. At any rate the change in the domain size dependent on the number of hydrogens partaking in the impact is too small relative to the over-all dimensions of the molecules to affect the nature of the general conclusions to be drawn.

the molecule is again studded over with hydrogen atoms with a domain radius of 0.78 \AA .) of 26.4 sq. inches. This is too small. Clearly, the actual octane molecule possesses a shape somewhere between that of the most extended chain and the most compact helix. It is probably a loosely wound helix.

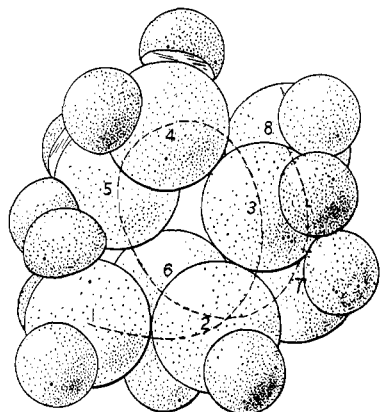


Fig. 5.

The tightness with which the helical chain can be packed together seems to be determined by the presence of hydrogen atoms of about the size found in organic liquids.¹⁴ Such atoms along the interior portions of the helix would not be subject to direct bombardment, would not be compressed as much as the hydrogen atoms on the surface and would prevent the formation of anything tighter than a very loose spiral. It is somewhat difficult to represent this form in a drawing,

but in Fig. 6 an attempt is made to show how the large-sized hydrogen atoms condition the coiling of the helix. A model constructed in this way, with hydrogen atoms of domain radius about 1.06 \AA . determining the tightness of the helix, and hydrogen atoms of domain radius 0.78 \AA . on the surface, gives an average shadow area of 35.9 sq. inches. This agrees extremely well with the observed value of 34.9 sq. \AA .

Table III presents the results also for heptane and nonane. In this table the shadow areas of the models are given both for a hydrogen atom domain radius of 0.78 \AA . (third power law) and for a domain radius of 0.70 \AA . (fourth power law).

Evidently the molecules of *n*-heptane and of *n*-nonane, as well as those of *n*-octane, assume an average shape which is a loosely wound helix. If the shadow area sizes are about correct for octane, then those reported in Table III for heptane are somewhat too large, and for nonane somewhat too small, because of the fact that in the case of heptane a somewhat smaller number and in the case of nonane a somewhat larger number of hydrogen atoms share in the impact of collision.

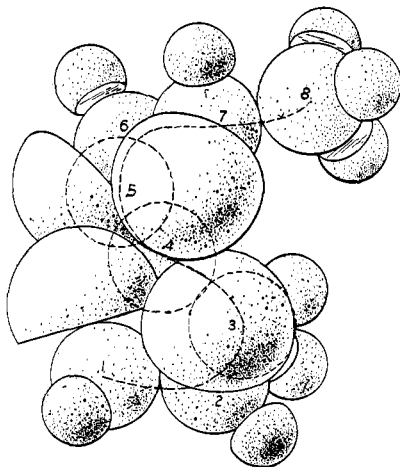


Fig. 6.

TABLE III
COMPARISON OF COLLISION AREAS AND SHADOW AREAS FOR HEPTANE, OCTANE
AND NONANE

	Collision area, sq. Å.	Average shadow area, sq. inches						Area of sphere of revolution of extended molecule
		Tight helix		Loose helix		Extended		
		0.70 Å.	0.78 Å.	0.70 Å.	0.78 Å.	0.70 Å.	0.78 Å.	
<i>n</i> -Heptane	26.7	23.7	25.2	30.0	31.1	34.8	35.9	93.3
<i>n</i> -Octane	34.9	25.0	26.4	34.5	35.9	38.7	40.0	116.8
<i>n</i> -Nonane	42.5	26.6	28.1	38.0	39.6	43.0	44.4	143.1

In the last column of Table III the cross-sectional areas of the improbable spheres of revolution of the extended molecules are listed. They are far too large to represent the actual collision areas. In so far as we have neglected the effect which end over end spin motion might have on the areas of our models, we have not disturbed in the slightest degree the validity of our general conclusions regarding the probable shape of these carbon chain molecules. Because, if the molecules are coiled up into a helix, as we have concluded that they are, rotation about the center of gravity would not appreciably affect the size, since the molecule is already approximately of spherical form. But, if the molecule were in reality extended, sufficiently rapid rotation would increase the shadow area values of the extended chain, by smearing the molecular domain over a larger space and make the decision in favor of the coiled-up form still more convincing.

In general it is to be expected that other long carbon chain molecules will coil up into loose helical forms: not only because the van der Waals forces acting between the atoms within the molecule will tend to draw the atoms closely together, and thus, in general, produce a molecular surface of minimum area, but also because the continuous punching which such a molecule suffers from its neighbors will pound it down to as compact and as closely pressed a form as rotation about chemical bonds and the special structural features of the organic molecule will permit.

Another feasible method of determining whether or not the carbon chain of a molecule such as *n*-heptane is coiled up in a helix, would involve a comparison of the collision areas (by the viscosity method) of the isomers of heptane. If the normal chain is a helix it should have very much the same collision area as the most highly branched isomers, which are already quite well bunched up into almost spherical form by their characteristic structure. Such an investigation is now under way in our laboratory.

Summary

The viscosities of gaseous *n*-heptane, *n*-octane and *n*-nonane are determined over the temperature range 100–250°, and the Sutherland constants and collision areas of the molecules calculated. These latter are, re-

spectively, 445 and 26.7 sq. Å. for heptane, 337 and 34.9 sq. Å. for octane, 276 and 42.5 sq. Å. for nonane.

The relationship between Sutherland's constants and boiling points is discussed and it is pointed out that Vogel's empirical equation, $C = 1.47 T_b$, can hardly be expected to hold for large molecules.

On the basis of a shadow-graphic estimation of the average cross-sectional area of plausible models of ethane, propane, butane and isobutane, and with due consideration of the spin motions of the molecules, collision areas for these molecules are predicted, which are found to be in fairly good agreement with Titani's experimental results.

By the same sort of treatment of models of heptane, octane and nonane, it is shown to be very probable that these carbon chain molecules do not exist in the extended form in the gas phase, but are coiled up on the average into the shape of a loose helix.

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

THE COLLISION AREA OF THE GASEOUS CARBON TETRACHLORIDE MOLECULE

BY ELMER H. SPERRY AND EDWARD MACK, JR.

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The recent determination by Mark and Wierl,¹ using an electron diffraction method, of the distance between the nuclei of the chlorine atoms within the gaseous carbon tetrachloride molecule makes it possible now to set up an approximate model of the carbon tetrachloride molecule, if the collision area of the molecule is known. This latter is necessary to an estimation of the size of the chlorine atom domain as conditioned by the impact of gaseous molecule collision. In the present paper the collision area of the molecule of carbon tetrachloride is determined by a gaseous viscosity method, and then the chlorine atom domain is shown to be of about the same size in the molecules of carbon tetrachloride and of chlorine. These results will be presented after the experimental procedure and data have been given.

Experimental Procedure and Data.—The viscosity of the vapor of carbon tetrachloride was determined with the same apparatus and in precisely the same manner already described in an accompanying paper.² The sample of carbon tetrachloride which was used boiled at 75.74–75.76° (742 mm.). The viscosities, η , at the several temperatures, were calculated with Meyer's transpiration formula, as before, and were corrected for slip, η_c . The results are listed in Table I.

¹ Mark and Wierl, *Naturwissenschaften*, **18**, 205 (1930).

² Melaven and Mack, *THIS JOURNAL*, **54**, 888 (1932).