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The Molecular Structure of P_4O_6 , P_4O_8 , P_4O_{10} and As_4O_6 by Electron Diffraction

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Molecular structures of P_4O_6 and As_4O_6 were determined from electron diffraction data. P_4O_6 was found to have the symmetry of the point group T_d with an angle P—O—P of $128.5 \pm 1.5^\circ$, and a P—O distance of $1.67 \pm 0.03\text{\AA}$. In this structure the phosphorus oxygen distances and the phosphorus valence angles were preserved with resulting deformation of the oxygen valence angle. The separation of the arsenic atoms in As_4O_6 was found to be $3.20 \pm 0.05\text{\AA}$. Because of the predominant scattering of the arsenic atoms it was difficult to determine the oxygen valence

angle, As—O—As. Values of 120° , 127.5° and 140° gave approximate agreement between the observed and calculated positions of maxima. Electron diffraction photographs obtained from P_4O_{10} differ considerably from those found for P_4O_6 . It was not possible to explain all of the features of the P_4O_{10} diffraction pattern by a model having the symmetry of the point group T_d and it is thought that the structure might be one of lower symmetry. Data were obtained on P_4O_8 which indicated that it has approximately the same electron diffraction pattern as P_4O_{10} .

INTRODUCTION

MOLECULAR structure determinations of phosphorus trioxide, phosphorus pentoxide, and arsenic trioxide by means of electron diffraction were undertaken as part of a general study of these compounds. Under the experimental conditions used the molecular forms of these gases are known to be P_4O_6 , P_4O_{10} and As_4O_6 . An attempt was also made to study antimony trioxide but the extreme corrosive character of the molten compound caused the work to be abandoned. Arsenic pentoxide could not be studied since it dissociates upon heating to give oxygen and the trioxide. The results obtained for the molecules investigated give further information about the valence angles of

oxygen and phosphorus as well as the inter-nuclear distances.

ARSENIC AND PHOSPHORUS TRIOXIDES (As_4O_6 AND P_4O_6)

These molecules are expected to have the symmetry of the point group T_d and their structures are fixed by two parameters. For convenience these are taken as the P—P or As—As distance and the P—O—P or As—O—As valence angle. Cartesian coordinates of the atomic positions are:

$$\begin{aligned} \text{As or P;} & u u u, \bar{u} \bar{u} u, u \bar{u} \bar{u}, \bar{u} u \bar{u} \\ \text{O;} & v o o, o v o, o o v, \bar{v} o o, o \bar{v} o, o o \bar{v}. \end{aligned}$$

Intensity of electron scattering $I_1(\theta)$ from this structure is given by

$$\begin{aligned} I_1(\theta) = & 4\psi_P^2 \cdot A_s \left(1 + 3 \frac{\sin s \cdot (8u^2)^{\frac{1}{2}}}{s \cdot (8u^2)^{\frac{1}{2}}} \right) + 24\psi_P \cdot A_s \psi_O \left(\frac{\sin s \cdot [(u-v)^2 + 2u^2]^{\frac{1}{2}}}{s \cdot [(u-v)^2 + 2u^2]^{\frac{1}{2}}} + \frac{\sin s \cdot [(u+v)^2 + 2u^2]^{\frac{1}{2}}}{s \cdot [(u+v)^2 + 2u^2]^{\frac{1}{2}}} \right) \\ & + 6\psi_O^2 \left(1 + \frac{\sin s \cdot 2v}{s \cdot 2v} + \frac{4 \sin s \cdot (2v^2)^{\frac{1}{2}}}{s \cdot (2v^2)^{\frac{1}{2}}} \right) + I'_{inc}(\theta), \quad (1) \end{aligned}$$

where ψ_P , A_s and ψ_O represent the atomic electron scattering amplitudes, $I'_{inc}(\theta)$ the incoherent electron scattering¹ and $s = 4\pi(1/\lambda) \sin \frac{1}{2}\theta$. For the purpose of comparing the theoretical electron scattering with the observed interference pattern it is desirable in certain instances to modify the theoretical scattering formula in such a manner

as to provide a direct comparison with the visual measurements. A method followed by other investigators² uses a modified scattering formula in which ψ_i is replaced by Z_i and the incoherent scattering is omitted. Theoretical curves obtained in this manner show prominent maxima which are then compared with the ob-

¹ See L. Bewilogua, *Physik. Zeits.* **33**, 688 (1932).

² See for instance L. Pauling and L. O. Brockway, *J. Chem. Phys.* **2**, 867 (1934).

served interference maxima as determined visually. Another method³ for transforming the calculated scattering curves into many real maxima involves only a plot of $I_1(\theta) \cdot s^2$. This procedure is considerably less drastic than the former method and gives correctly the relative atomic scattering probabilities of the different constituents of the molecule. In the present case several models were calculated according to the two different methods and a comparison of the results obtained is shown in Table I where

$$x_{i-i} = s \cdot (8u^2)^{\frac{1}{2}} = 4\pi l_{i-i} (1/\lambda) \sin \frac{1}{2}\theta \quad (2)$$

and l_{i-i} is the distance between nearest phosphorus or arsenic atoms. It is noticed that the positions computed from $I_1(\theta) \cdot s^2$ are usually less than those obtained by the approximate method, however the difference is generally not greater than 2 percent. In some cases the relative intensities of the maxima are different. In order to reduce the labor involved the approximate method was used to a considerable extent with a realization of the approximations involved. We have thus shown in Figs. 1, 2, 3 and 4 theoretical curves calculated for P_4O_6 and As_4O_6 using the approximate method.

³ L. R. Maxwell, S. B. Hendricks and V. M. Mosley, J. Chem. Phys. 3, 699 (1935).

Electron diffraction photographs were obtained using the electron diffraction camera and boiler previously described.^{3, 4} A reproduction of a typical photograph obtained from As_4O_6 is shown in Fig. 5. Positions of the interference maxima as measured visually are shown in Table II and are indicated for comparison with the theoretical curves in Figs. 1, 2, 3 and 4.

Arsenic trioxide (As_4O_6)

Since the arsenic atoms are responsible for a large amount of the electron scattering their positions can be determined but it is difficult to obtain the oxygen valence angle. By a comparison between the experimental and the theoretical positions for the various interference maxima as shown in Fig. 3 and Fig. 4 it is noticed that fair agreement is found for 120° , 127.5° and 140° while all of the other angles considered can definitely be excluded. The model with an oxygen valence angle of 140° appears to give somewhat better agreement than the other possible angles. An As-As distance of $3.20 \pm 0.05A$ is thus obtained from a consideration of the agreement existing for these angles. The good agreement

⁴ S. B. Hendricks, L. R. Maxwell, V. M. Mosley and M. E. Jefferson, J. Chem. Phys. 1, 549 (1933).

TABLE I. Comparison of methods used for transforming theoretical electron scattering curves into a form possessing real maxima in all cases.

	No.	Position of Maxima in Terms of x_{i-i}		$I(\theta) \cdot s^2$		% Difference
		$\psi_i = Z_i$				
P_4O_6 , P-O-P = 130°	1	7.5	(7)*	7.35	(10)	2.0
	2	13.75	(10)	13.5	(7)	1.5
	3	19.1	(1)	absent		—
	4	25.5	(6)	25.1	(3)	1.6
	5	32.5	(1)	32.0	(1)	1.6
	6	38.0	(3)	37.6	(1)	1.1
As_4O_6 , As-O-As = 130°	1	7.5	(10)	7.5	(10)	0
	2	13.8	(9.3)	13.75	(8.5)	.4
	3	20.0	(2.5)	19.75	(1.5)	1.3
	4	26.0	(5.5)	25.5	(3.5)	2.0
	5	32.7	(1.5)	32.3	(.8)	1.2
	6	38.5	(2.5)	37.75	(.5)	2.0
P_4O_{10} Model No. 1	1	8.0	(3)	7.7	(5)	3.9
	2	13.5	(10)	13.3	(10)	1.5
	3	22.25	(4)	21.75	(3)	2.3
	4	26.8	(3)	26.70	(1.5)	0.4
	5	33.9	(5)	33.7	(1.5)	0.6
	6	39.2	(2)	39.0	(.5)	0.5
P_4O_{10} Model No. 5	1	8.5	(4)	8.0	(2.5)	6.2
	2	14.0	(10)	13.70	(10)	2.2

* Numbers in parenthesis represent an estimated relative intensity.

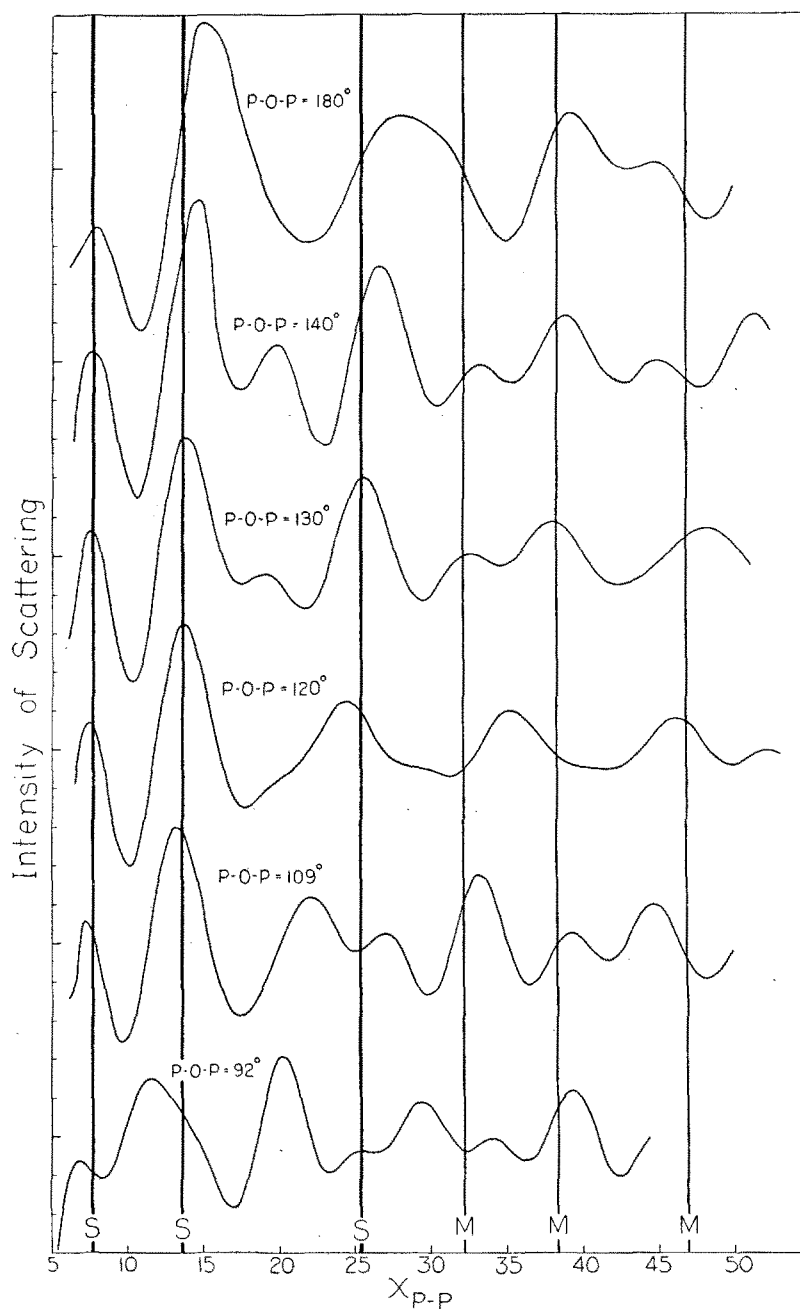


FIG. 1. Electron scattering curves for P_4O_6 where ψ_i is replaced by Z_i calculated for various P—O—P valence angles. Vertical lines give the position of the experimental maxima where $l_{p-p} = 3.00\text{\AA}$. The incoherent scattering has been omitted.

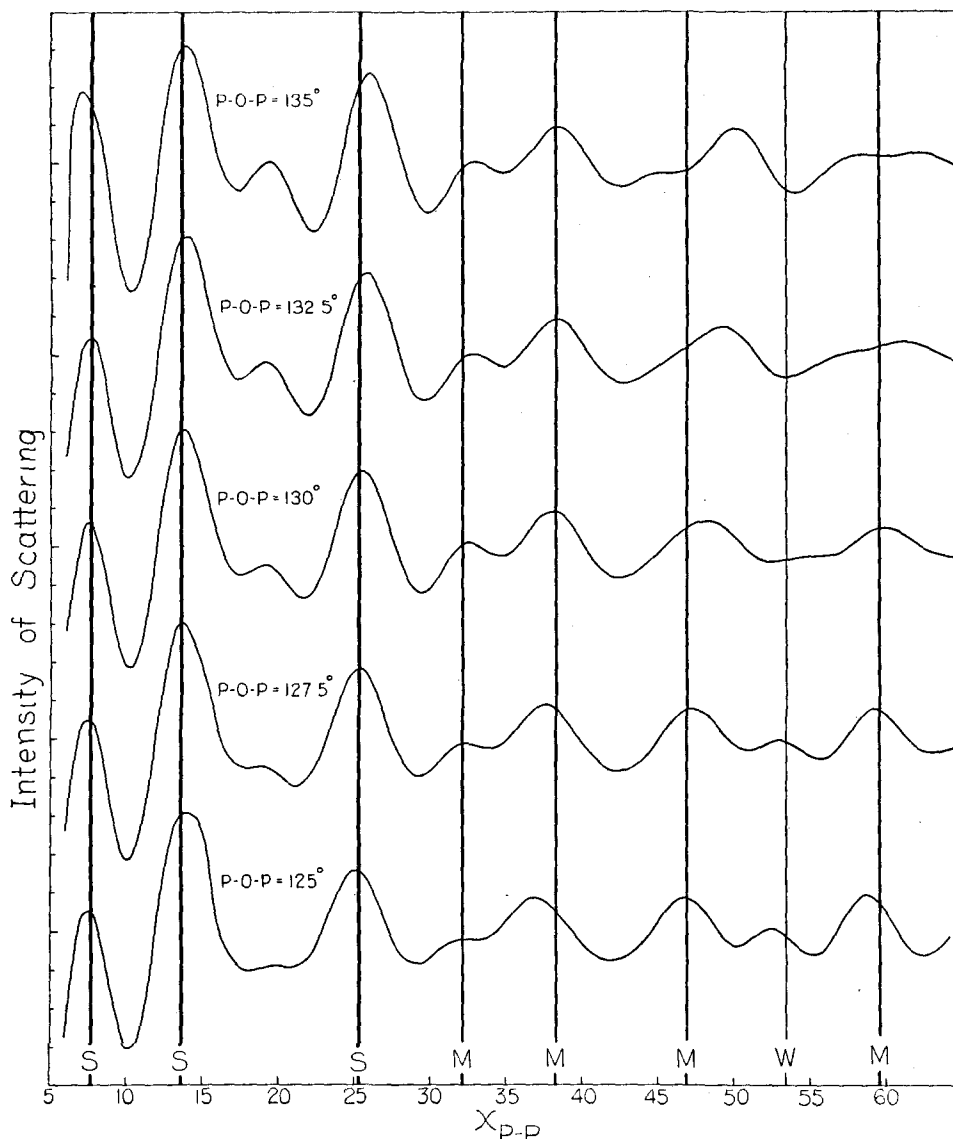


FIG. 2. Electron scattering curves for P_4O_6 where ψ_i is replaced by Z_i calculated for P-O-P valence angles near 130° . Vertical lines give the position of the experimental maxima where $l_{p-p} = 3.00\text{\AA}$. The incoherent scattering has been omitted.

between experiment and theory shows that the arsenic atoms have a regular tetrahedral arrangement and that the symmetry of the molecules is probably that of the point group T_d .

Phosphorus trioxide (P_4O_6)

A value of $l_{p-p} = 3.00\text{\AA}$ was found to give the best agreement with the position of the theoretical maxima, as illustrated in Figs. 1 and 2. Although the model for P-O-P = 130° shows

quite good agreement it is noticed that the weak seventh maximum does not appear for this model. For an angle of 127.5° the seventh maximum is present, however, the fourth ring has weakened considerably. Therefore the valence angle probably lies between these two values since all other angles considered are excluded. Thus we arrive at $128.5 \pm 1.5^\circ$ as the final value for the oxygen valence angle. This leads to the following complete structure for

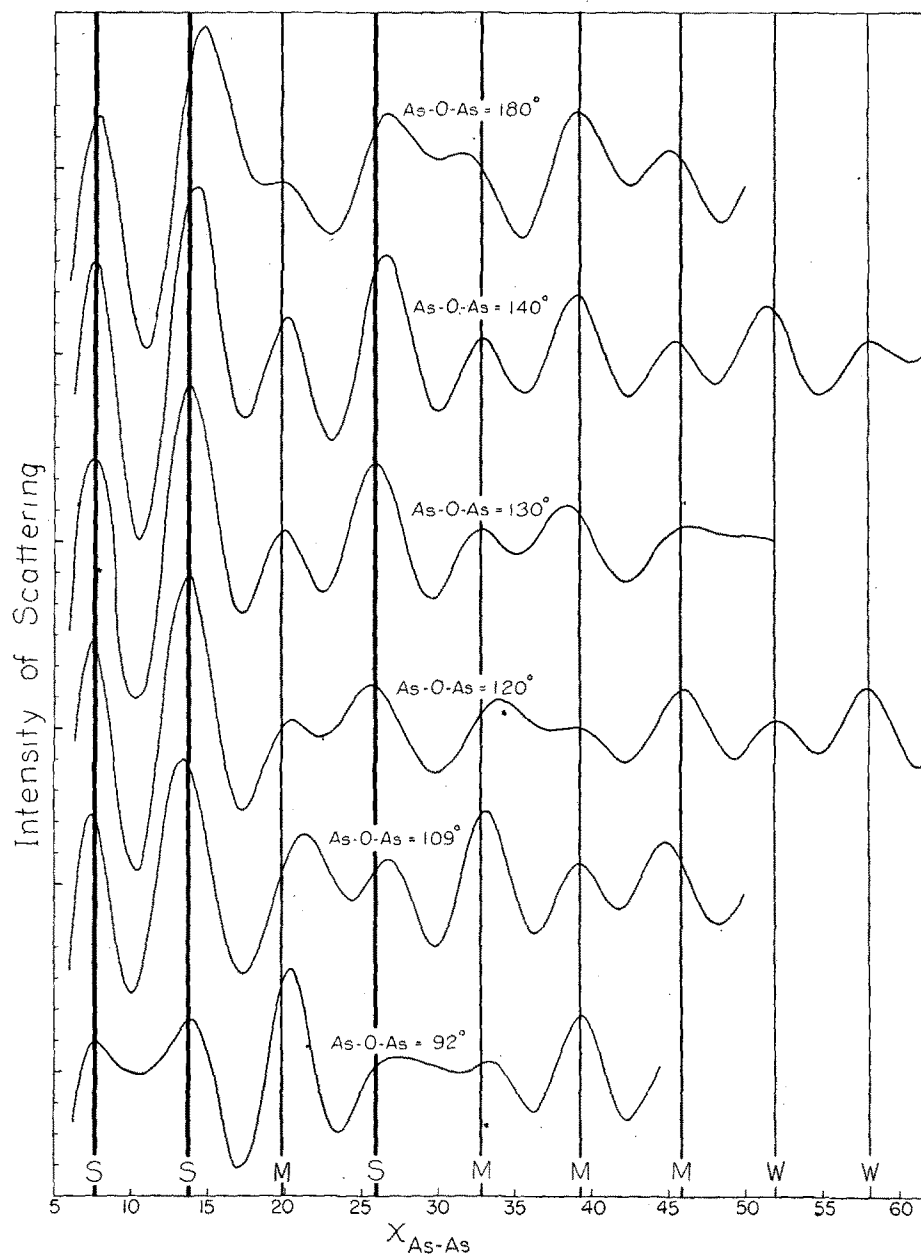


FIG. 3. Electron scattering curves for As_4O_6 where ψ_i is replaced by Z_i calculated for various As-O-As valence angles. Vertical lines give the position of the experimental maxima where $l_{\text{As-As}} = 3.20\text{\AA}$. The incoherent scattering has been omitted.

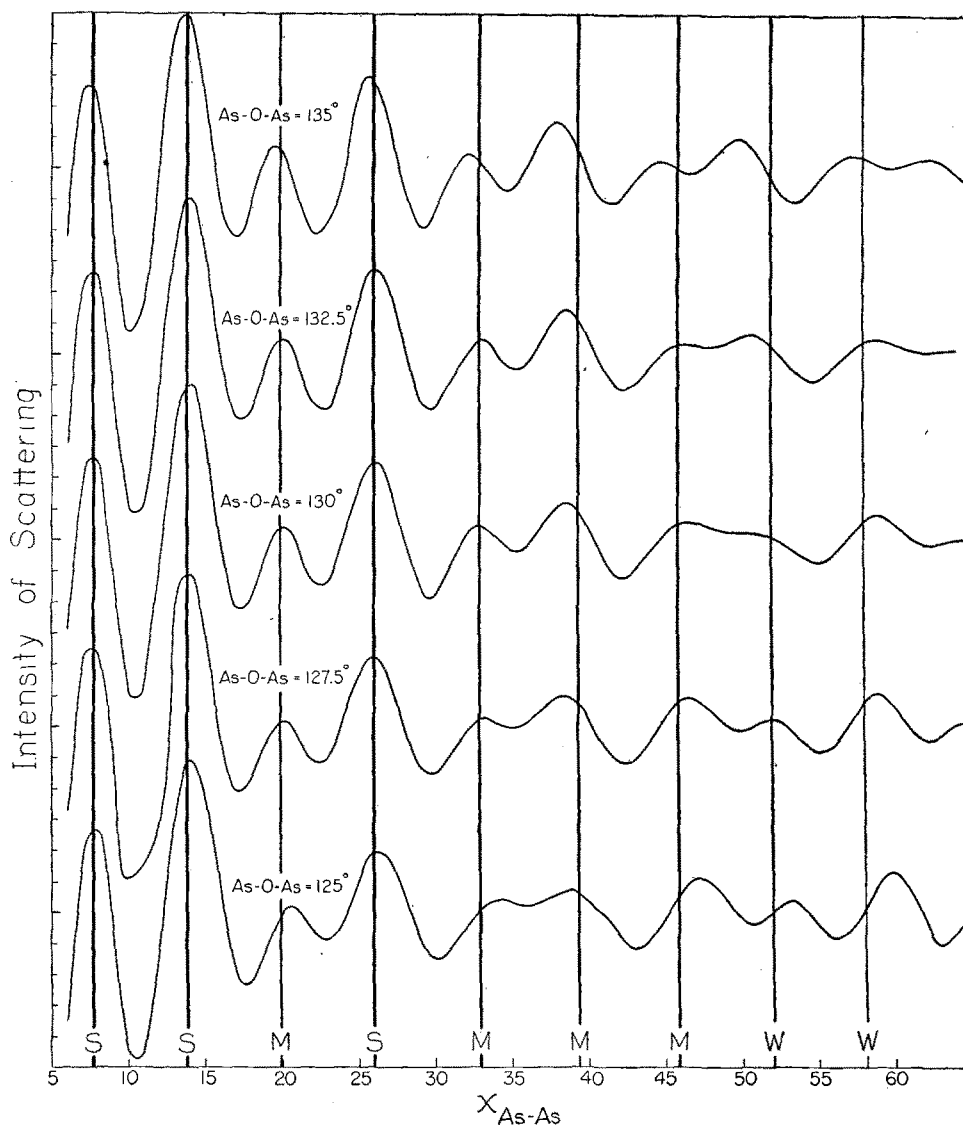


FIG. 4. Electron scattering curves for As_4O_6 where ψ_i is replaced by Z_i calculated for As-O-As valence angles near 130° . Vertical lines give the position of the experimental maxima where $l_{As-As} \approx 3.20\text{\AA}$. The incoherent scattering has been omitted.

P_4O_6 .

$$\begin{aligned} P-O-P &= 128.5 \pm 1.5^\circ, \\ P-P &= 3.00 \pm 0.05\text{\AA}, \\ P-O &= 1.67 \pm 0.03\text{\AA}. \end{aligned}$$

There are some features of the visual measurements from P_4O_6 which support the theoretical data computed by using $I_1(\theta) \cdot s^2$ as compared to the approximate method. For example the weak third theoretical maximum noticed in Figs. 1 or 2 for an oxygen valence angle of 130° is not

observed experimentally in accordance with the calculations made using $I_1(\theta) \cdot s^2$ as shown in Table I. Also the fourth and fifth experimental maxima which correspond to the fifth and sixth theoretical maxima listed in Table I appear from visual measurements to be of approximately equal intensity. This observed intensity relationship is in considerably better agreement with the $I_1(\theta) \cdot s^2$ computations in contrast to the approximate method. These additional theoretical confirmations of the visual measurements

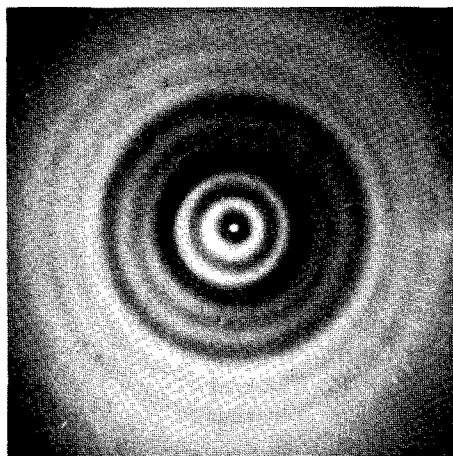


FIG. 5. Reproduction of electron diffraction photograph obtained from As_4O_6 .

further support the correctness of the chosen model.

The complete scattering curve in the region of the second maximum for an oxygen valence angle of 130° was computed according to Eq. (1). A real maximum was obtained at $x_{p-p} = 12.7$ as illustrated in Fig. 6. Fig. 7 illustrates a typical densitometer record of the second maximum whose position occurs at $(1/\lambda) \sin \frac{1}{2}\theta = 0.342$. From Eq. (2) we thus obtained a $l_{p-p} = 2.95\text{\AA}$ from the densitometer measurements. This provides a confirmation of the P-P separation rather than the oxygen valence angle since the position of the second maximum is a relatively insensitive function of this angle.

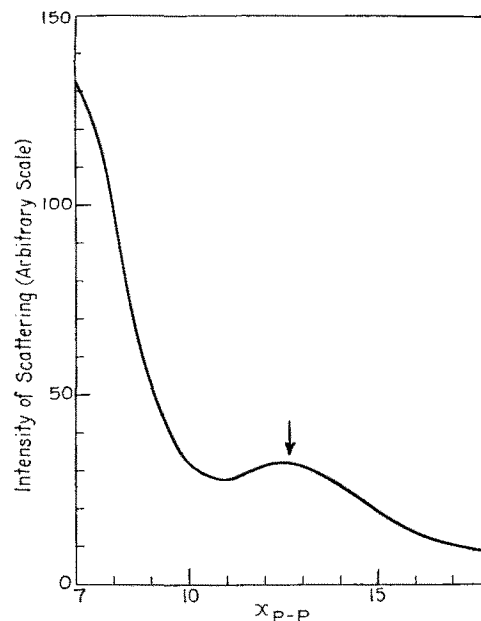


FIG. 6. Electron scattering curve for P_4O_6 using the complete scattering formula for an oxygen valence angle of 130° .

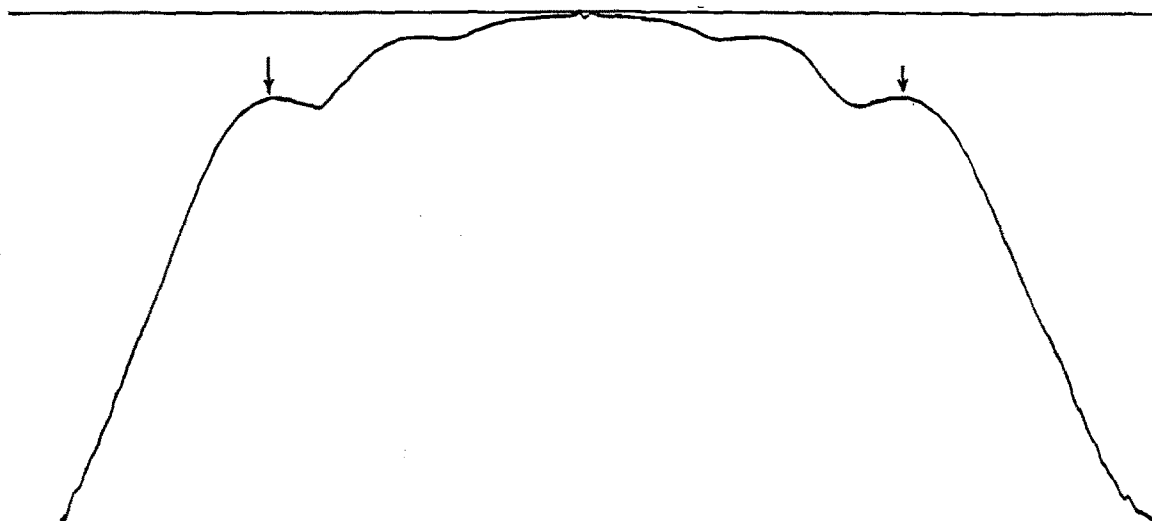
Phosphorus pentoxide (P_4O_{10})

In the first instance it is assumed that P_4O_{10} has the molecular symmetry of the point group T_d and that the atomic positions are given by the parameters used for P_4O_6 with additional oxygen atoms at www , $\bar{w}\bar{w}w$, $w\bar{w}\bar{w}$, and $\bar{w}w\bar{w}$. The general formula for the intensity of electron scattering $I_2(\theta)$ becomes

TABLE II. Visual measurements of $(1/\lambda) \sin \frac{1}{2}\theta$ for the electron interference maxima obtained from P_4O_6 , P_4O_{10} and As_4O_6 .

No.	P_4O_6	P_4O_{10}	As_4O_6
1	$0.205 \pm .001$ (2)* s.	$0.163 \pm .004$ (4) sharp, w.	$0.1916 \pm .0004$ (3) s.
2	$0.361 \pm .001$ (2) s.	$0.388 \pm .001$ (5) v. s.	$0.3436 \pm .001$ (3) s.
3	$0.672 \pm .006$ (5) s.	$0.498 \pm .003$ (6) barely resolved	$0.4935 \pm .002$ (5) m.
4	$0.852 \pm .005$ (3) m.	0.66 approx. (diffuse band)	$0.6457 \pm .004$ (7) s.
5	$1.016 \pm .014$ (3) m.	$1.020 \pm .003$ (6) medium	$0.8181 \pm .003$ (7) m.
6	$1.244 \pm .006$ (6) m.	$1.275 \pm .004$ (6) medium	$0.9756 \pm .004$ (7) m.
7	1.418 (1) w.	$1.618 \pm .006$ (3) v. w.	$1.138 \pm .003$ (10) m.
8	$1.580 \pm .006$ (4) m.	—	$1.293 \pm .005$ (6) w.
9	—	—	$1.445 \pm .004$ (5) w.
Two very prominent minima occur at 0.315 ± 0.003 and 0.561 ± 0.005 , respectively.			

* Number in parenthesis gives number of photographs taken. Variations shown are the average deviations obtained between measurements taken on different photographs.

FIG. 7. Densitometer record taken of P_4O_6 showing the presence of a real second maximum.

$$I_2(\theta) = I_1(\theta) + 8\psi_p\psi_o \left(\frac{\sin s \cdot [3(w-u)^2]^{\frac{1}{2}}}{s \cdot [(3(w-u)^2)^{\frac{1}{2}}]} + \frac{3 \sin s \cdot [2(w+u)^2 + (w-u)^2]^{\frac{1}{2}}}{s \cdot [2(w+u)^2 + (w-u)^2]^{\frac{1}{2}}} \right) \\ + 4\psi_o^2 \left(1 + \frac{6 \sin s \cdot [(w-v)^2 + 2w^2]^{\frac{1}{2}}}{s \cdot [(w-v)^2 + 2w^2]^{\frac{1}{2}}} + \frac{6 \sin s \cdot [(w+v)^2 + 2w^2]^{\frac{1}{2}}}{s \cdot [(w+v)^2 + 2w^2]^{\frac{1}{2}}} + \frac{3 \sin s \cdot (8w^2)^{\frac{1}{2}}}{s \cdot (8w^2)^{\frac{1}{2}}} \right) + I_{inc}''(\theta), \quad (3)$$

where $I_{inc}''(\theta)$ represents the additional amount of incoherent scattering arising from the 4 extra oxygen atoms.

Table I contains a summary of the visual measurements. This interference pattern showed a rather sharp inner ring occurring at $(1/\lambda) \sin \frac{1}{2}\theta = 0.16$ followed by a prominent minimum at 0.315. A very strong second maximum was observed which was followed by a strong second minimum. At approximately $(1/\lambda) \sin \frac{1}{2}\theta = 0.66$ there occurred a diffuse band-like scattering with a sharp inner edge. It can be seen from the general characteristics of the interference pattern that considerable departure is shown from the P_4O_6 scattering.

Fig. 8 illustrates theoretical scattering curves using $\psi_i = Z_i$ for various models as listed in Table III. Positions of the experimental maxima obtained by visual measurement are indicated on this figure; none of the models considered gives good agreement. Considerable disagreement is noticed for the innermost ring which corresponds to a distance in the molecule of approximately 3.7Å as would be given by a first interference maximum. Densitometer records were

taken of the strong second maximum and a typical trace is shown in Fig. 9. It is noticed that a real maximum is obtained and its position comes at $(1/\lambda) \sin \frac{1}{2}\theta = 0.379$ which is about 2 percent less than the value found by visual measurements. Intensity of electron scattering was calculated in the region of the second maximum according to Eq. (3) for model 5 using the exact values for ψ_i . Fig. 10 shows the curve obtained in this manner with a real maximum at $x_{p-p} = 13.5$. Thus we obtained from

TABLE III. Models used for calculating electron scattering curves for P_4O_{10} .

Model No.	Type of Model	
1	P-O-P=109°30'	P-O=1.76Å
	P-P=2.87Å	P-O=1.60Å
2	P-O-P=114°	P-O=1.68Å
	P-P=2.82Å	P-O=1.52Å
3	P-O-P=120°	P-O=1.67Å
	P-P=2.89Å	P-O=1.60Å
4	P-O-P=120°	P-O=1.68Å
	P-P=2.89Å	P-O=1.52Å
5	P-O-P=130°	P-O=1.68Å
	P-P=3.04Å	P-O=1.60Å
6	P-O-P=130°	P-O=1.68Å
	P-P=3.04Å	P-O=1.50Å

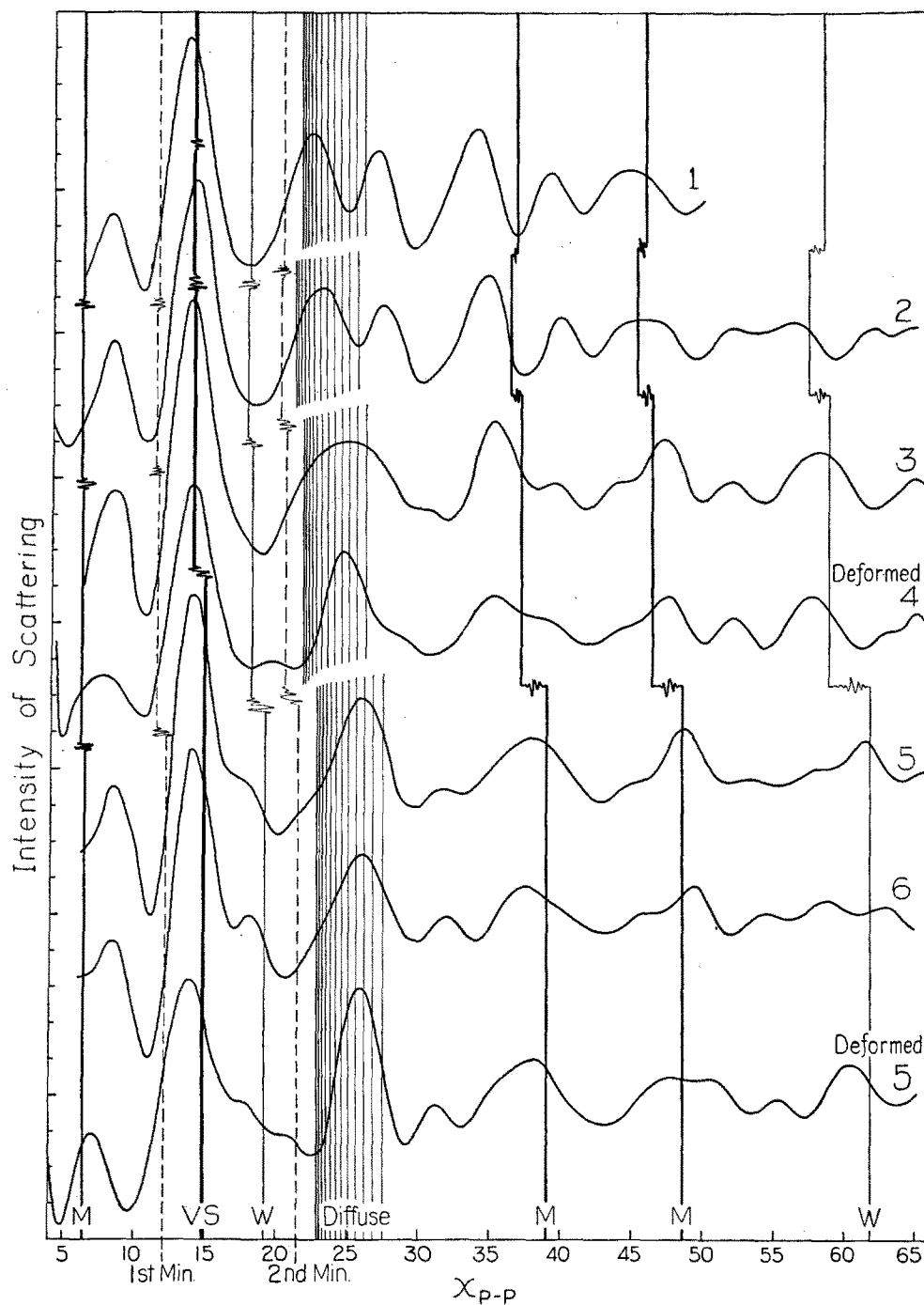


FIG. 8. Electron scattering curves for P_4O_{10} where ψ_i is replaced by Z_i calculated for various models listed in Table III. Vertical lines give the relative position of the experimental maxima and minima as governed by the models considered. The incoherent scattering has been omitted.

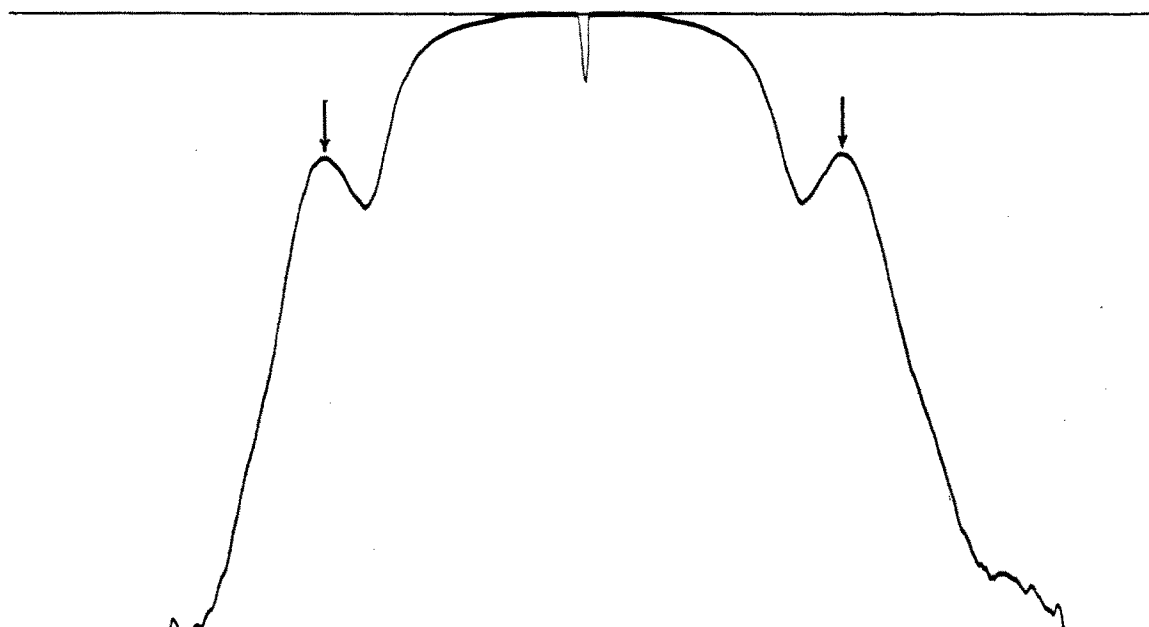


FIG. 9. Densitometer record taken of P_4O_{10} showing presence of a real second maximum.

Eq. (2) a $l_{p-p} = 2.83\text{\AA}$ which is in poor agreement with the actual assumed separation of 3.04\AA .

In the various models computed as shown in Fig. 8 it is noticed that the position of the second maximum does not greatly change as various alterations of the molecule are made so that one can estimate that the P-P separations must be near 2.9\AA as determined by the densitometer records.

From simply an inspection of the models calculated it is possible to exclude many other models for P_4O_{10} . For example, if model 5 were reduced in size to give a $P-P = 2.89\text{\AA}$, $P-O = 1.60\text{\AA}$, $P=O = 1.52\text{\AA}$, maintaining the oxygen valence angle constant, the theoretical scattering curves expressed in terms of x_{p-p} would be identical with the curve given for model 5 in Fig. 8. The experimental maxima would all be proportionally decreased in position for comparison with the theoretical curve and hence give poor agreement especially for the outer maxima. This analysis can be applied to all the other models with subsequent disagreement as long as the oxygen valence angles are maintained unchanged. It is also possible to eliminate other models by a study of the theoretical curves shown for P_4O_6 , for several of the

prominent diffraction features of P_4O_6 are maintained in the P_4O_{10} scattering curves.

Calculations were also carried out for distorted models having the symmetry of the point group $V_d \equiv D_{2d}$. The constants were those given for

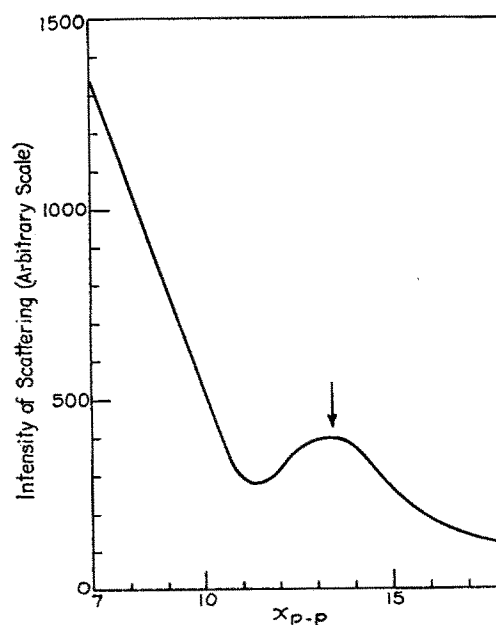


FIG. 10. Electron scattering curve for P_4O_{10} using the complete scattering formula for model 5.

models 4 and 5 of Table III with oxygen to oxygen distances (*www'* to *voo* and *ovo*) equal to 2.38Å and 2.28Å, respectively. Curves calculated for these models are also shown in Fig. 8. The agreement with the experimental data is not improved by these particular deformations which were used chiefly to facilitate calculations.

DISCUSSION

There are essentially three determining factors that can be obtained from the structure found for P_4O_6 , the valence angle of the oxygen and phosphorus atoms and the P to O single bond separation. The observed oxygen valence angle of 128.5° is greater than the angles of 100° to 118° as found for compounds not having a closed structure.⁶ The P—O separation was found to be 1.67Å which is less than the sum of the single bond radii 1.76Å as given by Pauling and Huggins.⁵ This departure is in the same direction as that observed for PCl_3 , PF_3 and PF_5 .⁶ From the standpoint of the directed valence of the phosphorus atom the angle O—P—O comes out to be $98^\circ \pm 2^\circ$ for P_4O_6 which does not differ greatly from values found for black phosphorus 102° ,⁷ PCl_3 101° ⁶ and $POCl_3$, 104° .⁶ Thus it appears that the phosphorus oxygen distances and the phosphorus valence angles are preserved with resulting deformation of the oxygen valence angle.

For As_4O_6 several possible values were obtained for the oxygen valence angle. A final choice was not made although the model with a valence angle of 140° seemed to be slightly preferable. Crystal structure data from As_4O_6 ⁸ give an As—O—As angle of 109° a value which is excluded by the electron diffraction results. The As—As distance in the crystal is 3.28Å which is close to the electron diffraction value of $3.20 \pm .05$ Å.

Satisfactory explanation of the electron diffraction results from P_4O_{10} was not obtained for models having the symmetry of the point group T_d . Closest agreement for the outermost maxima

was obtained for model 5 which has the same constants as the P_4O_6 structure with a P=O distance of 1.60Å. In the case of P_4O_6 the character and calculated positions of the first three maxima were in good agreement with observation. However, this was not the case for P_4O_{10} and it is quite improbable that the additional oxygen atoms could produce the observed changes if the T_d symmetry were maintained. On the basis of the above considerations it seems logical to propose that the actual structure of P_4O_{10} is one of lower symmetry in which none of the atoms is in the position required by the symmetry T_d . However, there can be but little doubt that the phosphorus atoms have approximately the same arrangement as in P_4O_6 .

No information is available on the crystal structure of the phosphorus oxides, however some prediction can be made in that regard. When yellow phosphorus changes to black phosphorus there is a transformation from a lattice consisting of small groups of atoms sharing covalent bonds to an extensive space network or homopolar lattice. This results in a change in valence angle of phosphorus from 60° to 102° or more nearly the valence angle found in PCl_3 , $POCl_3$ and P_4O_6 . Thus one expects that this larger angle would be preserved in a possible homopolar lattice of the pentoxide. Single bonds of the P_4O_{10} molecule could be rearranged in the transition for this compound and the resulting structure might be expected to be one with less distortion of the oxygen valence angle.

The authors wish to thank Mr. J. Floyd Shultz for preparing the samples of P_2O_3 and P_2O_5 which were used in this work. P_2O_3 may have contained only a small amount of phosphorus as an impurity while the P_2O_5 was completely purified by distilling commercial P_2O_5 in O_2 in an iron furnace at 800°C .

We also wish to acknowledge the assistance of Mr. V. M. Mosley who operated the electron diffraction camera used.

Note on Phosphorus Tetroxide (P_4O_8) Added in Proof July 9th, 1937:

The above work was submitted for publication without information on phosphorus tetroxide because no suitable samples of the material were available. Dr. Emmett and Mr. Shultz of this laboratory have now prepared phosphorus tetroxide as a mixture with phosphorus pentoxide. Analysis by Mr. Shultz of the material condensed from

⁵ L. Pauling and M. Huggins, *Zeits. f. Krist.* **87**, 205 (1934).

⁶ L. O. Brockway, *Rev. Mod. Phys.* **8**, 231 (1936). Also H. Braune and P. Pinnow, *Zeits. f. physik. Chemie* **35**, 239 (1937).

⁷ R. Hultgren, N. S. Gingrich and B. E. Warren, *J. Chem. Phys.* **3**, 351 (1935).

⁸ R. M. Bozorth, *J. Am. Chem. Soc.* **45**, 1621 (1923).

the molecular beam in the electron diffraction camera showed approximately 50 percent phosphorus tetroxide and 50 percent phosphorus pentoxide. They will later describe the method of preparation used. Electron diffraction photographs obtained from this mixture gave an interference pattern almost identical to that found for P_4O_{10} . Values of $(1/\lambda) \sin \frac{1}{2}\theta$ for the interference maxima Nos. 2, 3, 5 and 6 agreed with the data given for P_4O_{10} in Table II above to within less than 1 percent. The first maximum appeared to be slightly weaker than the similar

one found for P_4O_{10} but it had approximately the same position. Both first and second minima differed by less than 2 percent in position from the corresponding minima for P_4O_{10} . It was possible to see an additional weak maximum for the mixture at $(1/\lambda) \sin \frac{1}{2}\theta = 0.87$ which was previously too weak for measurement in the case of P_4O_{10} .

Since the resultant diffraction pattern of this mixture is practically the same as for a pure sample of P_4O_{10} it is thus concluded that the true interference pattern of P_4O_8 must be approximately the same as found for P_4O_{10} .

AUGUST, 1937

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VOLUME 5

The Temperature Variation of Some Thermodynamic Quantities*

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The quantity, $(F^0 - E_0^0)/T$, calculated from spectroscopic data has been fitted to a five constant equation in T for 19 molecules. It may be differentiated and integrated to give values of S^0 , E^0 , H^0 and C_p^0 between 298.1 and 3000°K and is sufficiently exact for most purposes. The equilibrium constant for exchange reactions involving isotopes has been calculated and in each case, maxima exist and in one case a minimum also. This effect probably occurs at some temperature for all reactions involving isotopic molecules although not for other equilibria. An optimum temperature therefore exists for separation of isotopes by exchange reactions.

THE calculation of thermodynamic quantities from spectroscopic data has usually resulted in numerical values of these functions at a series of temperatures, 100° or so apart.¹ Since most experiments are performed at some odd temperature, interpolation in these tables is necessary in order to make comparison with the calculations. This may be done graphically from a large scale plot or by some method of numerical interpolation, either of which may be rather tedious. It is obvious that an analytical expression to represent these quantities as a function of the temperature would be useful. This has been done for the heat capacity of a number of molecules by Spencer and Justice² but a suitable expression for the variation of the free energy with temperature appears more satisfactory as this may be differentiated and integrated to give other thermodynamic quantities without the

involved summation necessary to obtain them directly from the spectroscopic data.

The constants for a satisfactory analytical equation have been given recently³ for H_2 , D_2 , HI and DI and it is the purpose of this paper to give the constants for other molecules and to apply the results in calculating the variation with temperature of the equilibrium constant of certain exchange reactions.

If we represent the free energy function by the equation⁴

$$-(F^{0*} - E_0^0)/T = a/T + b \log T + cT + dT^2 + \dots + i, \quad (1)$$

the well-known methods of thermodynamics⁵ lead immediately to expressions for the additional quantities:

$$S^{0*} = -dF^0/dT = -b\{\log e + \log T\} + 2cT + 3dT^2 + \dots + i, \quad (2)$$

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¹ For a review of the methods of calculation and references to molecules for which calculations have been made, see Kassel, *Chem. Rev.* **18**, 277 (1936).

² Spencer and Justice, *J. Am. Chem. Soc.* **56**, 2311 (1934).

³ Murphy, *J. Chem. Phys.* **4**, 344 (1936); Blagg and Murphy, *ibid.* **4**, 631 (1936).

⁴ For the meaning of the symbols used here, see Giauque, *J. Am. Chem. Soc.* **52**, 4808 (1930).

⁵ See any text-book on thermodynamics, as Lewis and Randall, *Thermodynamics* (McGraw-Hill Book Co., New York, 1923).