

ess was impracticable but it appeared to be possible to extract a small quantity of neodymium which was present in praseodymium. Accordingly, we selected a mixture which was composed of 94 per cent praseodymium and 6 per cent neodymium and extracted the latter with ether. The residue contained such a small quantity of neodymium that it could not be detected by spectroscopic means and we believe that this method of separation may also be applied in other cases.

*THE DETERMINATION OF THE STRUCTURES OF THE HEXA-
FLUORIDES OF SULFUR, SELENIUM AND TELLURIUM BY
THE ELECTRON DIFFRACTION METHOD**

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The application of electron diffraction methods in the study of gas molecules was first made by Mark and Wierl,¹ who investigated the structure of a large number of molecules in this way. Using methods closely similar to theirs, and briefly discussed in the following paragraphs, we have determined the atomic configuration and interatomic distances in SF₆, SeF₆ and TeF₆.

The Debye formula² for the relative intensity as a function of the scattering angle θ for x-radiation diffracted by widely separated gas molecules with random orientation is

$$I = k \sum_i \sum_j f_i f_j \frac{\sin x_{ij}}{x_{ij}}, \quad (1)$$

in which

$$x_{ij} = 4\pi l_{ij} \frac{\sin \theta/2}{\lambda} \quad (1a)$$

with l_{ij} the distance between the i th and the j th atoms, λ the wave-length of the incident radiation, and k a constant for given experimental conditions. The summations extend over all the atoms in one molecule. For electron diffraction the x-ray-scattering factors f_i and f_j for the atoms are replaced by electron-scattering factors ψ_i and ψ_j , which were shown by Mott³ to be given by the expression

$$\psi_i = \frac{Z_i - f_i}{\left(\frac{\sin \theta/2}{\lambda}\right)^2}, \quad (2)$$

in which Z_i is the atomic number of the atom and f_i , as before, the x-ray-scattering factor, essentially a function of $\frac{\sin \theta/2}{\lambda}$.

The interpretation of an electron diffraction photograph is made by comparing it with theoretical intensity curves calculated for each of several models (corresponding to different relative positions of the atoms), among which a choice can then be made. An approximate treatment can be based on the comparison of the maxima and minima shown by calculated curves obtained on substituting for f_i in Equation 1 the value Z_i (rather than ψ_i) with the apparent maxima and minima seen on visual examination of the films. The most probable model for any substance is that leading to the curve which permits the best correlation of maxima and minima with the measured diameters of the rings on the photograph. Application of Equation 1a then provides values of the interatomic distances. A complete interpretation of the photograph would require recalculation of the theoretical intensity curve with the use of the ψ -values corresponding to the interatomic distances given by the simpler treatment, and the quantitative comparison of this curve with the observed intensity curve. It has been found, however, that the very rapid decrease in intensity with increasing angle θ makes an accurate knowledge of the behavior of photographic emulsions toward electrons necessary for the interpretation of micro-photometer records of diffraction photographs. Until this knowledge is obtained, use must be made of the simpler treatment, this procedure being justified by the self-consistency of the results it leads to and by their agreement with the results of x-ray diffraction and band-spectral investigations. Wierl in this way determined interatomic distances for a large number of molecules with a probable error estimated by him at $\approx 2\%$. Our own experience supports this estimate, and indicates that still greater accuracy can be obtained by standardizing the technique of preparing and measuring the photographs.

The experiments consist in causing a well-defined beam of electrons traveling with a uniform velocity to intersect a jet of gas, the scattered electrons being recorded on a photographic film set at right angles to the direction of the initial beam. The source of electrons was a hairpin-shaped hot filament set asymmetrically in a focussing cup which could be charged to various potentials with respect to the filament. The accelerating potential of about fifty thousand volts was taken directly from the secondary winding of a transformer. The electron beam was defined by 0.2 mm. holes in two platinum foils set 130 mm. apart. The gas jet was introduced through a nozzle with a rectangular opening of dimensions 1×0.1 mm. placed with the long dimension parallel to the electron beam. The nozzle was connected through a stopcock to a small reservoir of gas maintained at a pressure of about $1/2$ atmosphere. The exposures in all cases were of the order of $1/2$ second.

A calibration of the wave-length furnished by the accelerating potential was obtained with the aid of photographs of gold. The structure of gold determined by electrons was checked by Thomson⁴ with the generally accepted one determined by x-rays; hence, measurement of gold photographs constitutes a convenient method of standardization. The sharpness of the rings in the photographs used for this purpose indicated that all of the electrons were traveling with nearly the same velocity.

TABLE 1
CARBON TETRACHLORIDE

MAXIMUM	MINIMUM	x	FILM NO. 123, LIGHT		FILM NO. 126, DARK	
			$\sin \theta/2\lambda$	$a = \text{C-Cl}$	$\frac{\sin \theta/2}{\lambda}$	a
1		0.765	0.212	1.80 Å	0.220	1.74 Å
	2	1.04	0.292	1.778	0.290	1.795
2		1.35	0.376	1.798	0.385	1.752
	3	1.69	0.474	1.784	0.484	1.746
3		2.01	0.558	1.801	0.569	1.766
	4	2.31	0.648	1.809	0.659	1.754
4		2.58	0.730	1.767	0.735	1.756
	5	2.90			0.826	1.756
5		3.215	0.905	1.777	0.905	1.777
Weighted mean				1.788 Å		1.761 Å

SULFUR HEXAFLUORIDE

MAXIMUM	MINIMUM	x	FILM NO. 66, DARK	
			$\sin \theta/2\lambda$	$a = \text{S-F}$
1		1.05	0.310	1.69 Å
	2	1.29	0.417	1.548
2		1.51	0.506	1.491
	3	1.86	0.619	1.502
3		2.255	0.729	1.547
	4	2.70	0.907	1.49
4		3.10	1.027	1.51
Corrected value S-F = 1.58 ± 0.03 Å				

SELENIUM HEXAFLUORIDE

Second maximum $x = 2.250$

	FILM NO. 70, DARK	FILM NO. 71, DARK
$\sin \theta/2\lambda$	0.685	0.676
$a = \text{Se-F}$	1.643 Å	1.666
Corrected a	1.69 Å	1.71 Å

Average Se-F = 1.70 ± 0.03 Å

TELLURIUM HEXAFLUORIDE

Second maximum $x = 2.248$

	FILM NO. 80, DARK	FILM NO. 81, MEDIUM	FILM NO. 82, DARK
$\sin \theta/2\lambda$	0.618	0.620	0.628
$a = \text{Te-F}$	1.819	1.812	1.789
Corrected a	1.86	1.84	1.83

Average Te-F = 1.84 ± 0.03 Å

It was found for a series of photographs made with carbon tetrachloride that the measured maxima and minima on any one photograph gave consistent values for the C-Cl separation, but that the value depended somewhat on the apparent density of the photograph. Thus the light film No. 123 and the dark film No. 126, for which data are included in table 1, lead to C-Cl = 1.79 and 1.76 Å, respectively, while very dark films lead to values as low as 1.73 Å, 4% smaller than the value C-Cl = 1.80 Å which we assume to be correct. In interpreting photographs of the hexafluorides we have compared the apparent density of each film with that of CCl₄ photographs, and have then made a corresponding

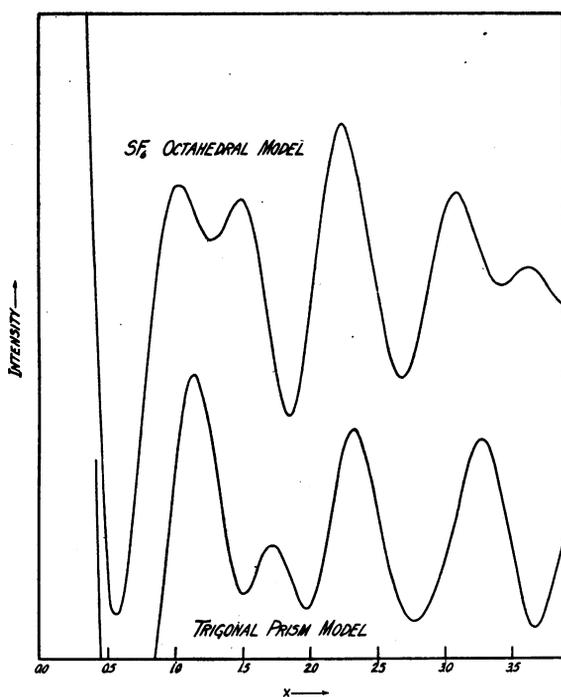


FIGURE 1

correction in the interatomic distances, which, however, was always less than 3%.

Interatomic distances obtained in this way from rather indistinct photographs made with Br₂ and Cl₂ lay within 2% of the values known from band-spectral data.

Two models were considered for each of the hexafluorides, in one the fluorine atoms being placed at the corners of a regular octahedron about the central atom, and in the other at the corners of a right trigonal prism with axial ratio unity; these were shown by Hultgren⁵ to be the only

probable structures for molecules containing a central atom with six equivalent bonds. The intensity formulas used are illustrated by the following one, for the octahedral model of SF₆:

$$I/k = 2\pi Z_S^2 + 12Z_S Z_F \frac{\sin x}{x} + Z_F^2 \left(12\pi + 24 \frac{\sin \sqrt{2}x}{\sqrt{2}x} + \frac{6 \sin 2x}{2x} \right)$$

with

$$x = 2a \frac{\sin \theta/2}{\lambda}$$

in which a is the S-F distance. The two curves for SF₆ are shown in figure 1.

The photographs from all three substances eliminate the prismatic models, the shapes and relative positions of the maxima and minima of the curves being in pronounced disagreement with the observed rings. Good agreement is obtained for the octahedral models, however. The two close inner maxima of the SF₆ curve appear as two distinct rings in the photograph. In SeF₆ and TeF₆ the increased scattering factors of the central atoms modify these two into a single broad maximum, and the photographs also show correspondingly a broad inner ring. The relative positions of maxima and minima when correlated with observed ring diameters lead to consistent values for the interatomic distances, as shown for SF₆ in the table. The error shown by the first maximum is probably due to the effect of the close second ring in causing low estimates of the ring diameter. The value 1.55 Å given by the sharp third maximum is the most reliable; this corrected by the factor 1.02 for the dark photograph leads to an S-F separation of 1.58 ± 0.03 Å. Measurements of the same sharp maximum on the SeF₆ and TeF₆ films lead to Se-F = 1.70 ± 0.03 Å and Te-F = 1.84 ± 0.03 Å.

The interatomic distances agree very well with those expected for an ionic structure. The sums of ionic radii⁶ are 1.65, 1.78 and 1.92 Å, respectively, and these sums are expected to be somewhat larger than the equilibrium distances between small highly charged cations and large anions. The differences, 0.07, 0.08 and 0.08 Å, are very close to that between the observed Si-F distance 1.68 ± 0.02 Å in the crystal (NH₄)₂SiF₆ and the ionic radius sum 1.77 Å.

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THE AGGLOMERATION THEORY OF SLEEP*

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Hollingworth¹ says that "normal sleep shows so many differences from the states of stupor and insensibility induced by anesthetics, narcotics and other drugs, that the resemblance between the two conditions must be regarded as superficial." Hollingworth represents a minority. Most physiologists and psychologists consider that sleep due to chloroform, morphine, alcohol and other drugs, is identical in principle with ordinary sleep,² though differing of course in detail. If this is true, sleep must be due in part to a reversible agglomeration of some proteins in the centers of consciousness, wherever these may be.

Many agglomeration theories of sleep have been advanced; but they have all been rejected on the ground that one would necessarily stay awake until the agglomerating agent reaches a certain concentration and would necessarily go to sleep as soon as that concentration was exceeded. Since not going to sleep is a matter of choice within certain limits, it was assumed that no agglomeration theory can be right. The flaw in the reasoning is that people have overlooked the effect due to the irritability of the sensory nerves. The more irritated these nerves are, the higher must be the concentration of the agglomerating agent necessary to overbalance the effect due to the sensory nerves and thus to produce sleep. It was a curious error to make, because everybody knows the extraordinary effect of external stimuli in keeping men awake. Laird and Muller³ say: "Soldiers on a forced march feel they can go no farther. They are on the verge of falling by the road from sheer exhaustion. An officer comes along. He cheers them with a few words. The regimental band breaks out with a stirring Sousa rhythm—and without rest the men become refreshed and march briskly off many more miles." If the fatigue becomes great enough, it is almost impossible to keep men awake. There would come a time