is almost entirely a dust reaction, for when the dust is removed the rate of oxidation is immeasurably slow.

The photochemical decomposition of hydrogen peroxide occurs largely on the surface of suspended dust; when this is removed, the quantum yield is very greatly diminished. It seems likely that when reactions of large quantum yield are studied in the dust-free condition the Einstein photochemical equivalence law will hold. We may explain this by assuming that the substrate is adsorbed in isolated aggregates, the average size of which is given by some multiple of the quantum yield of the reaction; a single quantum of light absorbed by one molecule of the aggregate is supposed to "explode" the whole aggregate.

There are two classes of reactions in which the phenomenon of negative catalysis appears. The first class is homogeneous and consists mainly of those reactions which occur in anhydrous organic solvents or 100% sulfuric acid and are inhibited by small amounts of water. The second class is heterogeneous and inhibitors or accelerators simply poison or promote the catalytic activity of dust particles or the walls of the containing vessel.

BALTIMORE, MARYLAND

[CONTRIBUTION FROM THE JEFFERSON PHYSICAL LABORATORY OF HARVARD UNIVERSITY]

PARAMETERS IN CRYSTAL STRUCTURE. THE MERCUROUS HALIDES

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In the analysis of crystal structure by means of X-rays it is necessary to make a calculation of the intensities of X-ray reflection from different crystal planes for various atomic arrangements and to compare the calculated intensities with those observed. Unless the atomic positions are completely determined by the symmetry of the crystal, there will be one or more undetermined parameters which can be evaluated only with the aid of the intensity data; the values obtained for the parameters will be correct if the method of calculating the intensity of reflection is correct. Unfortunately, the expression that is used in the calculation of the intensity of reflection contains an empirical factor called the "structure factor," depending upon the atomic and electronic arrangement in the crystal, which is but vaguely understood. The two points about which most uncertainty exists are: (1) the relation between the intensity of reflection and the structure factor and (2) the correct method of calculating the structure factor from any given atomic arrangement.

The purposes of this paper are: (1) to discuss the bearing of recent

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experiments by the author on these two points and (2) to describe a method of determining the parameters in a crystal which does not require a previous knowledge of the structure factor, and to apply this method to the determination of the parameters in the crystal structure of the mercurous halides.

The Structure Factor.—Darwin's expression[2] for the intensity of reflection of X-rays at an angle Θ from the face of a single crystal may be written

$$I \propto f^2 \, e^{-\frac{b^2 \sin^2\Theta}{\lambda^2}} \, \frac{1 + \cos^2 2\Theta}{\sin 2\Theta} = F^2 \, \frac{1 + \cos^2 2\Theta}{\sin 2\Theta} \qquad (1)$$

leaving out of consideration all the factors in the original equation which are independent of the angle of reflection for a certain crystal. The factor f is a function of $\lambda/\sin \Theta$ and of the electronic (and atomic) arrangement in the unit cell; $e^{-(b^2 \sin^2\Theta)/\lambda^2}$, the Debye temperature factor, is a similar function. Owing to the difficulty of evaluating the Debye factor, it may be included with f in a new factor F, called the "structure factor." This F represents the amplitude of the diffracted wave, and is equal to the number of electrons in the unit cell at zero angle of reflection, when $\sin \Theta = 0$; as the angle of reflection increases, F falls off in a manner dependent upon the electronic distribution in the unit cell. Each atom contributes to F and, since atoms of different kinds with different electronic arrangements may exist in the unit cell, the resultant value of F depends in a complicated way upon Θ.

In all efforts to get a working formula for the intensity of reflection, simplifying assumptions have been made. For example, Wyckoff[3] gives an expression which is generally used in this country

$$I \propto \left(\frac{d_{(hkl)}}{n}\right)^{2.35} (A^2 + B^2) \qquad (2)$$

where $A = \sum\limits_s \overline{N}_s \cos 2\pi n(hx_s + ky_s + lz_s)$ and $B = \sum\limits_s \overline{N}_s \sin 2\pi n(hx_s + ky_s + lz_s)$. $\overline{N}_s$ is the number of electrons in the sth atom located at x_s, y_s, z_s, and the summation is taken over each atom in the unit cell; $(A^2 + B^2)$ is the resultant intensity due to the superposition of diffracted waves from each atom in the unit cell, assuming the atom to have its diffracting power proportional to its electron content and concentrated at the atomic center—this factor is included in the F^2 of Equation 1; $\left(\frac{d_{(hkl)}}{n}\right)^{2.35}$ includes the part of Equation 1 which depends upon the angle of reflection, that is, the decrease of F with increasing Θ as well as the factor $(1 + \cos^2 2\Theta)/\sin 2\Theta$. *In the use of Expression 2 the tacit assumption is made that F varies with Θ in the same way for every atom in the unit cell,* an assumption evidently not based on fact.

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[2] Darwin, *Phil. Mag.*, **43**, 800 (1922).

[3] Wyckoff, "Structure of Crystals," Chemical Catalog Co., **1924**, p. 107.

However, very satisfactory results have been obtained by the use of expressions like Expression 2 for the determination of parameters in crystal structure. The reasons for the trustworthiness of determinations based upon this expression are: (1) a small change in the value of a parameter makes a large change in the structure factor for certain reflections; (2) if diffraction data are used to the fullest extent, so many comparisons of intensity are possible that a balancing of errors takes place; (3) the variation of F with Θ does not differ a great deal for heavy atoms at small angles of reflection, so that the assumption underlying Expression 2 perhaps becomes justified. Expression 2 fails completely for light atoms, consequently the parameters describing the positions of light atoms in crystals are rarely determined with accuracy.

Intensity of Reflection and the Structure Factor.—That the intensity of reflection is proportional to the square of the structure factor is indicated by Equation 1; but experimental data for certain very perfect crystals (diamond, calcite, aragonite) show that the measured intensity in these few instances is more nearly proportional to the first power of the structure factor. The theoretical treatment of X-ray reflection by Ewald[4] leads to the conclusion that the intensity should be proportional to the first power of the structure factor in the case of a *perfect* crystal. Darwin's treatment of reflection by a perfect crystal leads to the same result when we consider the abnormal absorption at the reflecting angle which he calls "extinction." In a perfect crystal with a thickness greater than 10^{-5} cm., the intensity of reflection will be modified by extinction. Darwin distinguishes two kinds of extinction: *primary* extinction, which occurs within each little block that acts as a perfect crystal, and *secondary* extinction, which represents the shielding of the blocks deep within the crystal by the reflection of the X-rays from the blocks near the surface. Extinction increases the effective absorption coefficient at the reflecting angle and, in case the crystal is nearly perfect, may cause an increase that quite swamps the effect of normal absorption. James and Wood[5] and W. L. Bragg[6] have shown that, since extinction is proportional to the intensity of reflection, the measured intensity would be proportional to the first power of the structure factor in the case of a perfect crystal.

Now it is doubtful whether many substances form even approximately perfect crystals. Microscopically, most crystals are probably mosaic structures, with the size of the perfect crystal blocks of the order of 10^{-4} cm. or even less. Secondary extinction, though, exists in an imperfect crystal and may cause a reduction of perhaps 40% in the intensity of the strongest reflections from a crystal. Consequently, intensity data from

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[4] Ewald, *Physik. Z.*, **26**, 29 (1925).

[5] James and Wood, *Proc. Roy. Soc.*, (London), **109A**, 598 (1925).

[6] W. L. Bragg, *Phil. Mag.*, **50**, 306 (1925).

single crystal measurements may well be greatly in error. Secondary extinction becomes negligible when the thickness of the crystal becomes less than 10^{-2} cm.; therefore powder measurements are free from its effect. Recent experiments by the author[7] on the intensity of reflection of crystal powders of various particle sizes have shown that primary extinction is absent from crystal powders that have been thoroughly ground. We may conclude, therefore, that the intensity of reflection from powdered crystals is proportional to the square of the structure factor.

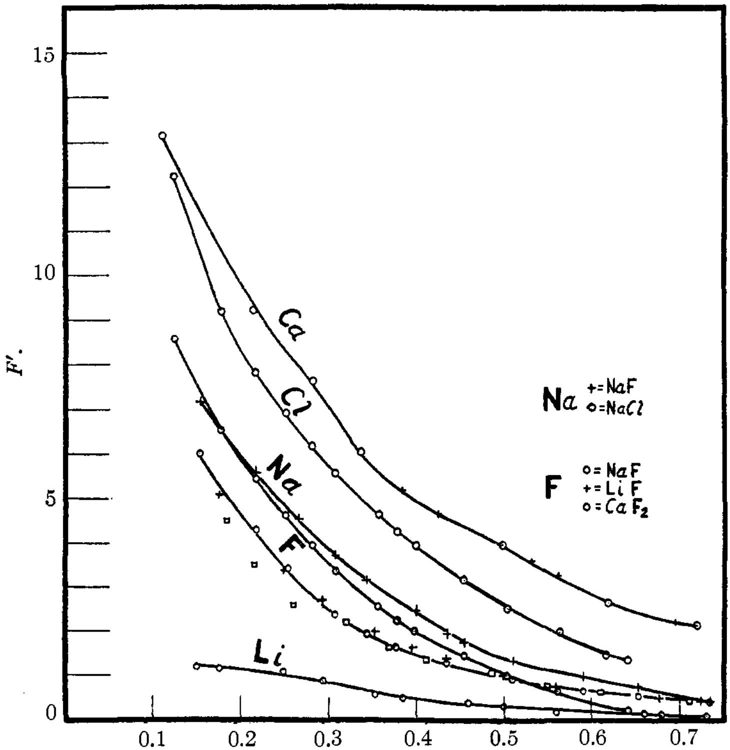

Fig. 1.—Atomic-structure factor curves.

Calculation of the Structure Factor.—We have seen that the ordinary method of calculating the structure factor in the expression by which we test the fitness of any proposed crystal structure assumes that the variation of F with Θ is the same for every atom in the unit cell. This assumption is in error, especially for light atoms, when the unit cell contains more than one kind of atom. The author has measured the relative intensities of reflection from different planes of pure sodium fluoride, lithium fluoride, calcium fluoride and sodium chloride, and obtained the F curves for the dif-

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[7] Havighurst, *Proc. Nat. Acad. Sci.*, **12**, 375, 380 (1926).

ferent atoms.[7] These curves are shown in Fig. 1, where the atomic structure factor is plotted against sin Θ. The structure factor is called F' because while the Na and Cl curves from sodium chloride are correct in absolute magnitude, the other curves have been evaluated indirectly and may be in error on the absolute scale by perhaps 10%. Curves from two different substances should not, strictly speaking, be compared unless their absolute magnitudes have been determined accurately; but curves for different atoms in the same crystal (sodium and fluorine, calcium and fluorine, lithium and fluorine, sodium and chlorine) are comparable. The ratios of the ordinates of the curves for different values of sin Θ have been tabulated in Table I. The ratios from any pair of curves should be constant if the variation of F with sin Θ is the same for the two atoms. Inspection of the table shows that these ratios vary widely.

TABLE I

RATIOS OF F CURVES

$\lambda = 0.710$ Å.

Sin Θ	0 (assumed)	0.15	0.20	0.20	0.40	0.50	0.60	0.70
Ca^{++}/F^-	1.8	1.90	2.10	2.84	3.41	3.95	4.54	4.85
Na^+/F^-	1.0	1.20	1.28	1.56	1.69	1.40	1.46	1.22
Na^+/Cl^-	0.55	0.70	0.72	0.62	0.51	0.40	0.25	(0.15)
Li^+/F^-	.20	.20	.24	.33	.34	.30	.31	.22
Cl^-/F^-	1.8	1.76	1.79	2.30	2.72	2.60	2.46	2.23
$Ca^{++}/Na^+_{(NaF)}$	1.8	1.58	1.65	1.82	2.02	2.82	3.00	3.96
$Na^+_{(NaF)}/Li^+$	5.0	6.12	5.30	4.70	5.00	4.67	4.75	5.50

Two conclusions may be drawn from these results: (1) a positive ion has a larger F value than a negative ion with the same number of electrons, because the excess positive charge draws the electronic atmosphere in toward the nucleus, and electrons close to the nucleus reflect more strongly in the angular domain covered by ordinary crystal structure work; (2) a heavy ion has larger relative F values than a light ion of the same sign; this, too, because the heavier ion has its electrons nearer the nucleus. It is evident that the use of Expression 2 in calculating the structure factor is especially undesirable in the case of crystals containing ions of opposite sign, or in the case of crystals containing both heavy and light atoms.

The use of experimental F curves of the type shown would allow much more accuracy in the calculation of the structure factor. Here too, however, there is an objection, because the F curve depends not only on the specific atom or ion, but also upon the crystal lattice forces to which the atom is subjected; for example, the curve for sodium in sodium fluoride differs from that for sodium in sodium chloride. On the other hand, the curves for fluorine from lithium fluoride, sodium fluoride and calcium fluoride are all quite similar. The crystal lattice forces in the two sodium salts must be of an appreciably different magnitude, while in the fluorides they are nearly equal.

Another method of determining F curves is that of Hartree,[8] which is based upon the dimensions of the electronic orbits as determined from spectral data, and the distribution of the electrons in these orbits as given in Stoner's scheme. James and Wood[5] have used these curves with satisfactory results. Hartree's method does not take into consideration the effect of thermal vibration, which greatly reduces the actual F curves at large angles; for this and perhaps other reasons, his curves are not in good agreement with experimental curves in the few cases where comparison is possible.

There is no existing method of predicting the structure factor with quantitative accuracy, although crystal structure work based on the use of F curves gotten experimentally or by Hartree's method would be superior to that based only on the use of Expression 2. Yet at least a qualitative knowledge of the structure factor has been essential to every determination of a parameter in a crystal. *There is another method of determining the parameters in a crystal* which depends only upon experimental data and upon assumptions that are more easily defended than those upon which the theory of the structure factor is based. This method consists in the determination of the positions of greatest density of diffracting power in the unit cell of a crystal by the use of a Fourier's series.

The Use of Fourier's Series in Determining Parameters.—Duane[9] has shown that the distribution of density of diffracting power (we shall call it "electron density") in a crystal may be represented by a Fourier series whose general term is

$$A_{n_1n_2n_3} \sin\left(2\pi\frac{n_1X}{a_1} - \delta_{n_1}\right) \sin\left(2\pi\frac{n_2Y}{a_2} - \delta_{n_2}\right) \sin\left(2\pi\frac{n_3Z}{a_3} - \delta_{n_3}\right) \qquad (3)$$

where $n_1n_2n_3$ are the Miller indices (multiplied by the order of reflection) of any reflecting plane; a_1, a_2, a_3 are the lengths of the sides of the unit cell; the δ's are phase constants; $An_1n_2n_3$ is the F of Equation 1. Duane's work was based upon a quantum theory of diffraction, but A. H. Compton[10] has recently obtained a similar expression for the electron density on the basis of the classical theory of diffraction. In order to determine the positions of the atoms with the aid of this series, we must make two assumptions: (1) the distribution of diffracting power conforms to the symmetry of the crystal; (2) a point of maximum density is the center of an atom. As a result of the first assumption we are often enabled to fix the phase constants in Expression 3. Then, if the series is evaluated with the aid of experimental data on the intensity of reflection from the different crystal planes, there will be maxima in the curve representing electron density which we assume to be the centers of atoms;

[8] Hartree, *Phil. Mag.*, **50**, 289 (1925). W. L. Bragg, *ibid.*, **50**, 306 (1925).

[9] Duane, *Proc. Nat. Acad. Sci.*, **11**, 489 (1925).

[10] Compton, *Phys. Rev.*, **27**, 510 (1926).

there is no *a priori* assumption of the existence of atoms or molecules in the crystal. Electron-density curves have been obtained by the author[11] for some simple crystals. In many cases the difficulty of this procedure is very great because the symmetry of the crystal is so low that the series expressing electron density is a complicated one containing both sines and cosines; but sometimes the crystal possesses so much symmetry that the parameters may readily be obtained from a simple series. For example, if the plane of the X and Y axes of a crystal is a plane of symmetry and the intersection of the two axes is taken as the origin, the series representing the electron density in a direction Z, perpendicular to the plane of symmetry, will contain cosines only, for the electron density must be symmetrical with respect to the plane of symmetry. The δ_{n_3} of Expression 3 is, therefore, an odd multiple of $\pi/2$. Such a series may easily be evaluated. As an example of the method, the parameters the mercurous halides will be determined.

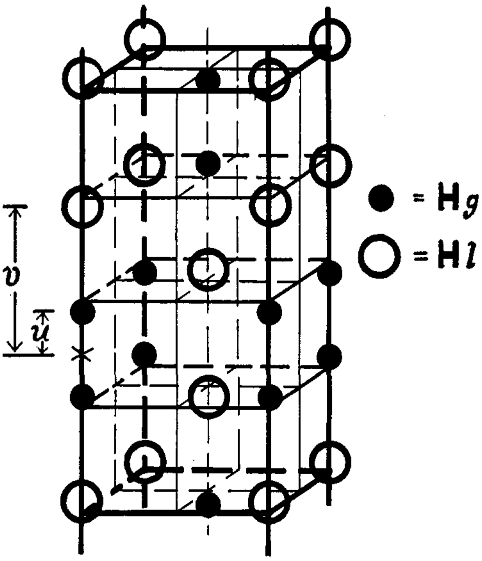

Fig. 2.—Atomic arrangement of mercurous halides.

Parameters of the Mercurous Halides.—The crystal structure of these substances has been investigated by the author,[12] who used the powdered-crystal method of X-ray analysis supplemented by reflections of the tungsten K series from single crystal faces of calomel. The crystals are tetragonal, with two molecules of mercurous halide (Hg_2Hl_2) in the unit cell. The atomic arrangement can be obtained from any of the space groups D_{4h}^{17}, D_{4h}^{15}, D_{4h}^{14}, D_{4h}^{12}, D_{4h}^{6}, D_{4h}^{4}, D_{4}^{9}, D_{4}^{6}. There are four mercury atoms at $00u$; $00\bar{u}$; $^1/_2, {}^1/_2, {}^1/_2 + u$; $^1/_2, {}^1/_2, {}^1/_2 - u$; and four halogen atoms at $00v$; $00\bar{v}$; $^1/_2, {}^1/_2, {}^1/_2 + v$; $^1/_2, {}^1/_2, {}^1/_2 - v$. The dimensions of the unit cells and the values of the parameters as previously determined are given in Table II. Fig. 2 shows the unit cell. The molecule Hl-Hg-Hg-Hl seems to exist in the crystal, the orientation of this molecule being the reason for the unique character of the Z axis. Expression 2 was used in the determination of the parameters, and further simplifying assumptions were made as follows: (1) the absolute distance Hg-Hg

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[11] Havighurst, *Proc. Nat. Acad. Sci.*, **11**, 502, 507 (1925).

[12] Havighurst, *Am. J. Sci.*, **10**, 15 (1925).

is the same in each substance; (2) $v - u = 0.25$ in each crystal. Although it was recognized that these assumptions might lead to inaccuracy in the values of the parameters, they were introduced for the sake of simplicity in the calculations.

TABLE II

CRYSTAL STRUCTURE OF THE MERCUROUS HALIDES

Crystal	c, Å.	a, Å.	u	v
Hg_2Cl_2	10.89	4.47	0.110	0.360
Hg_2Br_2	11.10	4.65	.108	.358
Hg_2I_2	11.61	4.92	.105	.355

Recently Hylleraas[13] has published some work on the crystal structure of the mercurous halides. His structure is identical with that of the author, but he does not claim to have located the parameters accurately.

It is evident that the origin of the unit cell is a center of symmetry. Consequently the Fourier's series expressing the electron density at a point in the unit cell will be a simple cosine series,

$$\rho_{(XYZ)} = \sum_{n_1}\sum_{n_2}\sum_{n_3} A_{n_1n_2n_3} \cos 2\pi\frac{n_1X}{a}\cos 2\pi\frac{n_2Y}{a}\cos 2\pi\frac{n_3Z}{c} \qquad (4)$$

for the phase constants are all odd multiples of $\pi/2$; but the origin is midway between two atoms, and therefore is a point of minimum (probably zero) electron density. Some of the coefficients must accordingly be negative, so that the sum of the series shall be approximately zero at the origin. A qualitative knowledge of the values of the parameters, such as can be obtained by inspection of the relative intensities, is sufficient to determine the signs of the coefficients.

We are interested in evaluating the series representing the electron density along the Z axis. This series is

$$\rho_{(OOZ)} = \sum_{n_1}\sum_{n_2}\sum_{n_3} A_{n_1n_2n_3} \cos 2\pi\frac{n_3Z}{c} \qquad (5)$$

A preliminary study of the relative intensities shows that the values of u and v must be slightly less than $^1/_8$ and $^3/_8$, respectively. Now it seems probable that when Z/c is slightly less than $^1/_8$, at the center of the mercury atom, the series will have its maximum value and the coefficients will all be positive. The assumption that the coefficients of the first few terms of the series (which are all that we can measure experimentally) are positive at the center of a mercury atom, that is, when Z/c is slightly less than $^1/_8$, fixes the signs at the origin. This method of determining the signs of the terms in the series may be considered too intuitive, but it is substantiated by a rigorous method which we shall carry through.

The unit cell of Hg_2Hl_2 is composed of four interpenetrating body-centered lattices, two of mercury and two of halogen, with origins at $00u$, $00\bar{u}$, $00v$, $00\bar{v}$, respectively. The electron density, due to its

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[13] Hylleraas, *Physik. Z.*, **26**, 811 (1925).

own electrons, at a point in any of these lattices (the origin of each is a center of symmetry for that lattice) may be represented by a Fourier's series as in Equation 4. We wish to superimpose these four series, so as to get an expression for the total electron density due to all four lattices.

The coefficients in the four series are $A'_{n_1n_2n_3}$, $A''_{n_1n_2n_3}$, $B'_{n_1n_2n_3}$, $B''_{n_1n_2n_3}$, where $A' = A'' \propto F_{\mathrm{Hg}}$ and $B' = B'' \propto F_{\mathrm{Hl}}$. Now change the origin of each of the four lattices to the point (000). The total electron density is the sum of the contributions from the four separate lattices:

$$\rho_{(XYZ)} = \sum_{n_1}\sum_{n_2}\sum_{n_3} A'_{n_1n_2n_3} \cos 2\pi \frac{n_1X}{a} \cos 2\pi \frac{n_2Y}{a} \cos \left(2\pi \frac{n_3Z}{c} + 2\pi n_3u\right) + \sum_{n_1}\sum_{n_2}\sum_{n_3} A''_{n_1n_2n_3}$$
$$\cos 2\pi \frac{n_1X}{a} \cos 2\pi \frac{n_2Y}{a} \cos \left(2\pi \frac{n_3Z}{c} - 2\pi n_3u\right) + \sum_{n_1}\sum_{n_2}\sum_{n_3} B'_{n_1n_2n_3} \cos 2\pi \frac{n_1X}{a} \cos 2\pi \frac{n_2Y}{a}$$
$$\cos \left(2\pi \frac{n_3Z}{c} + 2\pi n_3v\right) + \sum_{n_1}\sum_{n_2}\sum_{n_3} B''_{n_1n_2n_3} \cos 2\pi \frac{n_1X}{a} \cos 2\pi \frac{n_2Y}{a} \cos \left(2\pi \frac{n_3Z}{c} - 2\pi n_3v\right)$$
$$= \sum_{n_1}\sum_{n_2}\sum_{n_3} (A' + A'')_{n_1n_2n_3} \cos 2\pi \frac{n_1X}{a} \cos 2\pi \frac{n_2Y}{a} \cos 2\pi \frac{n_3Z}{c} \cos 2\pi\ n_3u + \sum_{n_1}\sum_{n_2}\sum_{n_3}$$
$$(B' + B'')_{n_1n_2n_3} \cos 2\pi \frac{n_1X}{a} \cos 2\pi \frac{n_2Y}{a} \cos 2\pi \frac{n_3Z}{c} \cos 2\pi n_3v$$
$$= \sum_{n_1}\sum_{n_2}\sum_{n_3} [(A' + A'') \cos 2\pi n_3u + (B' + B'') \cos 2\pi n_3v]_{n_1n_2n_3} \cos 2\pi \frac{n_1X}{a} \cos 2\pi \frac{n_2Y}{a}$$
$$\cos 2\pi \frac{n_3Z}{c} \qquad (6)$$

The F^2 of Equation 1, which is what we actually measure, is proportional to the square of the quantity in the brackets, while the sign of the quantity in the brackets is determined by the signs of $\cos 2\pi n_3u$ and $\cos 2\pi n_3v$. In case the signs of these two factors are different, it will be remembered that $(A' + A'') > (B' + B'')$. From Equation 6 we find that the first few coefficients are all positive at the center of a mercury atom (when $u = Z/c$), which is the conclusion at which we had previously arrived.

We are now in a position to evaluate Series 5. As coefficients in the series we shall use the F values obtained from the estimated intensities of the powder reflections as follows[7]

$$F^2 \propto \frac{I}{j} \frac{\sin^2\Theta \cos \Theta}{1 + \cos^2 2\Theta} \qquad (7)$$

where j is the number of planes belonging to the form which is reflecting the X-rays. Intensity estimates from powder-method photographs are not at all accurate, but a purpose of this work is to show that the parameters may be determined from the same data as those used previously. As a matter of fact, the inaccuracy of the estimated intensities is of surprisingly small moment; this will be shown later.

The intensity data, given in Table III, are those used in the previous determination of the parameters. The only difference is that the intensity of the hazy reflections from the (200) and (204) planes, which was underestimated because of the diffuseness of the lines of the films, has been

TABLE III

INTENSITIES OF X-RAY REFLECTION FOR THE MERCUROUS HALIDES

	Hg_2Cl_2					Hg_2Br_2			Hg_2I_2		
		Ionization method		Photographic method							
	Plane	*I*	*F*	*I*	*F*	Plane	*I*	*F*	Plane	*I*	*F*
8	101	100	5.40	90	5.13	101	40	3.32	101	15	1.87
4	110	100	10	100	10	110	100	10	110	100	10
8	103	25	2.39	10	2.52	004	40	10.7	004	30	9.21
2	004		6.61	30	9.06	200	40	9.21	200	40	9.01
4	200	39	8.94	40	9.05	114	60	8.46	114	55	8.39
8	114	44	7.28	50	7.77	121	15	3.17	121	6	1.97
16	121	58	4.26	70	4.64	105	35	7.00	105	30	6.43
8	105		6.46		7.05	204	35	7.81	204	35	7.90
16	123	34	1.60	35	1.60	220	15	8.01	220	20	9.05
8	204		7.37		7.49	125	25	5.63	125	20	4.97
4	220	11.5	7.02	15	8.01	130	10	5.19	130	15	6.28
2	004		6.61	30	9.06	224	20	7.67	224	20	7.52
8	301	27	3.51	25	3.33	008	4	7.00	008	4	6.97
16	125		5.20		4.96	134	20	6.00	134	20	5.86
8	130	9.5	5.07	8	4.64	231	15	2.35			
8	224	10	4.86	15	5.96	118		5.10	118	10	4.03
2	008		4.86		5.44	305		4.71	305		4.46
16	134	22	4.41	20	5.14	109	20	6.90	109	20	7.38
8	118		4.20		4.08	208		6.23	208		5.41
16	231		2.33	8	2.69	235	5	3.53	235	7	4.11
8	305		3.30		3.81				330	4	6.27
8	109	12	5.38	15	5.76	404	15	5.82	404	4	4.64
8	208		4.55		4.99	129		4.45	228	15	4.03
16	141	5	2.23	6	2.23	228		3.36	129		5.70
16	235		3.16		3.16	334	4	3.06	334	4	4.85
16	129	14	4.37	15	4.52	138		2.17	138	4	2.49
8	404		4.67		4.96	145		2.17	145		2.49
8	228		4.05		4.05	244	4	3.21	244	6	3.86
8	334	5	3.04	4	2.49	309		2.63	309		3.16
16	138		2.49		2.15						
16	145		2.49		2.15						
8	309	3.5	2.62	6	3.20						
16	244		2.93		3.93						

increased. The relative intensities of the reflections from powdered mercurous chloride were remeasured by an ionization method previously described,[7] and are also shown in Table III. They show that the powder-method estimates, although only approximate, contain no systematic error.

One difficulty inherent in the application of the powdered-crystal method to any crystal analysis is that reflections are often superimposed, and the total intensity must be divided arbitrarily among the components. By analogy with single reflections from the same classes of planes, this division may be made with some accuracy, or the structure factor approximated by Expression 2 may be used. In either case a certain amount of uncertainty is introduced.

The powder-method estimates of intensity in Table III have been used to evaluate Series 5 for each of the mercurous halides, and the curves of electron density, $\rho_{(OOZ)}$, are shown in Fig. 3. The parameters may be read directly from the curves. It is remarkable that these parameters should be so nearly equal for the three substances; this equality means that, as bromine is substituted for chlorine and iodine for bromine, the distance between mercury atoms increases in proportion to the increase in size of the unit cell. The best values for the parameters are u = 0.116, v =

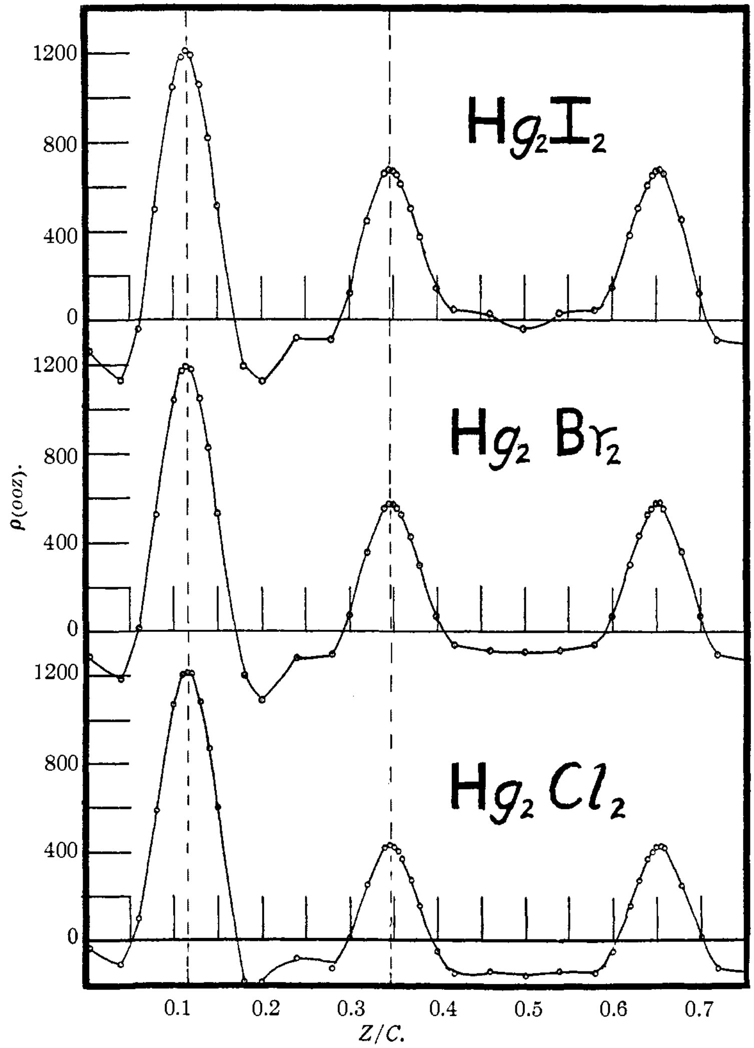

Fig. 3.—Electron-density curves.

0.347.[14] The ionization measurements on mercurous chloride when used in the series give a curve agreeing so nearly with that of Fig. 3 that it can not well be drawn in as a separate curve. Upon consideration it will be seen that fortuitous errors in the intensity estimates will not cause much error in the electron density curves at their maxima, because the density is the sum of contributions from a number of different terms, the errors of which have a tendency to neutralize each other.

The chief advantage of this method of determining the parameters in a crystal is that it automatically sums up all of the available data and gives a result which depends upon no assumed knowledge of the structure factors of the atoms in the crystal. It must be remembered that we have used relative intensities only in evaluating the series, so our electron-density values are only relative. To get the absolute electron density, it would be necessary to have the absolute values of F for all the planes of the crystals. Reflections of such small intensity that they are not observed on the powder-method photographs would have to be measured. Such a procedure would change the scale of ordinates in Fig. 3 to an absolute scale of electron density, and smooth off the minima, bringing them up to the zero line at the same time. Curves of this type have been obtained by the author for the alkali halides, but such refinements would have little effect upon the positions of the maxima on the curves, which are what we are primarily interested in here.

The author is indebted to Professor William Duane for his suggestions and advice in connection with this work.

Summary

In the determination of parameters in crystal analysis, the intensity of reflection of X-rays must be used to evaluate the structure factor. Experiments show that intensities of reflection measured by the powdered-crystal method are accurately proportional to the square of the structure factor. The usual method of calculating the structure factor for a crystal is based upon the assumption that the atomic structure factors of the component atoms vary in the same manner with the angle of reflection. This assumption is not valid, and is particularly in error for crystals containing light elements and ions of opposite charges, as is shown by F curves obtained experimentally for the atoms in lithium fluoride, sodium fluoride, calcium fluoride and sodium chloride.

For accurate determination of parameters in crystal structure, either F curves for the individual atoms should be used, or some method requiring no knowledge of the F curves. Such a method consists in the use of a

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[14] Huggins and Megill, working at the California Institute of Technology, have recently worked out the structure of mercurous iodide, using Laue photographs and rotation spectra. Their values for the parameters are $u = 0.117$, $v = 0.353$.

Fourier's series to determine the electron density at points in the unit cell of a crystal, the coefficients of the series being evaluated from the measured intensities of X-ray reflection. This method, when applied to mercurous chloride, mercurous bromide and mercurous iodide, sets the values of the parameters at $u = 0.116$, $v = 0.347$ in the unit cell containing two molecules of mercurous halide with mercury atoms at $00u$; $00\bar{u}$; $^1/_2, {}^1/_2, {}^1/_2 + u$; $^1/_2, {}^1/_2, {}^1/_2 - u$; and halogen atoms at $00v$; $00\bar{v}$; $^1/_2, {}^1/_2, {}^2/_2 + v$; $^1/_2, {}^1/_2, {}^1/_2 - v$.

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NOTES

Reaction of "Aluminon" with Hydroxides of Beryllium, Rare Earths, Zirconium and Thorium.—The new reagent for aluminum, proposed by Hammett and Sottery[1] and now on the market under the trade name "Aluminon," has proved very satisfactory in our Laboratory. Its value for the detection of very small amounts of aluminum has been shown recently by Lundell and Knowles.[2]

It appears worth recording that lakes are formed by this reagent with the hydroxides or basic acetates of beryllium, yttrium, lanthanum, cerium, neodymium, erbium, zirconium and thorium. All these are deeper red than the aluminum lake, the color being a rich bright crimson, that with cerous hydroxide much darker than the others. All, except that of beryllium, are either dissolved or decolorized by moderate additions of ammonium carbonate. Accordingly, the reagent does not distinguish aluminum from beryllium in mixtures of the two hydroxides. The lakes are not affected by moderate concentrations of ammonia except that of zirconium which is partially decolorized and flocculates as a rose-pink precipitate. All are distinctly more insoluble than the corresponding hydroxides or basic acetates.

From the commercial pure nitrates, solutions were made up containing approximately 10, 1 and 0.1 mg. of the element per cc., except the beryllium solutions which contained 2, 0.2 and 0.02 mg. of the element per cc. To 1 cc. of these solutions was added 5 cc. of 1 N hydrochloric acid, 5 cc. of 3 N ammonium acetate, 5 cc. of 0.1% Aluminon solution and, after mixing, 3 cc. of 6 N aqueous ammonia. Further addition of 2 cc. of 9 N aqueous ammonium carbonate sufficed to dissolve or decolorize the precipitates except in the case of beryllium. Distinct precipitates were formed by 1 mg. of each of the elements tested (0.2 mg. of beryllium). Pink solutions, but no precipitates formed when 0.1 mg. (0.02 mg. of beryllium) was taken. The pink color of these very dilute solutions was not

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[1] Hammett and Sottery, THIS JOURNAL, **47**, 142 (1925).

[2] Lundell and Knowles, *Ind. Eng. Chem.*, **18**, 60 (1926).