oxide to silicon dioxide ranging from 1:1 to 2:1. Since the materials used by Kühl and Mann were synthetic melts and the products at equilibrium not formed by the combination of the basic constituents calcium oxide and silica but by hydrolysis or hydration of the silicates, the results do not lend themselves to a direct comparison with the observations reported here.

Summary

On the basis of the results secured by means of the conductivity method and under the conditions of the experiment, the reactions between calcium oxide and silica proceed in the following manner:

With dilute solutions the silica adsorbs calcium oxide in accordance with the Freundlich adsorption isotherm. Above an initial ratio of CaO/SiO_2 of 0.30 and up to 0.60, chemical combination takes place, and a reaction product is formed in which the ratio of CaO/SiO_2 is 1 to 2. This product is stable in a solution containing 1.5 m. e. of calcium oxide per liter.

On increasing the calcium oxide concentration further above an initial ratio of 0.60, adsorption takes place again, which proceeds until the initial ratio of CaO/SiO_2 is 0.90 and the ratio of combined CaO/SiO_2 is 4 to 5.

The reaction product with the ratio of 4CaO to $5SiO_2$ is stable up to an equilibrium concentration of 10 m. e. of calcium oxide per liter. With higher concentrations of calcium oxide and initial ratios from 1.3 to 3.75, a third range of adsorption reactions takes place. As the point of saturation of the calcium oxide solution at equilibrium is reached, the ratio of CaO/SiO_2 in the reaction product approaches 2:1, indicating the probable existence of a hydrated $2CaO{\cdot}SiO_2$ in saturated calcium oxide solution.

CHICAGO, ILL. RECEIVED APRIL 23, 1938

[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY No. 648]

The Electron Diffraction Investigation of the Molecular Structures of (1) Phosphorus Oxytrichloride, Oxydichlorofluoride, Oxychlorodifluoride, Oxytrifluoride, Fluorodichloride, Pentafluoride, and Trifluorodichloride, and of (2) Disilane, Trichlorosilane, and Hexachlorodisilane

BY L. O. BROCKWAY[1] AND J. Y. BEACH[2]

The molecular structures of the halogen derivatives of the non-metals are of special interest because of the systematic deviations from additivity of bond radii which are observed in many of these substances.[3,4] With the exception of those of the first row elements, the observed distances in the halogen derivatives are all smaller than the sum of the corresponding radii for single covalent bonds. This decrease is apparently greatest in the silicon compounds and is less marked in the elements toward the right and in the lower rows of the periodic table. The effect, moreover, is greatest in the fluorides and decreases in order with the other halogens. While the regular way in which the effect varies from one element to another suggests that the same causes are operating in all of them, the nature of the causes is not entirely certain. It seemed desirable to extend the investigation of phosphorus and silicon compounds, where the effect is greatest, and we have determined the structures of a number of mixed fluorine and chlorine derivatives of phosphorus, including some oxygen compounds, as well as those of three silicon compounds.

The diffraction patterns were obtained in the usual way,[5] whereby a beam of electrons traverses a sample of the vapor and the diffracted electrons are recorded on a photographic emulsion. The apparent maxima as well as some of the minima were measured visually on a comparator, and the observed diameters were converted to the s_0 values [equal to $4\pi (\sin \theta/2)/\lambda$] listed in the tables below. The s_0 values for the maxima were used with the visually estimated intensities, I_k, in the calculation of the functions shown in Figs. 1 and 8 representing the observed radial

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[3] L. O. Brockway and F. T. Wall, THIS JOURNAL, **56**, 2373 (1934); L. O. Brockway and H. O. Jenkins, *ibid.*, **58**, 2036 (1936).

[4] A. H. Gregg, G. C. Hampson, G. I. Jenkins, P. L. F. Jones and L. E. Sutton, *Trans. Faraday Soc.*, **33**, 852 (1937).

[5] L. O. Brockway, *Rev. Modern Phys.*, **8**, 231 (1936).

distributions[6] of scattering matter for the various substances. In cases where the total range of estimated intensities was greater than ten to one, a "corrected intensity" was used, namely, $s^2e^{-as^2}I_k$, with a given the value which made the range of "corrected intensities" equal to ten to one.[7] The principal peaks in the distribution functions correspond to internuclear distances in the molecules. While the positions of the peaks are most reliable in the curves based on eight or nine measured maxima, curves are shown for all of the substances having more than three measurable maxima in the photographs. For the sake of comparison the vertical lines in Figs. 1 and 8 mark the internuclear distances as determined with the aid of theoretical intensity curves; the heights of the lines show the relative scattering powers associated with the atom pairs.

The other figures show various theoretical intensity curves calculated from the approximate scattering function, $I = \Sigma_{ij} Z_iZ_j(\sin sr_{ij})/sr_{ij}$, in which the summation extends over all of the atoms in the molecule, Z_i is the atomic number of the ith atom and r_{ij} is the separation of the ith and jth atoms. A choice was made among the molecular models on the basis of the selection of the curve which best reproduces the qualitative features of the observed diffraction pattern. In the tables the s values, corresponding to the maxima and minima in the curve, are compared quantitatively with the s_0 values, and the r_{ij} values assumed in the model are multiplied by the average of the s/s_0 ratios to obtain the observed interatomic distances. Wherever the measured diameter is unreliable because of excessive back-intensity or a marked asymmetry in the maximum, the corresponding s/s_0 ratio has been excluded in taking the average.

The samples of POF_3, POF_2Cl, $POFCl_2$, and $PFCl_2$ were provided by Professor H. S. Booth, A. R. Bozarth, and Fred Dutton of Western Reserve University. For $POCl_3$ the commercial product was used after fractional distillation. Preparations of PF_5 and PF_3Cl_2 were made by V. Schomaker and J. B. Hatcher under the direction of Professor D. M. Yost in this Laboratory. The sample of Si_2Cl_6 was prepared by Dr. Fred Stitt, and those of Si_2H_6 and $SiHCl_3$ were furnished by Professor Warren C. Johnson of the University of Chicago.

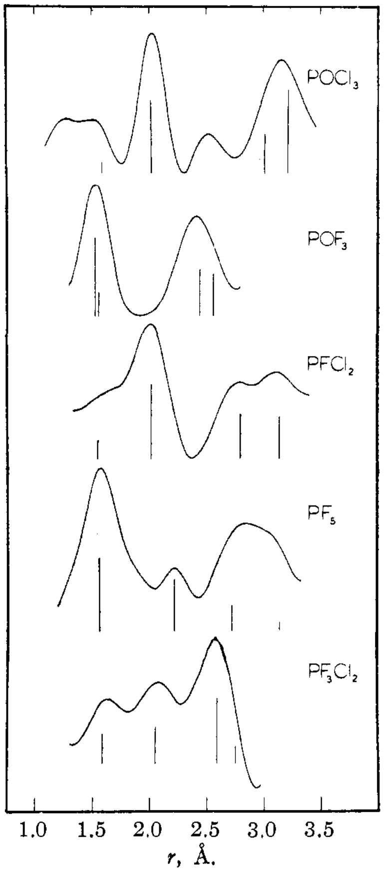

Fig. 1.—Observed radial distributions of scattering matter in the phosphorus compounds. The vertical lines represent the internuclear distances as determined by the comparison of the photographs with theoretical intensity curves.

TABLE I

PHOSPHORUS OXYTRICHLORIDE

Max.	Min.	I_k	s_0	s^a	s^b	s^a/s_0	s^b/s_0
1		8	(2.54)	2.58	2.55		
2		20	4.34	4.33	4.26	0.998	0.982
3			5.55	5.45	5.42	.982	.977
3		16	6.60	6.61	6.59	1.002	.998
4		4	(8.20)	8.44	8.09		
5		12	10.18	10.25	10.11	1.007	.993
	6		11.71	11.48	11.35	0.980	.969
6		10	13.04	12.80	13.50	.981	1.035
	7		14.85	14.98	14.78	1.009	0.995
7		6	16.21	16.30	15.97	1.006	.985
8		2	19.25	19.77	19.64	1.027	1.020
9		1	22.21	22.09	21.86	0.994	0.984
					Average	0.999	0.994
					Cl–Cl, Å.	3.207	3.240
					P–Cl	2.018	2.008

[a] Calculated for P–Cl = 2.02 Å., P–O = 1.58 Å., and ∠ClPCl = 105°. [b] Calculated for P–Cl = 2.02 Å., P–O = 1.58 Å., and ∠ClPCl = 107.5°.

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(6) L. Pauling and L. O. Brockway, THIS JOURNAL, **57**, 2684 (1935).

(7) The significance of the correction factors will be discussed by V. Schomaker and C. Degard in a later paper.

Phosphorus Oxytrichloride.—The photographs of $POCl_3$ show nine rings with the relative intensities and s_0 values given in Table I. With the exception of the first and fourth maxima the decline in intensity is fairly regular. The fourth maximum is very faint in comparison with the third and fifth, while the sixth is relatively broad with a slight shelf on the outer edge. The radial distribution curve (Fig. 1) shows two principal peaks. The first at 2.02 Å. represents the P–Cl distance and the second near 3.2 Å. represents the O–Cl and Cl–Cl distances unresolved.

Six theoretical curves were calculated having the assumed distances P–Cl = 2.02 Å., P–O = 1.58 Å., and ∠ClPCl = 90, 100, 105, 107.5, 110, and 120°, respectively. The first and last failed to reproduce any of the distinguishing features of the observed diffraction pattern. The other four are shown in Fig. 2. The 100° model is incorrect because its curve shows a too strong fourth maximum and an extra maximum between the sixth and seventh. In the 110° curve the fourth maximum has turned into a shelf and an extra maximum appears between the fifth and sixth, and this, too, is incorrect. The best general agreement is given by a model lying between those for 105 and 107.5°; and on the basis of the observed appearance of the fourth and sixth maxima the ClPCl angles are fixed at 106 ± 1°. The data of Table I and the radial distribution curve lead to the distances P–Cl = 2.02 ± 0.03 Å., and Cl–Cl = 3.22 ± 0.03 Å. A preliminary value of 104 ± 4° for the angle was reported previously.[5]

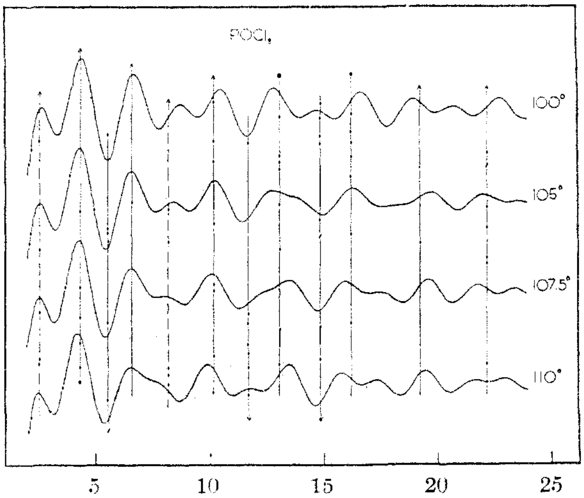

Fig. 2.—Theoretical intensity curves for phosphorus oxytrichloride. The arrows show the positions of the maxima and minima as measured on the photographs.

The low scattering power of the oxygen atom relative to that of the phosphorus and chlorine atoms means that its position cannot be as accurately fixed. The value, 3.01 Å., for the Cl–O distance occurring in the model accepted above is supported by the position of the second strong peak in the radial distribution curve. The displacement of this peak toward the Cl–Cl position is in agreement with the greater scattering power associated with the Cl–Cl terms. The corresponding P–O distance, 1.58 Å., is supported within 0.02 Å. by the more direct determination in POF_3.

Phosphorus Oxytrifluoride.—Photographs of POF_3 were obtained over the same range of scattering angle as observed for $POCl_3$, but on account of the smaller size of the POF_3 molecule only five maxima appeared. These are quite regular except for the shelf on the second. The five term radial distribution function shows peaks at 1.53 and 2.42 Å., the first representing P–F and P–O and the second F–F and O–F.

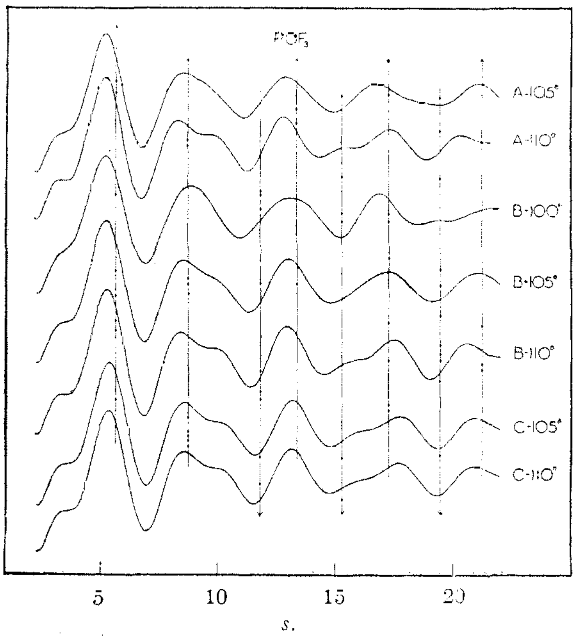

Fig. 3.—Theoretical intensity curves for phosphorus oxytrifluoride.

Thirteen intensity curves were calculated covering a range of the ratio P–O/P–F from 0.90 to 1.07° and a range of the FPF angle from 95 to 115°. The seven shown in Fig. 3 were calculated with the following parameter values: P–F = 1.56 Å., in all curves; A, P–O = 1.67 Å., ∠FPF = 105, 110°; B, P–O = 1.58 Å., ∠FPF = 100, 105, 110°; C, P–O = 1.49 Å., ∠FPF = 105, 110°. Among those not shown three curves were calculated having P–O = 1.40 Å. and P–F bond angles from 100 to 110°. These have two maxima instead of one between s = 14 and 19. The C curves with P–O = 1.49 Å. are somewhat better but the fourth maximum still lacks the symmetrical shape observed in the photographs. It may be noted that C-105° and C-110° are scarcely distinguishable because the change in angle has only the effect of interchanging the F–F and O–F distances. In the B curves (P–O = 1.58 Å.) the 100° model has no shelf on the second maximum, the 110° model has a faulty fourth maximum, while the 105° curve is reasonably satisfactory. In the A curves (P–O = 1.67 Å.) the small maximum preceding the fourth in the 110° model is incorrect, while the 105° curve is much better.

TABLE II

PHOSPHORUS OXYTRIFLUORIDE

Max.	Min.	I_k	s_0	s^a	s/s_0
1		8	(5.63)	5.23	(0.929)
2		10	8.71	8.45	.970
	3		11.82	11.29	.955
3		8	13.35	12.92	.968
	4		15.27	14.67	.961
4		3	17.25	17.20	.997
	5		19.43	19.11	.984
5		1	21.24	20.84	.981
				Average	0.974
				P–F, Å.	1.519
				P–O	1.568
				F–F	2.442

[a] Calculated for P–F = 1.56 Å., P–O = 1.61 Å., and ∠FPF = 107°.

A survey of all the models shows that among those definitely eliminated are all those with FPF bond angles as large as 110° and those in which the O–F distances are not larger than the F–F distances. On the other hand, the angle is not less than 105°, so that the P–O distance cannot be appreciably less than the P–F distance. The most probable values for the P–O/P–F ratio and the FPF bond angle chosen for the best qualitative agreement between curve and photographs are 1.03 and 107°. In the table the s values for the model having these parameter values are compared with the s_0 values. The final results for the distances are P–F = 1.52 ± 0.02 Å., P–O = 1.56 ± 0.03 Å., and F–F = 2.44 ± 0.02 Å., with ∠FPF = 107 ± 2°.

Phosphorus Oxydifluorochloride and Oxyfluorodichloride.—Six rings were observed in the photographs of POF_2Cl and $POFCl_2$, but in each case a heavy background obscured the first three and only the outer ones were really distinctly resolved. Because of the lack of reliable measurements on the inner rings radial distributions were not calculated. For the same reason it was scarcely possible to make a complete treatment of the several parameters required to fix the molecular model. On the other hand, the occurrence of the same bond angles in $POCl_3$ and POF_3 suggested that there would be no appreciable variations in the structures of the two intermediate compounds. Accordingly, a theoretical curve was calculated for each with the distances and angles observed in the two previous cases, *i. e.*, P–Cl = 2.02 Å., P–F = 1.52 Å., P–O = 1.57 Å., and ∠FPF = ∠FPCl = ∠ClPCl = 106°.

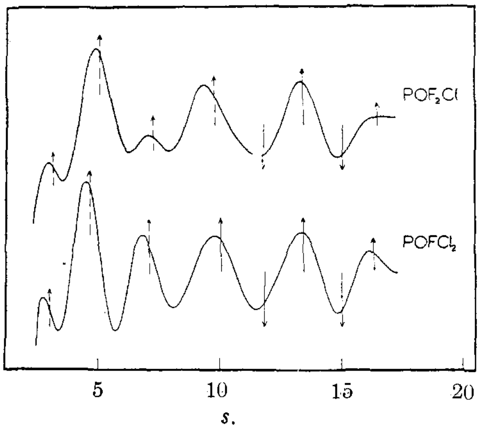

Fig. 4.—Theoretical intensity curves for phosphorus oxydifluorochloride and -fluorodichloride.

The two curves in Fig. 4 represent very well the qualitative feature in the photographs. In particular, the third ring in POF_2Cl is observed to be much weaker than the fourth, whereas in $POFCl_2$ the third and fourth rings are nearly equal. In the quantitative comparisons in Tables III and IV only the outer rings are used as indicated. Although the results for the two compounds differ by 1%, this is not significant in view of the probable experimental error which is estimated to be ±2% in this case. The values for POF_2Cl are P–Cl = 2.01 ± 0.04 Å., P–F = 1.51 ± 0.03 Å., P–O = 1.55 ± 0.03 Å., and ∠FPF = ∠FPCl = 106 ± 3°; for $POFCl_2$, P–Cl = 1.99 ± 0.04 Å., P–F = 1.50 ± 0.03 Å., P–O = 1.54 ± 0.03 Å., ∠FPCl = ∠ClPCl = 106 ± 3°.

Table III

Phosphorus Oxydifluorochloride

Max.	Min.	s_0	s^a	s/s_0
1		(3.10)	3.00	(0.968)
2		(5.07)	4.94	(.974)
3		(7.26)	7.11	(.979)
4		(9.82)	9.42	(.959)
	5	11.82	11.67	.987
5		13.45	13.35	.993
	6	15.07	14.88	.987
6		16.47	16.53	1.004
			Average	0.993
			P–Cl, Å.	2.006
			P–F	1.509
			P–O	1.549

[a] Calculated for P–Cl = 2.02 Å., P–F = 1.52 Å., P–O = 1.56 Å., ∠FPF = ∠FPCl = 106°.

Table IV

Phosphorus Oxyfluorodichloride

Max.	Min.	s_0	s^a	s/s_0
1		(2.99)	2.75	(0.920)
2		(4.67)	4.53	(.970)
3		(7.11)	6.86	(.965)
4		10.08	9.80	.972
	5	11.84	11.49	.970
5		13.45	13.39	.996
	6	15.02	14.86	.989
6		16.36	16.18	.989
			Average	0.983
			P–Cl, Å.	1.986
			P–F	1.495
			P–O	1.535

[a] Calculated for P–Cl = 2.02 Å., P–F = 1.52 Å., P–O = 1.56 Å., ∠FPCl = ∠ClPCl = 106°.

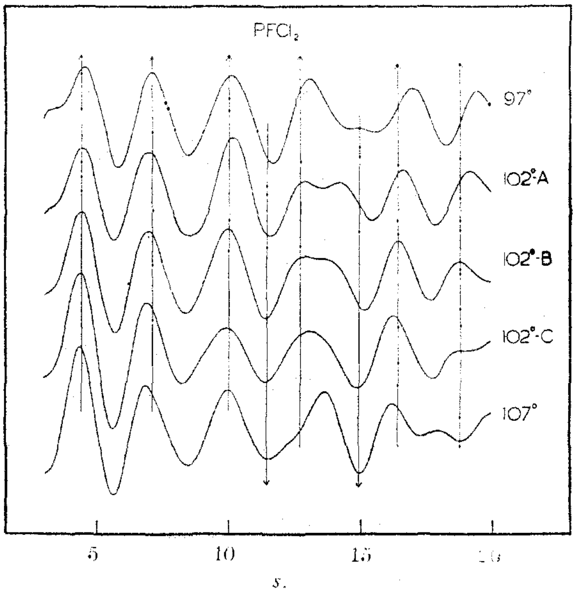

Fig. 5.—Theoretical intensity curves for phosphorus fluorodichloride.

Phosphorus Fluorodichloride.—The six term radial distribution function for $PFCl_2$ (Fig. 1) has a sharp peak at 2.01 Å., corresponding to the P–Cl distance in the molecule. The F–Cl and Cl–Cl distances are also represented but are not well enough resolved for distance determinations. In the calculation of theoretical curves the three bond angles were assumed to be equal and were varied from 90 to 120° with P–Cl = 2.02 Å. and P–F = 1.52 Å. Angle values outside of the range 97 to 107° (Fig. 5) were rejected because the curves showed extra maxima not observed in the photographs. The 97 and 107° curves are not satisfactory because they do not reproduce the rather broad fourth maximum followed by a sharp minimum. For the 102° curves the P–F distance has the assumed values A, 1.42 Å., B, 1.52 Å., C, 1.62 Å. A shows a doubled fourth maximum, which is not observed. Comparison of B and C suggests that the correct model lies between the two but nearer to B.

The data of Table V show how little the positions of the maxima are affected by the change in P–F distance in going from 102°-B to 102°-C (Fig. 5). This distance may be fixed within rather broad limits by the qualitative comparison. The final values are P–Cl = 2.02 ± 0.03 Å., P–F = 1.55 ± 0.05 Å., ∠FPCl = ∠ClPCl = 102 ± 3°. These are consistent with the observed radial distribution curve. The preliminary value for P–Cl reported earlier[5] has been increased by 0.02 Å. in the complete analysis.

Table V

Phosphorus Fluorodichloride

Max.	Min.	I_k	s_0	s^a	s^b	s^a/s_0	s^b/s_0
1		5	4.40	4.42	4.38	1.005	0.995
2		7	7.08	6.93	6.92	0.979	.977
3		6	10.01	10.00	9.92	.999	.991
	4		11.46	11.43	11.45	.997	.999
4		4	12.70	12.93	13.10	1.016	1.031
	5		14.93	15.19	14.94	1.017	1.001
5		2	16.42	16.46	16.31	1.002	0.993
6		1	18.81	18.84	18.85	1.002	1.002
					Average	1.002	0.999
					P- Cl, Å.	2.024	2.018
					P–F	1.523	1.618
					Cl–Cl	3.146	3.137
					F–Cl	2.774	2.832

[a] Calculated for P–Cl = 2.02 Å., P–F = 1.52 Å., bond angles = 102°. [b] Calculated for P–Cl = 2.02 Å., P–F = 1.62 Å., bond angles = 102°.

Phosphorus Pentafluoride.—In the six ring pattern observed in the PF_5 photographs the first ring is very heavy and broad and difficult to measure, while the fourth ring is the weakest of all those observed. The principal peak in the radial distribution function occurs at 1.58 Å., and is to be identified with the P–F distance.

Of the two types of molecular models considered the first is the trigonal bipyramid with the phosphorus atom at the center of an equilateral triangle of three fluorine atoms and the other two fluorine atoms on opposite sides of the phosphorus atom on a line perpendicular to the triangle. Curve A (Fig. 6) represents this model with P–F = 1.60 Å. The other models (designated B) are square pyramids with one fluorine atom at the apex and the other four at the corners of the square base. The angles between the P–F bond directed toward the apex and the bonds directed to the corners of the base were varied from 90 to 120°.

The B models with bond angles greater than 95° are unsatisfactory in that the fourth maximum is missing. Model B-90° and model A both show good agreement with the photographs; and since they differ only in the first maximum, which is poorly defined in the photographs, a choice between these two models cannot be made by means of the electron diffraction curves. It may be argued, however, that if the PF_5 molecule were based on a square pyramidal model the angles between the apex bond and the other bonds would be greater than 90° because of the unbalanced repulsions between the fluorine atoms. A simplified calculation based on Coulomb forces between the fluorine atom pairs leads to an angle value of 105° for the configuration of minimum potential energy. Such a model is definitely eliminated by the observed diffraction pattern.

TABLE VI

PHOSPHORUS PENTAFLUORIDE

Max.	Min.	I_k	s_0	s^a	s/s_0
1		10	(4.86)	4.96	(1.021)
2		8	9.17	8.98	0.979
	3		11.02	10.72	.973
3		6	12.34	12.17	.986
4		2	14.29	14.00	.980
	5		15.73	15.25	.969
5		4	17.18	16.86	.981
	6		19.04	18.73	.984
6		3	20.43	20.45	1.001
				Average	0.982
				P-F, Å.	1.571

[a] Calculated for trigonal bipyramid with P–F = 1.60 Å.

The dipole moment of the gas has been measured and found to be zero.[8] This could be true of a square pyramidal model having equal bond moments only if the angle between the apex bond and the others were 104.5°, a value in disagreement with the diffraction evidence. The trigonal bipyramidal model, on the other hand, agrees both with the observed dipole moment and the electron diffraction pattern; and it may be concluded with certainty that this is the correct model for PF_5. The quantitative comparison of Table VI leads to a value of P–F = 1.57 ± 0.02 Å. in excellent agreement with the radial distribution curve.

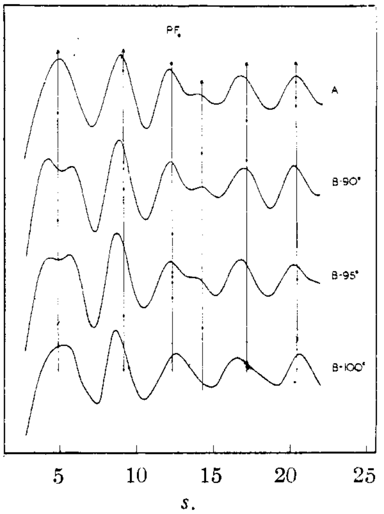

Fig. 6.—Theoretical intensity curves for phosphorus fluoride.

A preliminary report of this value was given in 1936.[5] In the meantime Braune and Pinnow[9] have investigated PF_5 by electron diffraction and have also chosen the configuration of the trigonal bipyramid. Their value for P–F is 1.54 Å., 2% smaller than reported in the present investigation.

Phosphorus Trifluorodichloride.—The eight rings observed in the PF_3Cl_2 photographs lead to a radial distribution curve with a sharp peak at 2.57 Å. and less reliable ones at 2.07 Å. and 1.63 Å. These correspond to F–Cl, P–Cl, and P–F distances. In the diffraction pattern the first five rings are much stronger than the last three. The third and fourth are weaker than the fifth, and the sixth is weaker than the seventh.

Because of the constancy of the bond angles in the PX_3 and in the POX_3 groups of compounds, it was assumed that the PX_5 group would also show no variation. Accordingly, only models of the trigonal bipyramidal configuration were calcu-

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(8) R. Linke and W. Rohrmann, *Z. physik. Chem.*, **B35**, 256 (1937).

(9) H. Braune and P. Pinnow, *ibid.*, **B35**, 239 (1937).

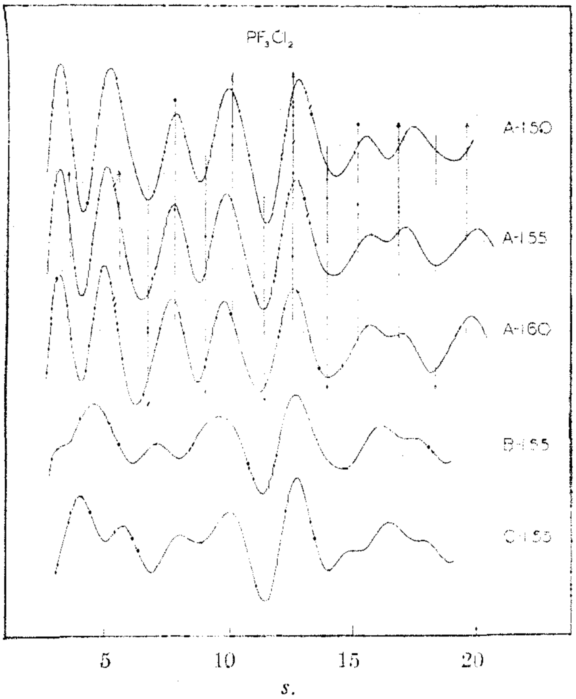

Fig. 7.—Theoretical intensity curves for phosphorus trifluorodichloride. The scale of the molecular models has been changed in plotting the curves by a factor of 1.023.

lated. In the A models (Fig. 7) the three fluorine atoms are in the equatorial plane and the two chlorine atoms at the poles, with P–Cl = 2.00 Å. and P–F = 1.50, 1.55, and 1.60 Å., as indicated. The B model has one chlorine atom in the equator with P–Cl = 2.00 Å., and P–F = 1.55, Å., and the C model has both chlorine atoms in the equator with P–Cl = 2.00 Å. and P–F = 1.55 Å.

Table VII

Phosphorus Trifluorodichloride

Max.	Min.	I_k	s_0	s^a	s/s_0
1		12	(3.70)	3.38	(0.914)
2		9	(5.70)	5.28	(.926)
	3		(6.80)	6.71	(.987)
3		7	7.89	8.04	1.019
	4		9.09	9.05	0.996
4		6	10.18	10.14	.996
	5		11.47	11.69	1.019
5		9	12.61	13.06	1.036
	6		14.05	14.59	1.038
6		1	(15.00)	16.12	
7		2	16.88	17.58	1.041
	8		18.27	18.85	1.032
8		2	19.63	20.53	1.046
				Average	1.026
				P–F, Å.	1.589
				P–Cl	2.050
				F–Cl	2.593

[a] Calculated for trigonal bipyramid with fluorine atoms in equator and P–F = 1.55 Å., P–Cl = 2.00 Å.

The B and C models show pronounced qualitative disagreements with the photographs throughout the range observed; and it is evident that the agreement would not be much improved with any reasonable value for the P–F/P–Cl ratio. Model A-1.55 agrees quite well with the photographs; it is superior to A-1.50 and A-1.60 in the region of the sixth and seventh maxima. The final results based on the data of Table VII and the radial distribution curve are P–F = 1.59 ± 0.03 Å., P–Cl = 2.05 ± 0.03 Å., and F–Cl = 2.59 ± 0.03 Å.

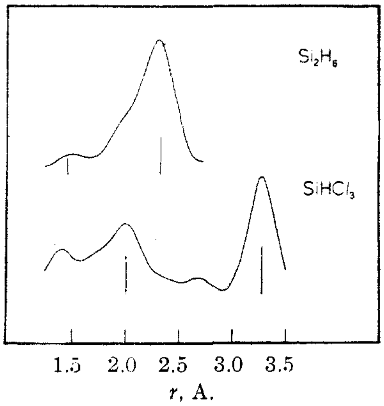

Fig. 8.—Observed radial distributions of scattering matter in disilane and trichlorosilane.

Disilane.—The seven maxima observed in photographs of Si_2H_6 with the s_0 and intensity values shown in Table VIII give a radial distribution with a strong peak at 2.31 Å. This represents the Si–Si bond distance.

Table VIII

Disilane

Max.	Min.	I_k	s_0	s^a	s/s_0
1		15	(3.56)	3.27	(0.918)
2		20	6.10	6.02	.987
	3		7.52	7.41	.985
3		15	8.69	8.74	1.006
4		8	11.49	11.08	0.964
	5		12.66	12.70	1.003
5		12	13.96	14.12	1.011
	6		15.47	15.50	1.002
6		5	16.69	16.78	1.006
7		3	19.26	19.10	0.992
				Average	0.995
				Si–Si, Å.	2.329
				Si–H	1.473

[a] Calculated for Si–Si = 2.34 Å., Si–H = 1.48 Å., ∠HSiSi = 109.5°.

For comparison with theoretical intensity curves five models were assumed with Si–Si distances of 2.34 Å., Si–H bond angles of 109.5°, and Si–H bond distances ranging from 1.35 to 1.55 Å. The H–H terms were neglected. The curves differ mainly in the fourth maximum, which is too strong in those corresponding to Si–H distances of 1.45 Å. or less, and too weak in those corresponding to Si–H distances of 1.50 Å. or more. The intermediate curve in Fig. 9 shows good agreement with the photographs. The final values for the interatomic distances are Si–Si = 2.32 ± 0.03 Å., Si–H = 1.47 ± 0.03 Å.

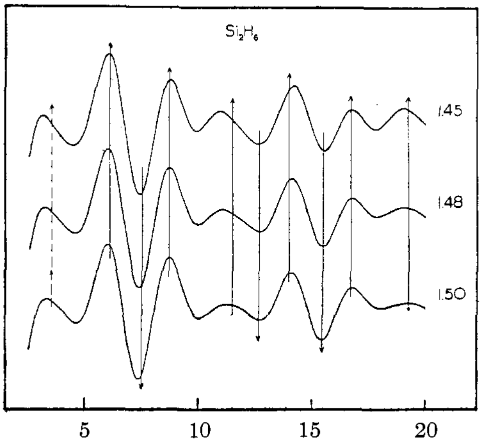

Fig. 9.—Theoretical intensity curves for disilane.

Trichlorosilane and Hexachlorodisilane.—The photographs of $SiHCl_3$ are exceptionally clear, showing a characteristic pattern of nine rings. Two well-resolved peaks in the radial distribution curve occur at 3.28 and 2.00 Å., corresponding to Si–Cl bond angles of 110°. Intensity curves (Fig. 10) were calculated for the molecular models having Si–Cl distances of 2.00 Å. and Si–Cl bond angles of 109.5 and 112°. The observed pattern is very well represented by the first of these, while in the second curve the third maximum is too strong relative to the second and the eighth is too strong relative to the seventh. While the bond angle may be 110° as suggested by the radial distribution curve, it can scarcely be as large as 112°.

In the comparison of s_0 and s values in Table IX it will be noted that the observations on the second and third maxima are displaced in opposite directions with respect to the corresponding s values. This is in accordance with the St. John effect previously observed when two maxima lie close together and are separated by only a shallow minimum. The s/s_0 values from these maxima are not included in the average value of the ratio. The values reported on the basis of the radial distribution curve and the quantitative and qualitative comparison of the intensity curves with the photographs are Si–Cl = 2.01 ± 0.03 Å., Cl–Cl = 3.29 ± 0.03 Å., ∠ClSiCl = 110 ± 1°.

TABLE IX

TRICHLOROSILANE

Max.	Min.	I_k	s_0	s^a	s/s_0
1		30	(4.36)	4.16	(0.954)
2		25	6.27	6.46	(1.031)
3		20	7.92	7.78	(0.982)
	4		9.04	8.92	.987
4		25	10.06	10.08	1.002
	5		11.11	11.27	1.015
5		10	12.04	12.15	1.010
6		15	13.82	13.71	0.992
	7		14.85	14.85	1.000
7		10	15.82	16.09	1.017
8		4	17.60	17.48	0.993
9		8	19.29	19.66	1.020
				Average	1.004
				Si–Cl, Å.	2.008
				Cl–Cl	3.283

[a] Calculated for Si–Cl = 2.00 Å., ∠ClSiCl = 109.5°.

Since the preliminary report of this value was given,[5] another electron diffraction investigation[10] has been made, with the reported values Si–Cl = 2.05 Å., Cl–Cl = 3.39 Å., ∠ClSiCl = 111 ± 4°. The determination of the Cl–Cl distance is not affected by small uncertainties in the value of the bond angle, and the 3% difference between this

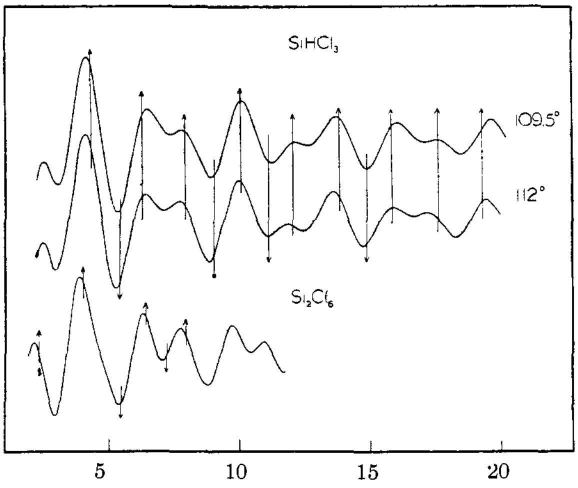

Fig. 10.—Theoretical intensity curves for trichlorosilane and hexachlorodisilane.

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[10] M. de Hemptinne and J. Wouters, *Nature*, **138**, 884 (1936); *ibid.*, **139**, 928 (1937).

value for Cl–Cl and that found in the present investigation is larger than the experimental error of the present result.

A sample of Si_2Cl_6 was photographed some time ago with a diffraction camera allowing a range of pattern only to $s = 11$. Five rings were observed in this range although the last was too faint to be measured. Since the inner rings show the usual displacement characteristic of measurements made at s values below about five, only two maxima could be measured well, and the radial distribution function was not calculated.

Tests were made, however, on two models. In each the assumed Si–Cl distance, 2.00 Å., was based on the observed values in $SiHCl_3$ and $SiCl_4$, the Si–Si distance was assumed to be 2.32 Å. from the value observed in Si_2H_6, and tetrahedral angles were used throughout. In the "*cis*" model the $SiCl_3$ groups were oriented so that the plane of each Si–Cl bond with the Si–Si bond also contained an adjacent Si–Cl bond in the other half of the molecule. In the "*trans*" model one $SiCl_3$ group was rotated by 60° around the Si–Si bond direction. In the "*cis*" curve the third maximum is partially resolved into two. The "*trans*" curve (shown in Fig. 10) is superior in this respect and it reproduces the qualitative features of the photographs. The quantitative measurements (Table X) suggest a decrease in the lengths of the more important interatomic distances. The curves calculated for the mixture of "*cis*" and "*trans*" molecules, most of the molecules being "*trans*," give somewhat better quantitative agreement with the photographs. This suggests that there is some freedom of rotation around the Si–Si bond. From the meager quantitative data it is impossible to determine the degree of freedom of internal rotation if the bond angles are different from the tetrahedral angle. A calculation of the steric repulsion of the six chlorine atoms indicates that the potential energy of the "*cis*" configuration is 650 cal./mole higher than that of the "*trans*" model. It may be concluded that the "*trans*" model is approximately correct with Si–Cl = 2.00 ± 0.05 Å. and Si–Si = 2.32 ± 0.06 Å.

TABLE X

HEXACHLORODISILANE

Max.	Min.	s_0	s^a	s/s_0
1		(2.32)	2.14	(0.923)
2		(4.05)	3.88	(.959)
	3	5.48	5.38	.982
3		6.40	6.32	.988
	4	7.23	7.05	.975
4		7.96	7.74	.973
			Average	0.980

[a] Calculated for "*trans*" model with tetrahedral bond angles, Si–Cl = 2.00 Å., Si–Si = 2.33 Å.

Discussion

The observed bond distances and angles in the phosphorus compounds including PF_3 and PCl_3[3,6] are collected in Table XI.

The P–F bonds ranging in length from 1.50 to 1.59 Å. represent three types of molecules, but the variations in bond length accompanying the change from one to another of these types are much smaller than those occurring among the molecules ordinarily classed together in the PX_3 type. The PX_3 molecules represent the normal valence compounds of phosphorus; there are apparently two distinct types of bonding within this group according to whether the attached radical X has unshared electron pairs, which by "back coördination" to the phosphorus may under certain conditions produce a degree of double bond character in the P–X bonds. When X is a methyl radical or another phosphorus atom, the bond is a normal single covalent bond. The observed distances in P_4 molecule, 2.21 Å.,[11] and in phosphorus trimethyl, 1.84 Å.,[12] give a phosphorus radius of 1.10 Å. in agreement with the value in the table of covalent radii. The sum of this radius and that for fluorine, 0.64 Å.,[13] is 1.74 Å. and is the length of a normal single covalent P–F bond. The observed bond distances in PF_3 and $PFCl_2$ fall below this by 0.2 Å. and indicate a considerable departure from the bond type occurring in P_4 and $P(CH_3)_3$. While the present results throw no new light on the nature of this change in bond type, it is evident that the change in going from PX_3 to POX_3 and PX_5 with constant X is less pronounced than the change occurring among the different PX_3 molecules. These effects are shown to a lesser degree by the observed P–Cl bond lengths, whose deviations from their average value, 2.01 Å., are smaller than the fall below the P–Cl radius sum, 2.09 Å.

The apparent difference in the P–F bond lengths in PF_3 and $PFCl_2$ may have some significance in spite of the large experimental errors. It has

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

[12] H. D. Springall and L. O. Brockway, THIS JOURNAL, **60**, 996 (1938).

[13] This value for the fluorine radius is obtained both by extrapolation of the carbon, nitrogen, and oxygen radii and from the observed distance in methyl fluoride.

TABLE XI

BOND DISTANCES AND ANGLES IN PHOSPHORUS COMPOUNDS

	P–F, Å.	P–Cl, Å.	P–O, Å.	∠FPF	∠ClPCl
PF_3	1.52 ± 0.04			104 ± 4°	
PCl_3		2.00 ± 0.02			101 ± 2°
$PFCl_2$	1.55 ± .05	2.02 ± .03			102 ± 3°
POF_3	1.52 ± .02		1.56 ± 0.03	107 ± 2°	
$POCl_3$		2.02 ± .03	(1.58)		106 ± 1°
POF_2Cl	1.51 ± .03	2.01 ± .04	1.55 ± 0.03	106 ± 3°	
$POFCl_2$	1.50 ± .03	1.99 ± .04	1.54 ± .03		106 ± 3°
PF_5	1.57 ± .02			90°; 120°; 180°	
PF_3Cl_2	1.59 ± .03	2.05 ± .03		120°	±180°

been observed that in the fluoromethanes and fluorochloromethanes[14] the C–F bond length decreases by about 0.05 Å. in going from the molecules with one fluorine atom to those with two or more. This effect may also occur in phosphorus compounds, but in the two substances investigated here having only one fluorine atom per molecule ($PFCl_2$ and $POFCl_2$) the more powerfully scattering chlorine atoms interfere with a precise location of the fluorine atom. Investigations are to be made on more suitable substances.

In the POX_3 compounds the P–X bond distances are not different from those in the PX_3 compounds for either fluorine or chlorine. From a comparison of the observed P–O distance, 1.56 Å., with the P–O double bond radius sum, 1.57 Å., and the P–O distances observed in phosphates, 1.56–1.61 Å., we conclude that the oxygen is held to the phosphorus atom by a double bond. The formation of the bond involves the previously unshared pair of electrons on the phosphorus atom and a pair from the oxygen atom, but in spite of the use of an additional bond orbital on the phosphorus atom the P–X bonds are not disturbed seriously.

While the increase in coördination number from three to four has no effect, the increase to five lengthens the bonds by 0.05 or 0.06 Å. In PF_5 the shortest F–F distances are just equal to that in CH_2F_2, 2.22 Å. This fact suggests that the mutual fluorine atom repulsions have lengthened the bonds in PF_5, but the conclusion is not certain because the tetrahedral bond angle in CH_2F_2 shows that at 2.22 Å. the fluorine atoms may not be as close as the critical distance of approach. In PF_3Cl_2 the P–F and P–Cl bonds have both been lengthened, and the F–Cl distance, 2.59 Å., is just that in CH_2FCl; but here again the lack of an increase in the bond angle in the substituted methane leaves the conclusion in doubt. An alternative explanation for the increase in the P–X bond lengths is that the degree of double bond character in each bond is decreased with the formation of additional bonds, *i. e.*, some of the 3*d* orbitals on phosphorus are utilized more easily than others.

The change of bond angles in going from PX_3 to POX_3 is of interest especially in view of the constant bond lengths. In the former compounds the XPX angles are close to 102° and in the latter they have risen to 106°. The angles between the P–O bond and the P–X bonds are 112°. This is additional evidence that the four atoms are not held by ordinary tetrahedral bonds. The small importance of repulsions between the attached atoms here is illustrated by the 106° ClPCl angle compared with the 112° OPCl angle.

There are many questions about the nature of phosphorus–halogen bonds which cannot be answered at the present state of information, and the problem remains of collecting data on many related substances before a complete discussion can be given.

The silicon compound measurements reported here illustrate the variation in bond type among the normal valence compounds of silicon. The Si–Si distance, 2.32 Å., observed in Si_2H_6 agrees with that in the crystalline form of the element, and the bond is of the normal single covalent type. In $SiHCl_3$ the SiCl bond is 2.01 Å. or 0.15 Å. less than the Si–Cl radius sum. The same situation exists in $SiCl_4$[3,6] with bonds of 2.00 Å. In Si_2Cl_6 the silicon atoms show both bond types in the same molecule. The Si–H distance, 1.47 Å., in Si_2H_6 leads to a hydrogen radius of 0.30 Å. in agreement with the values from other non-metallic hydrides. The bond angle of 110 ± 1° in $SiHCl_3$ does not show the increase above the tetrahedral value which is observed in $CHCl_3$. The increase in size of the central atom has increased the chlorine atom separations from 2.93 to 3.29 Å., and their mutual repulsions are not great enough to

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[14] L. O. Brockway, *J. Phys. Chem.*, **41**, 185, 747 (1937).

distort the bond angles in the silicon compound.

We are indebted for the furnishing of materials to Professor H. S. Booth of Western Reserve University, Professor Warren C. Johnson of the University of Chicago, Professor D. M. Yost of this Laboratory, Dr. Fred Stitt, and their associates. We also wish to thank Messrs. V. Schomaker and K. J. Palmer for assistance in preparing some of the photographs. To Professor Linus Pauling we express our appreciation of unfailing encouragement and help.

Summary

The molecular structures of seven phosphorus compounds have been investigated with the results shown in Table XI. The P-F bond distances in the PX_3 and POX_3 molecules are all close to 1.52 Å., and in PF_5 and PF_3Cl_2 are 1.57 and 1.59 Å. An increase in bond length with coördination number occurs at coördination number five but not four. The observed lengths are all smaller than the covalent radius sum, 1.74 Å. The P-Cl bond lengths show similar variations but the decreases below the radius sum, 2.09 Å., are only from 0.04 to 0.08 Å.

The XPX bond angles increase by 4° in going from PX_3 (102°) to POX_3 (106°). The P-O bond, 1.56 Å. in length, is a double bond and stands at angles of 112° to the three P-X bonds.

In Si_2H_6 the Si-Si bond length is 2.32 ± 0.03 Å., within 0.02 Å. of the length in elementary silicon. In $SiHCl_3$ and Si_2Cl_6 the Si-Cl bonds are 2.01 ± 0.03 Å., and 2.00 ± 0.05 Å.; the same value has been observed in $SiCl_4$. This value is 0.15 Å. below the Si-Cl radius sum. The ClSiCl angle in $SiHCl_3$ is distorted from the tetrahedral value by less than 1°.

PRINCETON, N. J. RECEIVED MAY 31, 1938

[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 650]

The Crystal Structure of Cesium Aurous Auric Chloride, $Cs_2AuAuCl_6$, and Cesium Argentous Auric Chloride, $Cs_2AgAuCl_6$

BY NORMAN ELLIOTT AND LINUS PAULING

The substances cesium aurous auric chloride, $Cs_2AuAuCl_6$, and cesium argentous auric chloride, $Cs_2AgAuCl_6$, discovered by Wells,[1] are of interest because of their jet black color, which has been ascribed[2] to the presence of the same element or two closely similar elements in two valence states.[3] In a preliminary investigation carried out some time ago[4] the substances were found to be diamagnetic, showing that they contain gold and silver in the univalent and trivalent oxidation states rather than the bivalent state. Powder photographs were also prepared with molybdenum X-radiation. These photographs, each with about fifteen lines, were interpreted as showing the crystals to have a structure closely related to the cubic perovskite type, the unit cube, with $a_0 \cong 5.33$ Å. for each substance, containing 1 Cs at 000, 1 (Au,Ag) at $\frac{1}{2}\frac{1}{2}\frac{1}{2}$, and 3 Cl at $\frac{1}{2}\frac{1}{2}0$, $\frac{1}{2}0\frac{1}{2}$, $0\frac{1}{2}\frac{1}{2}$. Although the agreement between the intensities of X-ray reflection calculated for this structure and the observed values was good in general, there were one or two points of pronounced discrepancy for each substance, and the conclusion was reached that the structures are actually distorted somewhat from the ideal perovskite arrangement.

In the course of the investigation described below X-ray powder photographs were prepared with copper and iron radiation, giving greater dispersion, and it was found that cesium aurous auric chloride is tetragonal, and contains the complex ions $[AuCl_2]^-$, which is linear, and $[AuCl_4]^-$, which is square. A similar structure occurs for heat-treated samples of cesium argentous auric chloride, which also exists in a cubic modification involving some randomness in atomic arrangement.

The Determination of the Structure of Cesium Aurous Auric Chloride.—Powder photographs of cesium aurous auric chloride were prepared with copper $K\alpha$ radiation filtered through nickel and with iron K radiation, the camera radius being 5.005 cm. The photographs show about fifty well-defined lines, occurring as multiplets near

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[1] H. L. Wells, *Am. J. Sci.*, **3**, 315 (1922).

[2] H. L. Wells, *ibid.*, **3**, 417 (1922).

[3] Norman Elliott, *J. Chem. Phys.*, **2**, 298 (1934); magnetic data for $(NH_4)_4Sb^{III}Sb^{V}Br_{12}$.

[4] Norman Elliott, *ibid.*, **2**, 419 (1934).