

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

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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).

TABLE I
VISCOSITIES

Temp., °C.	η	η_0
50	1.074×10^{-4}	1.082×10^{-4}
100	1.192×10^{-4}	1.203×10^{-4}
150	1.357×10^{-4}	1.371×10^{-4}
200	1.501×10^{-4}	1.519×10^{-4}
250	1.697×10^{-4}	1.703×10^{-4}

Here, as before,² Reynold's criterion was satisfied, that is, the flow of vapor through the capillary was slow enough to ensure viscous, and not permit turbulent, flow. From the data of Table I the Sutherland constant for carbon tetrachloride was found to be equal to 335; and the collision area, calculated from Chapman's equation, 22.0 sq. Å.

Model and Shadow Area.—Mark and Wierl obtained the value of about 3.14 Å. for the distance between the chlorine nuclei, which is probably more reliable than the somewhat larger result, 3.3 Å., found by Debye, Beuvilogua and Ehrhardt,³ by x-ray examination of carbon tetrachloride vapor. Since the nuclei of the four chlorine atoms are probably spaced around the carbon atom at the four corners of a regular tetrahedron, and since the tetrahedral edge length is 3.14 Å., it can readily be calculated that the distance from the carbon nucleus to a chlorine nucleus is 1.91 Å. It only remains to estimate what size of chlorine atom domain beyond the nucleus will give a collision area of 22.0 sq. Å. Application of the shadow-graphic method, previously described, to a determination of the average cross-sectional area of a model of the carbon tetrachloride molecule shows that the radius of the chlorine atom domain (based on the average of twelve shadows) is 1.32 Å. In arriving at this result the reëtrant angles, which are small, are assumed to have no effect on the area.

However, since the molecules of carbon tetrachloride are rotating, it is necessary to consider what alteration, if any, such rotation would make in the shadow-graphic collision area. If it is assumed that the rotation is similar to that in methane, the moment of inertia is readily calculated to be 566×10^{-40} . From the equipartition of energy, then, one can calculate (approximately) that the frequency of spin at 25° would be 13.5×10^{10} r. p. s., and the time for one complete rotation 74.1×10^{-13} seconds. But, since both molecules sharing in the impact are spinning, and since three chlorine atoms lie around the ring of revolution, and since the whole molecule possesses also other spin motions (expressible in terms of three axes of spin), it is to be expected that the molecule would present itself as a sphere of revolution if allowed a time of about 2×10^{-13} seconds. During such a time interval, the colliding molecule would travel through a distance of about 0.5 Å., and would probably invade to some extent the spherical envelope of revolution. If the molecule were actually able to present itself

³ Debye, Beuvilogua and Ehrhardt, *Physik. Z.*, **30**, 84 (1929).

as a total sphere of revolution, the value of the domain radius 1.32 Å. obtained above by the shadow-graphic method on the basis that the spin effect is negligible, would have to be trimmed down to about 0.78 Å. No doubt the radius of the chlorine atomic domain, considered as a hard spherical surface, would lie somewhere between these two limits, 0.78 and 1.32 Å., nearer to the latter and possibly about 1.2 Å.

It is interesting now to compare these limits of chlorine domain size with the chlorine atom in the diatomic molecule. Two spherical atoms of chlorine telescope together to form a chemically stable molecule. The distance between nuclei is about 1.98 Å., which is the distance deduced by Elliott⁴ for the normal molecule from his analysis of the absorption band spectrum of chlorine. The moment of inertia is about 113×10^{-40} calculated for two atoms of assumed average atomic weight (35.46), rather than for isotope pairs, 35-35, 35-37, etc. The frequency of spin would average about 30.2×10^{10} r. p. s., giving a rotational quantum number of roughly 21, which is about what is to be expected from Elliott's map of the absorption spectrum. The molecule makes a complete rotation in 33.1×10^{-13} seconds, and in view of the facts that both colliding molecules are spinning, and that each one would have to turn through about 90°, and that each one is also spinning end over end about two axes, the molecule would require a time of about 2×10^{-13} seconds to present itself as a sphere. During this time the colliding molecule would travel about 0.7 Å. On the whole, then, the chlorine molecule might be expected to behave less completely as a sphere of revolution than the carbon tetrachloride. If it did present itself completely as a sphere, the domain radius would have to be 0.86 Å. in order to give the observed collision area of 10.7 sq. Å. found by Rankine,⁵ if the spin motion were to play a negligible part in determining the collision area, the domain radius would be about 1.44 Å.

Thus, within the limits of resolution of the present method of treatment, the conclusion may be drawn that the chlorine atom domains are of approximately the same size in the two different molecules. It is to be noted further, however, that the values given are subject to the possible errors already² mentioned, principally those involved in the question of the validity of the Sutherland model, and the applicability of the Chapman equation in the present situation. The questions of whether Keesom orientation occurs at impact, and of whether the velocity of the invading molecule is increased appreciably as it approaches the point of impact, are also involved.

Summary

The viscosities of carbon tetrachloride vapor over the temperature range 50-250° have been measured. From them the Sutherland constant is

⁴ Elliott, *Proc. Roy. Soc. (London)*, **A127**, 638 (1930).

⁵ Rankine, *ibid.*, **A98**, 373 (1921).

calculated to be 335, and the collision area of the carbon tetrachloride 22.0 sq. Å.

The conclusion is drawn that the atomic domain size of the chlorine atom is roughly the same in the gaseous molecules of carbon tetrachloride and chlorine.

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[CONTRIBUTION FROM THE INORGANIC CHEMISTRY LABORATORY, PURDUE UNIVERSITY]

OXYCYANOGEN. II. THE FREE RADICAL

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Of the eight halogenoid free radicals $(\text{CN})_2$, $(\text{SCN})_2$, $(\text{SeCN})_2$, $(\text{SCSN})_2$, N_3 , $(\text{TeCN})_2$, $(\text{ONC})_2$ and $(\text{OCN})_2$, the latter four have not been isolated or satisfactorily described. The author¹ has failed to check the work of Lidov. A compound of carbon, oxygen and nitrogen such as he describes was not found.

Birckenbach and Linhard² treated silver cyanate with iodine in ligroin, carbon tetrachloride, ethyl chloride, benzene and ether solutions at -20° and obtained a product which they describe as IOCN. They state that it is impossible to obtain $(\text{OCN})_x$ by this process. $(\text{SCN})_2$ and $(\text{SeCN})_2$ have been prepared in a similar manner by Söderbäck³ and Kaufmann,⁴ respectively.

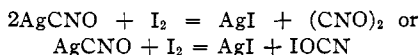
It is the purpose of this paper to describe the isolation and properties of $(\text{OCN})_x$.

Preparation

Fresh silver cyanate was prepared by precipitation from potassium cyanate and silver nitrate. The salt was carefully washed and dried. Analytical tests showed it to be free from any unchanged silver nitrate or oxidizing material. The salt was carefully dried over sulfuric acid in the dark to prevent decomposition.

The solvents which proved satisfactory for use were carbon disulfide and carbon tetrachloride. Several other common solvents, ether, alcohols and acetone, were tried but all gave difficulties of hydrolysis or side reactions. The solvents were thoroughly dried over soda lime and fractionally distilled before use.

Resublimed iodine was dissolved in the carbon tetrachloride or carbon disulfide to make a 0.05 normal solution. Greater concentrations do not react as rapidly. This solution was stirred in a mercury-sealed stirrer at room temperature for sixty days with a large excess of silver cyanate. No gas is given off but the iodine slowly disappears. This would indicate



¹ H. Hunt, *THIS JOURNAL*, **53**, 2111 (1931).

² Birckenbach and Linhard, *Ber.*, **62**, 2261 (1929); **63**, 2544 (1930); **64**, 961 (1931); **64**, 1076 (1931).

³ Söderbäck, *Ann.*, **419**, 217 (1919).

⁴ Kaufmann and Kögler, *Ber.*, **59**, 178 (1926).