Summary

The solubilities of the red and yellow forms of lead monoxide, of hydrated lead monoxide and of basic lead carbonate in dilute aqueous potassium hydroxide solutions at 25° have been determined.

The change of the stoichiometrical equilibrium constant with concentration shows that the activity coefficient of the plumbite ion is about the same as that of the nitrate ion in dilute solutions.

From the extrapolated values of the equilibrium constants, the free energies of solution have been calculated.

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[CONTRIBUTION FROM THE PHYSICAL AND CHEMICAL LABORATORIES OF THE OHIO STATE UNIVERSITY]

THE ATOMIC ARRANGEMENT IN THE CRYSTAL OF ORTHORHOMBIC IODINE

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The crystal structures of few of the non-metallic elements have been fully analyzed by the use of x-rays. Iodine has been studied recently by Ferrari[1] who has determined only the size of the unit cell, nothing being published concerning the arrangement of the atoms in the cell. A complete solution of the iodine structure is of special interest in connection with the question of the existence of molecules in crystals of non-polar substances and of the relationship of atomic to ionic radius.

The results presented by Ferrari were also obtained by the authors and presented in an unpublished thesis[2] at The Ohio State University in August, 1925. The methods used in this work were the same as those of Ferrari.[1] However, the results of the powder photographs obtained cannot be reconciled with those of Ferrari. These will be discussed in detail in the latter part of the present paper.

An extended study of the iodine symmetry was made by means of Laue photographs prepared with various crystal orientations and what is believed to be a unique solution of its structure was obtained in May, 1926. The definition of the structure involves two parameters which must be wholly evaluated from measurements of the intensities of reflection alone. Since the data obtained by the Laue and powder methods were not sufficient for as accurate a parameter determination as was desired, the crystal has since been re-analyzed by the oscillated crystal method.

The parameters have been evaluated from the intensity data in two ways, one being the well-known structure factor method[3] and the other the Four-

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[1] Ferrari, *Atti. Accad. Lincei*, [6] 5, 582 (1927).

[2] Thesis for the Master of Arts Degree by P. M. Harris.

[3] Wyckoff, "Structure of Crystals," Chemical Catalog Co., Easton, Pa., **1924**.

ier series method as formulated by Duane[4] and used by Havighurst.[5] This investigation thus serves as a test of the efficacy of the Duane method in the determination of parameters in crystals of relatively low symmetry.

Experimental

The cameras employed in the powder method have been described elsewhere.[6] The K_{α_1, α_2} characteristic from a water-cooled molybdenum target (Coolidge tube) was used. In some cases the incident and in other cases the reflected beams were filtered with zirconium oxide in order to remove the K_β line as well as a part of the general radiation. Pure aluminum and pure sodium chloride were used as reference standards, a_0 for the aluminum[7] being taken as 4.0438 Å., as measured in this Laboratory, and a_0 for salt as 5.6280 Å. Correction for penetration was made by the method[7] of Blake.

In the Laue method photographs were prepared with crystal to plate distances both of 4 and of 5 cm. A tungsten target Coolidge x-ray tube as a source of white radiation was operated at peak potentials of from 39 to 55 kilovolts as measured on a sphere gap.

The oscillated crystal photographs were prepared in a cylindrical brass camera of approximately 7.9 cm. radius, using a film 15 cm. wide and held in place inside the camera body at top and bottom by cast iron expansion rings similar to piston rings. The camera was provided with gold slits. The crystal table was mounted on a steel spindle fitted in a 6.3 cm. tapered bearing accurately turned to be co-axial with the body of the camera and actuated by a heart-shaped cam designed to give the crystal a constant angular velocity.[3]

Groth[8] gives the axial ratio for orthorhombic iodine as 0.6644:1:1.3653. The crystal has bipyramidal symmetry (determined by Mitscherlich). V. Federov[9] has given a description of a second crystalline variety of iodine which he found to be monoclinic. V. Kurbatow[10] has investigated the conditions under which the monoclinic modification is formed. He states that the monoclinic form is obtained by sublimation below 46.5°, or by crystallization by rapid evaporation of a volatile solvent such as ether. W. Wahl,[11] who worked with the orthorhombic form, was able to find no transition of the orthorhombic iodine into the monoclinic on cooling to below −180° and considers it improbable that there is such a point.

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

[5] Havighurst, THIS JOURNAL, **48**, 2113 (1926).

[6] Havighurst, Mack and Blake, THIS JOURNAL, **46**, 2368 (1924).

[7] Blake, *Phys. Rev.*, **26**, 60–70 (1925).

[8] Groth, "Chemische Kristallographie," Engelmann, Leipzig, **1906**, Vol. 1, p. 39.

[9] V. Federov, *Z. Krist. Mineral.*, **46**, 215 (1909).

[10] V. Kurbatow, *Z. anorg. allgem. Chem.*, **56**, 230 (1908).

[11] Wahl, *Proc. Roy. Soc. (London)*, **88A**, 352 (1913).

Wahl believes that the ordinary form is stable at all temperatures and that the monoclinic prism is a monotropic form having a marked temperature limit of formation and apparently a low velocity of transformation at ordinary temperatures. He states that v. Federov and v. Kurbatow were unable to determine whether the crystals used were pseudomorphosed, due to the metallic and opaque character of iodine. The crystals used in the present investigation were given several different treatments.

1. Baker's "Analyzed" iodine was used for powder photographs without treatment other than grinding.
2. Iodine from the same source was cooled to about −75° with a mixture of solid carbon dioxide and acetone. The iodine was ground while cold. This method was found to give a finer powder.
3. Iodine was sublimed at temperatures above 75°. Iodine prepared in this way was studied by all three photographic methods.
4. Sublimed crystals were prepared from a mixture of iodine with phosphorus pentoxide, to remove the water vapor. The temperature of the sublimation was above 75°. Iodine prepared in this way was used in both the powder and the Laue methods.
5. Iodine prepared by very rapid evaporation of the solvent (ethyl ether) was used in the powder method. The crystallization in this case took place below room temperature, the evaporation of the ether under reduced pressure cooling the system.

No differences in diffraction patterns prepared from the different samples were observed. Laue and oscillated crystal analysis showed the iodine used to be orthorhombic. Wahl's work is thus confirmed and doubt arises regarding the conditions under which the monoclinic variety of iodine is formed.

Determination of Structure

Gnomonic projections of Laue photographs taken with the x-ray beam perpendicular to the face of the crystal plate indicated that the sublimed crystals used were all tabular on $(010)_G$, where the subscript G refers to the axial ratio as stated by Groth. This is in agreement with the work of Ferrari.[1] Measurements gave an axial ratio $a:c$ agreeing with that of Groth within 1%. A complete analysis of the Laue photographs was then made on this basis and the values of $n\lambda$ calculated were plotted against the observed intensities of the corresponding spots.

The short wave length limit in the white radiation used to produce the Laue photographs, as defined by the quantum equation, $Ve = h\nu$, was never less than 0.2 Å. The analysis of the data on the basis of the one atom cell as calculated from the axial ratio and the density gave values of $n\lambda$ very much less than this. As a result, the computations were repeated for cells having each of the dimensions doubled, one at a time, then two at a time, and then for all three doubled. The last arrangement was the only one of the seven which gave values of $n\lambda$ greater than 0.2 Å. for all planes observed. Evidence of the correctness of these conclusions is given in the accompanying graphs, Fig. 1.

Iodine has a critical absorption limit at 0.374 and silver (in the film) at 0.48 Å. The graphs show clearly that the intensity drops off sharply on the short wave length side of the iodine limit and again on the long wave length side of the silver limit. A similar case (among many others) is that of sodium periodate[12] which shows the iodine and silver critical absorption limits.

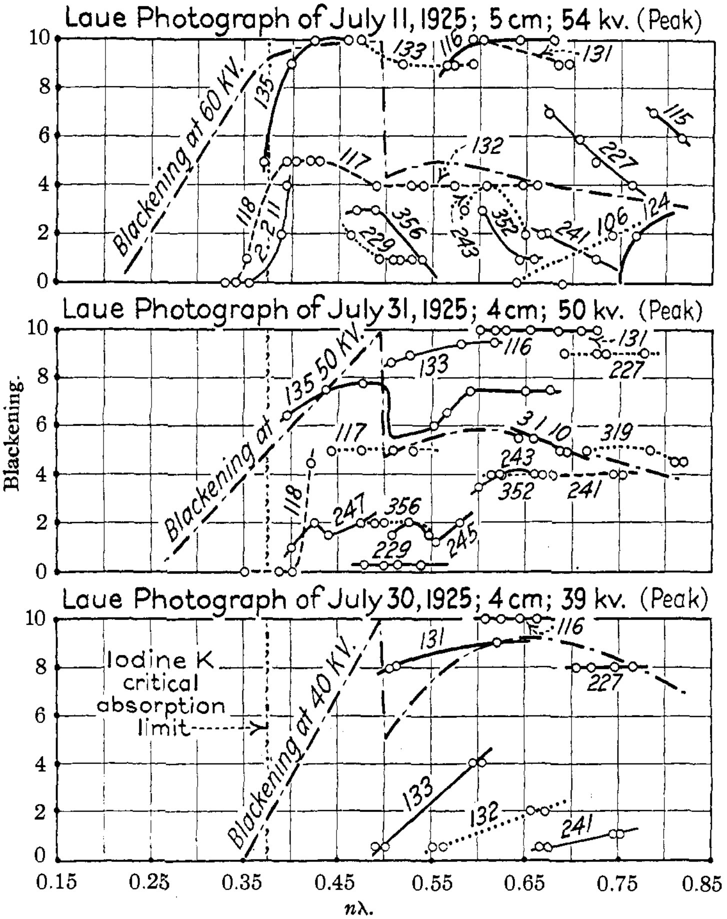

Fig. 1.

Photographs were made by oscillating crystals[13,14] about the c-axis$_G$, and the a-axis$_G$. The values of the primitive translations along the a

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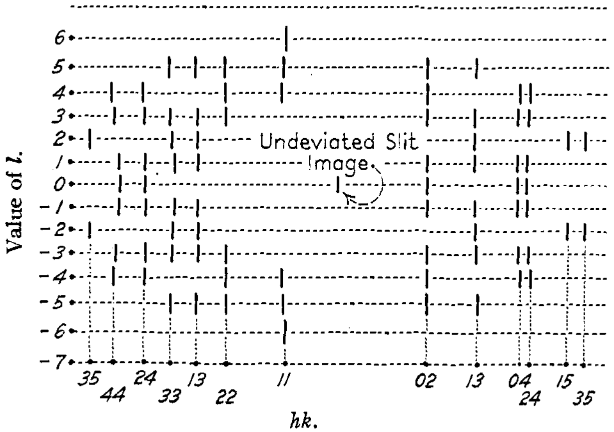
[12] Kirkpatrick and Dickinson, This Journal, **48**, 2327–34 (1926).

[13] Bernal, *Proc. Roy. Soc.*, **113A**, 117–160 (1926).

[14] Schiebold, *Fortschritte Mineral. Krist.*, **11**, 115–280 (1927).

and c axes of Groth calculated from oscillated crystal data agree with the values for the cell chosen from the Laue data. This also confirms the "set-up" of the crystals used with reference to the crystallographic axes. This latter method for the determination of cell size is the most trustworthy known at the present time.[13]



Tracing of photograph of iodine crystal oscillated through an angle of 30° about c axis.

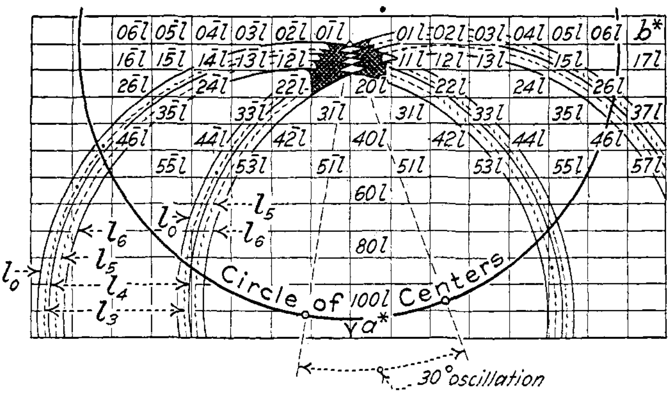


Fig. 2.—Oscillation diagram (about c axis). Projections of sections of sphere of reflection at maximum and minimum positions, showing lunes of reciprocal lattice for $l = 0, = 3, = 4, = 5$, and $= 6$.

An inspection of the accompanying tables and graphs shows that only those planes reflect in the first order which have $(h + k)_G$ even. This indicates[15] that the cell is end-centered on $(001)_G$ (has structure Γ_0).[16]

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[15] P. Niggli, "Geometrische Krystallographie des Discontinuums," Borntraeger, Leipsig, 1919, p. 496. See also Bozorth and Pauling, THIS JOURNAL, **47**, 1561 (1925).

[16] Wyckoff, "The Analytical Expression of the Results of the Theory of Space Groups," *Carnegie Institute Pub. No. 318,* Washington, 1922.

The space groups built on this basis are V_h^{17}...... V_h^{22} inclusive. These are further distinguished by the facts that (1) prism planes having $h + k + l$ even, cannot reflect in the first order for groups V_h^{18}, V_h^{21}, V_h^{22}; (2) prism planes having $h + k + l$ odd cannot reflect in the first order for V_h^{20} and V_h^{22}. The data (see Table I) show that first order reflections have been obtained from the plane $(403)_G$ and probably $(407)_G$, on Laue photographs. This indicates that the structure is different from V_h^{20} and V_h^{22}; these structures were also eliminated by consideration of the individual cases under them.

TABLE I

OSCILLATED CRYSTAL AND LAUE METHOD INTENSITY DATA

			Oscillated crystal				Laue method First order reflections		
				calculated intensities					
(h	k	l)SG	obs. intensity	$u = 0.150$ $v = 0.115$	0.150 0.119	0.160 0.119	Int.	λ	Photo No.
0	0	2	3.0	2.63	0.94	0.94			
0	0	4	30	31.1	32.4	32.4			
0	0	6	2	2.4	0.6	0.6			
0	0	8	9.6	5.1	6.0	6.0			
0	2	0	10.0	5.0	3.0	5.7			
0	2	1	30.6	11.5	12.2	11.1			
0	2	3	40.0	11.6	10.4	9.4			
0	2	4	7.5	1.3	1.3	2.5			
0	2	5	11.8	2.0	3.0	2.7			
0	2	7	20.0	5.1	4.4	3.9			
0	4	0	8.6	4.2	4.2	2.6			
0	4	1	2.4	0.9	1.0	1.7			
0	4	3	2.7	1.3	1.1	2.0	2	0.542	8
0	4	4	3.1	3.0	3.1	2.0			
0	4	7		1.0	0.8	1.4	1	.444	8
1	1	1	16.7	16.8	16.0	13.3			
1	1	2	50	36.8	37.2	40.5			
1	1	3	25	3.8	4.8	4.0			
1	1	4	7.5	0.9	0.3	0.4	3	.516	8
1	1	5	25	4.1	3.5	2.9	8	.652	8
1	1	6	33	6.0	6.6	7.2	10	.499	5
1	1	7		0.4	0.7	0.6	5	.431	1
1	1	8		.9	.3	.4	5	.394	1
1	3	1	17.9	5.6	5.4	4.3	9	.405	5
1	3	2	2.8	1.0	1.0	0.2	4	.384	5
1	3	3	8.9	2.5	3.1	3.4	10	.473	1
1	3	5	13.9	4.7	4.1	4.4	9	.398	11
1	3	6	2.0	0.5	0.5	0.1	3	.431	5
1	3	7	1.6	.6	1.0	1.1	3	.401	5
1	5	2	5.0	8.1	8.2	7.4			
2	0	0	40	81.3	81.3	81.3			
2	0	4	25	20.0	20.5	20.5			
2	2	1	2.5	7.7	8.1	7.4			
2	2	3	16.4	8.7	7.8	7.1			
2	2	4	6.6	1.0	1.1	2.0			
2	2	5	7.4	1.6	2.5	2.3			

TABLE I (*Concluded*)

			Oscillated crystal				Laue method First order reflections		
				calculated intensities					
(h	k	$l)_{SG}$	obs. intensity	$u = 0.150$ $v = 0.115$	0.150 0.119	0.160 0.119	Int.	λ	Photo No.
2	2	7	16.4	4.5	3.8	3.5	6	.450	4
2	4	0	8.1	3.6	3.6	2.2			
2	4	1	2.1	0.8	0.9	1.5	4	.517	5
2	4	3	2.5	1.2	1.0	1.8	5	.470	5
2	4	4	2.9	2.7	2.8	1.7			
2	4	5					2	.487	1
2	4	7					3	.466	1
3	1	1	18.0	4.5	4.3	3.6			
3	1	2	22	12.7	12.9	14.0			
3	1	3	5.0	1.7	2.1	1.8			
3	1	5	4.0	2.6	2.3	1.9			
3	3	1	8.0	3.9	3.8	4.2			
3	3	2	1.6	0.7	0.7	0.1			
3	3	3	5.0	1.9	2.3	2.6			
3	3	5	8.0	3.7	3.2	3.5			
3	3	6		0.4	0.4	0.1			
3	3	7		.6	.8	.9	3	.655	5
3	5	0		.0	.0	.0			
3	5	1		.0	.0	.2			
3	5	2	3.9	3.0	3.0	2.7	3	.603	1
3	5	3		.0	.0	.1			
3	5	4		.2	.1	.1			
3	5	5		.0	.0	.2			
3	5	6		2.0	2.2	2.0	3	.489	1
3	5	7		.0	.0	.1			
4	0	0	20	16.2	16.2	16.2			
4	0	4	13	9.1	9.5	9.5			
4	0	8	5.0	3.2	3.8	3.8			
4	2	1	10	3.7	3.9	3.5			
4	4	0	4.9	2.6	2.6	1.6			
4	4	1	0.5	0.6	0.6	1.1			
4	4	3	2.9	.9	.8	1.3			
4	4	4	2.4	2.1	2.2	1.4			
5	1	1	1.0	1.6	1.6	1.3			
5	1	2	1.1	5.1	5.1	5.6			
6	0	0	7.5	6.5	6.5	6.5			
6	0	4	4.5	4.7	4.9	4.9			
6	0	8	0.6	2.2	2.6	2.6			
8	0	0	2.0	3.7	3.7	3.7			
8	0	4	1.2	2.6	2.7	2.7			

Note: Indices $(hkl)_G$ may be obtained from $(hkl)_{SG}$ by interchanging h and k.

Bearing in mind the fact that the symmetry of the crystal is that of V_h^{17}, V_h^{18}, V_h^{19} or V_h^{21}, a further study of the powder photographs was made, an analysis based on the quadratic form of Runge being used to assign the indices. It was found that the plane $(001)_G$ gave observable reflections in the 4th order only. There is no evidence of a 1st, 2nd or 3rd order although such reflections could have been observed easily had they been present. It should be noted that the glancing angles for all of them are less than 8°, for which reflections the intensities are quite large unless the structure factor is quite small. Also, it was noticed in the Laue photographs that, in general, the intensities of the reflections from the zone $(31l)_G$ pass through a cycle of period $4l$. Reflections from planes $(310)_G$, $(314)_G$, $(318)_G$ are absent; reflections $(311)_G$, $(313)_G$, $(315)_G$, $(317)_G$ and $(319)_G$ are present and quite strong; reflections from $(312)_G$ and $(316)_G$ have been observed but they are not so strong as those from the planes for which l is odd.

Wyckoff has given the expression

> $I \propto (d/n)^{2.35} \times (A^2 + B^2)$, where $A^2 = [\Sigma_s \overline{N}_s \cos 2\pi n\ (hx_s + ky_s + lz_s)]^2$, $B^2 = [\Sigma_s \overline{N}_s \sin 2\pi n(hx_s + ky_s + lz_s)]^2$ and $\overline{N}_s$ is the atomic number and (x, y, z) are the coördinates of the sth atom in the cell, the summation being taken over every atom in the cell; n is the order of reflection.

The above expression is sometimes designated as the structure factor. An investigation of the structure factor for an 8-atom cell, end-centered on $(001)_G$ and having two 4-atom planes perpendicular to the z axis indicates that there is no arrangement with four atoms in the x,y plane which will satisfy the intensity relationships. The only possible way of explaining the absence of the first three orders of reflection from $(001)_G$ is by assuming that there are four 2-atom planes perpendicular to and distributed at nearly equal intervals along the z axis.

The relative intensities of the different orders of $(001)_G$ from oscillated crystal measurements also confirm this. This arrangement is indicated by the data given with regard to the $(31l)_G$ planes. Laue photographs do not show such a cyclic appearance of intensities in the case of the zone $(11l)$. Although the (114) plane reflects quite weakly, the (118) gives fairly strong reflections.

All possible combinations of the orthorhombic bipyramidal groups having the observed symmetry characteristics, having also eight atoms per unit cell, and having four planes of atoms distributed along the z axis have been fully investigated, the structure factor being derived where necessary. Since the corresponding planes of the forms $(11l)_G$ and $(31l)_G$ do not show similar intensities, it is evident that the structure factor must be a function of the h_G index. This requires that a parameter lie along the x axis. It may be shown that only the arrangements given by V_h^{18} case (f) and V_h^{17} cases (a) with (c), and (b) with (c) and case (f) satisfy these criteria.

Now V_h^{17} cases (a) with (c), and (b) with (c) are equivalent. A very roughly qualitative investigation of the intensities given by the structure factor for this arrangement shows its complete inadequacy for the explanation of the observed intensities. This is true also for case (f) of V_h^{17}. Therefore the arrangement is that of case (f) of V_h^{18}.

Inspection of the tables for the oscillated crystal data shows that all planes $(hk0)_G$ and $(0kl)_G$ are halved. These halvings demand space group V_h^{18}. This confirms the space group choice. The absences of first order reflections of $(hk0)_G$ are clearly shown on the microphotometer curves. Since the parameter must be taken along the x axis of Groth, the indices of a plane referred to the space group axes have the h and k indices interchanged and will be designated by $(hkl)_{SG}$.

Determination of Parameters

The relative intensities of spots on the oscillated crystal photographs were determined for certain of the vertical "layer lines" (*schichtlinien* of the second kind) by means of a Moll microphotometer. The intensities of other reflections were determined visually, using the photometric measurements as a comparison standard.

The crystals used for the oscillation films were extremely thin, the thickness probably never exceeding 0.01 mm. at the beginning of the exposure and decreasing due to evaporation. (To lower the rate of evaporation, the crystals were sealed in small cells made of microscope cover glasses.) Most of the Laue photographs show streaks indicating that the crystals were quite imperfect. As a result of the imperfections and the thinness of these crystals, both primary and secondary extinction (abnormal absorptions due to crystal perfection) should have been quite small; the effects of these extinctions were therefore neglected. It will be shown later that the accuracy of the parameter determinations by the Fourier series method is nearly independent of the perfection assumed for the crystal.

For single crystals, ideally imperfect, $I \propto F^2\ [(1 + \cos^2 2\theta)/\sin 2\theta]$, where[5] I is the intensity of the reflected beam, θ the glancing angle and F the structure factor. In the case of ideally perfect crystals, the intensity of the reflected beam is proportional to the first power of the structure factor.

The oscillation photographs were made by the transmission of the Mo K_α doublet through a crystal plate. The whole crystal was bathed in x-rays. Thus, a factor must be introduced to correct for the position of the crystal at the time of reflection and for absorption in the crystal. Since the crystal plates were so thin that practically no edge effect was introduced, $I \propto jF^2\ [(1 + \cos^2 2\theta)/\sin 2\theta]\ \cos \phi e^{-\mu l}$ where ϕ is the position angle of the crystal at time of reflection, μ the apparent absorption coefficient, l the length of path in the crystal and j the number of times a given plane contributes to a spot. When μ is constant (ideally imperfect crystal), the maximum variations in l for the reflections observed and for a decrease in intensity of one-half due to absorption give a variation of only 15% in the factor, $e^{-\mu l}$. Since for nearly all reflections the factor was practically unity, its effect was neglected. The factor $\cos \phi$ was used, however, ϕ being evaluated graphically. In eight cases the intensities were supplemented by a photograph taken by reflection from a crystal plate. Experimental values of F were computed from the above equation. These data were also supplemented by several values of F from powder method films using the relationship[5] $I \propto jF[(1 + \cos^2 2\theta)/\sin^2 \theta \cos \theta]$. Employing Wyckoff's expression for the intensity of reflection by a crystal plane, we obtain for the arrangement V_h^{18} case (f) (if all the iodine atoms diffract alike)

$$I \propto \frac{(d)^{2.35}}{n} \{[1 + \cos \pi kn \cos \pi ln \cos 4\,\pi ukn]\,[1 + \cos \pi kn \cos \pi ln \cos 4\pi vln]\}$$

Curves were drawn for the quantity in brackets for several zones. It was found that the Laue data demanded u and v to be approximately equal to 1/6 and 1/8, respectively. These values were confirmed by data from the oscillation photographs. The values of the relative intensities given by this formula have been calculated for several values of u in the neighborhood of 1/6 and v of 1/8. The results are listed in Table I with observed intensities. The closest agreement seems to be given by $u = 0.160$ and $v = 0.119$.

In the determination of the parameters u and v by the Duane Fourier series method we follow the work of Havighurst[5] on the mercurous halides. A simple, end-centered lattice in the orthogonal systems possesses three mutually perpendicular planes of symmetry passing through a common point and therefore may be fully described by a Fourier series consisting of cosine terms only. The electron density of such a lattice, provided it has the same elements of symmetry as the lattice, is given by ρ_{xyz} in

$$\rho_{xyz} = \Sigma_h\Sigma_k\Sigma_l\, A_{hkl} \cos 2\pi hx \cos 2\pi ky \cos 2\pi lz$$

the summations being taken over all integral values of h, k, and l, which have been substituted for Duane's n_1, n_2, and n_3 as have x, y, and z for Duane's X/a, Y/b, Z/c, the x, y, and z thus being used in the space group sense of the fractional part of the cell dimension, the full dimension being taken as unity.

Now the arrangement defined by case (f) of V_h^{18} is, on translation to (1/4,0,0)

$$0, u, v;\ 0, u + {}^1/_2, {}^1/_2 - v;\ {}^1/_2, u, {}^1/_2 - v;\ {}^1/_2, u + {}^1/_2, v$$
$$0, \bar{u}, \bar{v};\ 0, {}^1/_2 - u, v + {}^1/_2;\ {}^1/_2, \bar{u}, v + {}^1/_2;\ {}^1/_2, {}^1/_2 - u, v$$

If we take for the origins of four simple and end-centered lattices the four points having $x = 0$, then the sum of the contributions of the four lattices to the electron density is given by

$$\begin{aligned}\rho_{xyz} = \Sigma_h\Sigma_k\Sigma_l\, [&A^{1}_{hkl} \cos 2\pi hx \cos 2\pi k(y + u) \cos 2\pi l(z + v)\\ &+ A^{11}_{hkl} \cos 2\pi hx \cos 2\pi k(y - u) \cos 2\pi l(z - v)\\ &+ A^{111}_{hkl} \cos 2\pi hx \cos 2\pi k(y + \tfrac{1}{2} + u) \cos 2\pi l(z + \tfrac{1}{2} - v)\\ &+ A^{1V}_{hkl} \cos 2\pi hx \cos 2\pi k(y + \tfrac{1}{2} - u) \cos 2\pi l(z + \tfrac{1}{2} + v)]\end{aligned}$$

Setting $A^{\mathrm{I}} = A^{\mathrm{II}} = A^{\mathrm{III}} = A^{\mathrm{IV}}$ (assuming the four pairs of I atoms equivalent in diffracting power) and expanding and combining, we have

$$\rho_{xyz} = \Sigma_h\Sigma_k\Sigma_l\, 4A^1_{hkl} \cos 2\pi hx \,\{ [\cos 2\pi ku \cos 2\pi lv \cos 2\pi ky \cos 2\pi lz]_{(k+l)\ \mathrm{even}} + [\sin 2\pi ku \sin 2\pi lv \sin 2\pi ky \sin 2\pi lz]_{(k+l)\ \mathrm{odd}} \}$$

Since the crystal has a plane of symmetry perpendicular to x and passing through the origin used

$$\rho_{x00} = \Sigma_h\Sigma_k\Sigma_l\, A_{hkl} \cos 2\pi hx$$

Now from the developed expression

$$\rho_{x00} = \Sigma_h\Sigma_k\Sigma_l\, 4A'_{hkl} \cos 2\pi ku \cos 2\pi lv \cos 2\pi kx$$

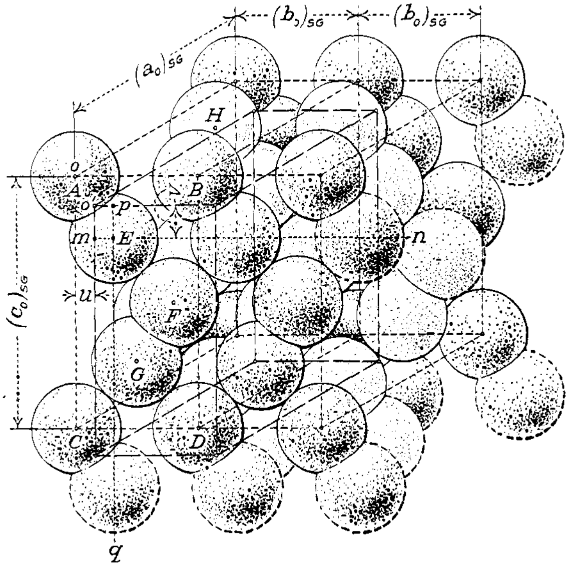
Hence

$$A_{hkl} = 4A'_{hkl} \cos 2\pi ku \cos 2\pi lv \text{ (for } (k+l)_{\mathrm{even}})$$

and by analogy

$$A_{hkl} = 4A'_{hkl} \sin 2\pi ku \sin 2\pi lv \text{ (for } (k+l)_{\mathrm{odd}})$$

Using the approximate values of u and v determined by the structure factor method, the signs of the terms have been determined and the series evaluated along $x = 0$, $y = 0.150$, $z = z$, $x = 0$, $y = y$ and $z = 0.115$, corresponding to the lines pq and mn, respectively, in Fig. 3, the results of which are shown in the accompanying graphs, Figs. 4 and 5. It is found that the portions of the curves beyond $z = 0.25$ and $y = 0.30$ are susceptible to considerable change by the omission of only one or two terms, while



Two unit cells shown. Space group V_h^{18}, case (f). Axes of Fourier series by translation of space group to ¼,0,0. Atoms in front and back planes heavy; atoms in mid-plane light; atoms in contiguous cells dashed.

Fig. 3.—Structure of orthorhombic iodine.

the position of the main peak is practically unchanged. This suggests that the series converges slowly because of its low symmetry and that the minor peaks are due to the fact that not enough terms have been used to straighten out the flat portion of the curve as well as to certain inaccuracies in the evaluation of the term coefficients.

The series used is slowly convergent also because the F curves for heavy atoms do not approach zero rapidly with increasing glancing angle. In the values of the series coefficients calculated from observed intensity data. the Debye temperature factor has been included, since it could not be evaluated even approximately. This practice, however, increases the rapidity with which the series converges.[17]

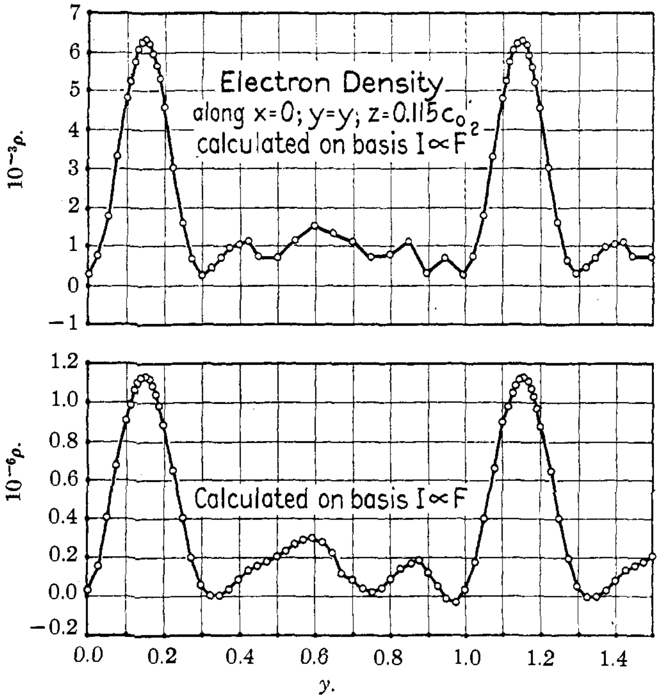


Fig. 4.

The series has also been evaluated for values of the structure factor derived on the basis of the ideally perfect crystal (values of F the squares of the former values). Now each of the coefficients consists of the sum of the squares of the terms which were summed to form the coefficients of the old series. *The resulting curve has its principal maximum at very nearly the same place as before.* The knowledge of this fact is of prime importance, since it makes it evident that in this method of parameter

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[17] Havighurst, *Phys. Rev.*, **29**, 9 (1927).

determination the question of crystal perfection is not serious, at least in the case of those parameters corresponding to peaks for the upper portions of which all terms of the series are positive.

VALUES OF PARAMETERS OBTAINED

	Structure factor method	Fourier series method $I \propto F^2$	Fourier series method $I \propto F$
u	0.160	0.150	0.150
v	.119	.117	.115
AE	2.788 Å.	2.703 Å.	2.670 Å.
CG	3.509 Å.	3.538 Å.	3.569 Å.
AH	4.348 Å.	4.348 Å.	4.348 Å.

Referring to Fig. 3 it would appear that the two atoms A and E correspond to a molecule of I_2 and similarly in the case of the two atoms G and F.

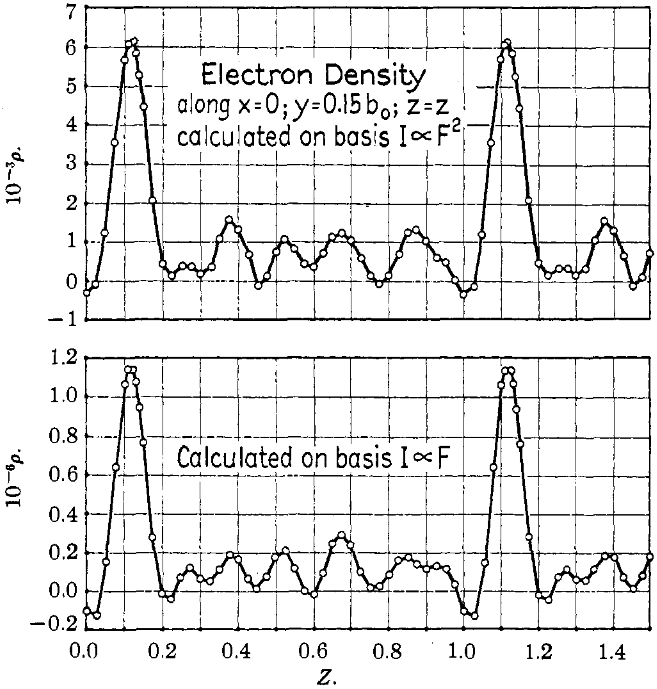

Fig. 5.

The spheres have been drawn so that G osculates C and D. Now the distance AE = GF = $2\sqrt{v^2c_0^2 + u^2b_0^2}$; and the distance CG = DG = $\sqrt{(1/2 - 2v)^2c_0^2 + b_0^2/4}$; and the distance AH = $1/2\sqrt{a_0^2 + b_0^2}$. The values obtained are shown in the above table. Values of iodine atom and ion dimensions calculated from x-ray crystal structure results, on assumption of constant atomic radii, and also calculations from viscosity and other data are shown in the following table.

IODINE ATOM AND ION DIMENSIONS

Distance	Source	Value, Å.	Authority
I^- radius	Alkali halides	1.40	W. L. Bragg, *Phil. Mag.*, **40,** 169 (1920)
	$CsCl_2I$	1.50	Wyckoff, *Proc. Nat. Acad. Sci.*, **9,** 33 (1923)
	$CsI(Cs^+ = I^-)$	1.974	Davey, *Chem. Rev.*, **2,** 349 (1926)
	Xe radius, from viscosity of Xe	1.75	Rankine, *Proc. Roy. Soc. (London)*, **98A,** 360 (1921)
	Alkali halides	2.10 (approx.)	W. L. Bragg, *Phil. Mag.*, [7] **2,** 258 (1926)
	Theoretical	2.19	Wasastjerna, *Soc. Sci. Fennica Comm.*, **1,** No. 38, 1–25 (1923)
$(I-I)/2$	Between two SnI_4	2.10^5	Dickinson, THIS JOURNAL, **45,** 958 (1923)
	CdI_2	2.10^5	Bozorth, THIS JOURNAL, **44,** 2232 (1922)
	Viscosity (and if I^- radius = 1.75)	1.40	Rankine (*loc. cit.*)
I atom radius		1.30	Walden, *Z. anorg. allgem. Chem.*, **113,** 125 (1920)
$Sn-I$	SnI_4	2.63	Dickinson (*loc. cit.*)
$Sn-Sn$	Gray tin	2.80	Bijl and Holkmeyer, *Proc. Roy. Soc. Ac. Amsterdam*, June-Sept. (1918)
I^- radius	SnI_4 and Sn	1.23	
$(I-I)/2$	HgI_2	2.05	Huggins and Magill, THIS JOURNAL, **49,** 2357 (1927)
$(Hg-Hg)/2$	Hg_2I_2	1.36	*Ibid.*
$(I-I)/2$	Hg_2I_2	1.71	*Ibid.*
$(Hg-I)$	Hg_2I_2	2.75	*Ibid.*
I	$(Hg-I)-(Hg-Hg)/2$	1.39	*Ibid.*
$(I-I)/2$ in I_2	Solid iodine	1.35^2	This paper
Between two I_2		1.769 and 2.17^4	This paper

It appears from the foregoing table that the iodine atom may have several radii of combination. In polar compounds, the radius probably corresponds to an ion radius of approximately 1.77 Å., (CG/2), or 2.17 Å., (AH/2). In the case of non-polar combinations, the radius seems to be approximately 1.35 Å., (AE/2), corresponding, perhaps, to the radius of the next to the outer shell of electrons in the iodine atom. This is in accordance with the anticipation of Rankine.

Finally, in considering the strength of the evidence for the proposed structure, we may say:

(1) No preliminary assumption regarding the existence of molecules has been made, and in the case of the Fourier analysis, the positions of the atoms have been found from a determination of the electron densities. This has placed the solution on as purely analytical a basis as is possible with methods in their present state of development.

(2) Such an ample quantity of data has been obtained that, after analysis, there is much left unused which agrees with the structure assigned. This is well illustrated by the zone (35l) on the oscillation diagram of Fig. 2. Only those planes with l = 0, 1, 2, 3, ...6, etc., were in position to reflect whose projections on the diagram were swept over by the circular arc, $l = l_n$, in a 30° oscillation of its center along the circle of centers. The diagram thus indicates that all planes of zone 35l for $0 \leqq l < 6$ were in position to reflect to the right during the exposure. The structure obtained gives calculated intensities for this zone such that the reflection $(352)_{SG}$ should be the only discernible one with $l < 6$ (see Table I). A small change in the parameters gives quite appreciable intensity to the other reflections of this zone. The reflection $(352)_{SG}$ is the only one of the group which appears and it is fairly strong.

(3) Although no speculations regarding the size or arrangement of the iodine atoms have been used in the solution, the dimensions of the iodine atom obtained from the structure are in good agreement with the results of other investigators.

The structure proposed is not only a necessary result of the analysis but is also sufficient for the explanation of the large amount of data obtained. The authors feel that such a solution may be said to be unique.

Cell Dimensions from Powder Photograph Data

The powder photographs were analyzed by application of the quadratic form obtained by squaring Bragg's equation and setting

$$\frac{d^2}{n^2} = \frac{1}{h^2/a_0^2 + k^2/b_0^2 + l^2/c_0^2}$$

so that

$$\sin^2\theta = \frac{\lambda^2}{4}\left(h^2/a_0^2 + k^2/b_0^2 + l^2/c_0^2\right)$$

Using this equation the indices were assigned by a cut and try method. Table II gives the arithmetical mean of the results of six powder films with values of d/n calculated from cell dimensions obtained from the powder data by an application of the Method of Least Squares. In the case of iodine only those values of d/n were used which seemed to correspond to single lines. All the values used also correspond to fairly low indices.

By this method we obtain a_{0G} = 4.795 Å., b_{0G} = 7.255 Å., and c_{0G} = 9.780 Å., or $a:b:c$ = 0.6609:1:1.3479. These cell dimensions give a calculated density of 4.913 g./cm^3. As has been stated, the axial ratio accepted for iodine is $a:b:c$ = 0.6644:1:1.3653 (Mitscherlich). Marignac[18] has given the ratio $a:b:c$ = 1:1.515:2.0586 which is equivalent to $a:b:c$ =

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[18] Marignac, "Handbuch der anorganischen Chemie," Abegg and Auerbach, Leipzig, **1913**, Vol. 4, pt. 2, p. 349.

Table II

Observed Powder Method Data Compared with Calculated Values

(h	k	l)SG	Observed mean d/n	Number of films	Calcd. d/n	Obs. intensity (visual)	Calcd. Intensity $u = 0.150$ $v = 0.115$	0.150 0.119	0.160 0.119
1[a]	1	1	3.698	6	3.702	25	16.8	16.0	13.3
2[a]	0	0	3.616	6	3.628	25	20.3	20.3	20.3
1[a]	1	2	3.094	6	3.096	30	36.8	37.2	40.5
1[a]	1	3	2.530	5	2.527	5	3.8	4.8	4.0
0[a]	0	4	2.453	6	2.445	10	7.8	8.1	8.1
0[a]	2	0	2.389	2	2.398	v.w.	1.3	0.8	1.4
0[a]	2	1	2.321	6	2.329	8	5.8	6.1	5.6
3	1	1	2.104	6	2.108	6	4.5	4.3	3.6
2	0	4	2.032	6	2.027	10	10.0	10.3	10.3
3[a]	1	2	1.978	6	1.975		12.7	12.9	14.0
2[a]	2	1	1.964	6	1.960	10	7.7	8.1	7.4
0[a]	2	3	1.929	6	1.931	7	5.8	5.2	4.7
2	2	2	1.877	2	1.851	v.v.w. broad	0.02	0.01	0.02
4[a]	0	0	1.809	6	1.814	7	4.1	4.1	4.1
1[a]	1	5	1.759	6	1.758	6	4.1	3.5	2.9
2[a]	2	3	1.706	6	1.704	10	8.7	7.8	7.1
1	3	1	1.541	6	1.540	7	5.6	5.4	4.3
0[a]	2	5	1.513	6	1.516	8	1.0	1.5	1.4
1	1	6			1.510		6.0	6.6	7.2
1	3	2	1.488	2	1.487	v.w.	1.0	1.0	0.2
4[a]	0	4	1.456	5	1.457	6	4.6	4.8	4.8
4[a]	2	1	1.432	5	1.431	2	3.7	3.9	3.5
2	2	5	1.404	6	1.398	4	1.6	2.5	2.3
1	3	3			1.408		2.5	3.1	3.4
5	1	1	1.375	4	1.375	1	1.6	1.6	1.3
5	1	2	1.336	5	1.336	5	5.1	5.1	5.6
3[a]	3	1	1.322	5	1.321	w.	3.9	3.8	4.2
3	1	6	1.299	3	1.301	w.	4.3	4.7	5.1
6	0	0	1.200	2	1.209	w.	1.6	1.6	1.6
0	4	0			1.199		1.1	1.1	0.7

[a] Values used in calculation of cell dimensions; w., weak; v.w., very weak; v.v.w., very, very weak.

0.6601:1:1.359. These different ratios proposed by good crystallographers indicate that the exact value of the ratio is probably somewhat different from either and the value obtained in this work may be much more nearly correct. Mitscherlich's values for the ratio were no doubt obtained from measurements on the good crystals which he describes as having been obtained by the slow air-oxidation of an aqueous solution of iodine in hydriodic acid.[19] It is now known that as much as several per cent. of water may be occluded by iodine crystals formed in the presence of water. The differences in the axial ratios may be due to variations in water content.

As has been stated, in no case were first order reflections obtained from

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[19] Mitscherlich, *Pogg. Ann.*, **98**, 554 (1856).

planes having $(h + k)$ odd. Ferrari's Laue data[1] are in accord with this observation. All of our oscillated crystal data also indicate this, as is shown by the diagram, Fig. 3. The zones (23*l*), (34*l*), (45*l*), etc., were in position to reflect to the left and the zones (12*l*), (14*l*), (23*l*), (25*l*), (34*l*), (36*l*), etc., were in position to reflect to the right during the exposure of the photograph whose tracing is shown. No reflections from these zones are observable.

Ferrari lists values of d/n to which he has assigned the indices (100), (012), (021), (004), (210), (131), (015) and (150), the axial ratio of Groth being used. Of these the only ones which could have other than zero intensity are (021), (004) and (131), since all prisms (*hk*0) are halved. Ferrari states that the sublimed crystals are tabular on $(010)_G$ (in accordance with our observations). Although Ferrari lists several orders of reflection for this plane in his rotated crystal data (and in our experience it reflects very strongly in the second order), no line corresponding to it is found in his powder data.

The writers employed powder cameras of approximately 330 mm. diameter while Ferrari used cameras about 57 mm. in diameter. The authors also used a comparison standard on every film as well as quite small sample tubes (0.4 mm.), thus obtaining distinct and fairly sharp diffraction patterns.

Since the indices assigned to powder data in this paper are in complete accord with the structure chosen from the Laue and oscillated crystal data, it seems that Ferrari's powder data must be in error.

The authors wish to express their appreciation for a grant from the funds of the American Association for the Advancement of Science.

Summary

1. By use of Laue and oscillated crystal photographs of the ordinary form of solid iodine, the unit cell having orthorhombic bipyramidal symmetry has been found to contain eight atoms. The best values of cell dimensions, obtained by an application of the Method of Least Squares to the observed values for d/n are: $a_0 = 4.795$ Å.; $b_0 = 7.255$ Å.; $c_0 = 9.780$ Å. These correspond to an axial ratio of 0.661:1:1.348 and a density of 4.913/cm.^{3} (axes chosen according to Groth).

2. The symmetry of the cell is that of space group V_h^{18}, the atoms being located according to the arrangement (f).

3. The values of the two parameters have been determined by use of both the structure factor method and the Fourier series method of Duane. By the latter, values of $u = 0.150$ and $v = 0.117$ are obtained. The parameter u is to be taken along the x-axis of Groth and the parameter v along the z-axis.

4. In the determination of the parameters by the Fourier series method,

the abnormal absorption effects due to crystal perfection are shown to be negligible in the case of iodine.

5. The atoms are found to be grouped in molecules of I_2. The distance between centers of the two atoms in one molecule is found to be 2.70 Å. Distances of closest approach of centers of 3.54 and 4.35 Å. exist in the crystal. Either of these may correspond to the ion radius of iodine.

Columbus, Ohio

[Contribution from the Chemical Laboratory of Harvard University and from the West Virginia Geological Survey]

A NEW EQUILIBRATOR: A DEVICE FOR THE DETERMINATION OF THE DISTRIBUTION RATIO OF A VOLATILE SOLUTE BETWEEN TWO MISCIBLE SOLVENTS

By Grinnell Jones and B. B. Kaplan

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In the course of an investigation on the normal potential of the iodine electrode to be described in a subsequent paper it became necessary to determine the free iodine present in a solution containing potassium iodide, iodine and tri-iodide. For this purpose we invented a device which we call an equilibrator, which permits the determination of the distribution ratio of a volatile solute between two miscible solvents. Since it is planned to use this device in several other researches in this Laboratory it seems desirable to describe it in a separate paper.

The equilibrator is a closed glass apparatus without mechanical valves and contains no liquids to produce seals except the two separated solutions under investigation and yet by mere rotation it causes a continuous circulation of gas or vapor so that it bubbles through the two solutions in turn for as long as the rotation continues. This ensures equality of vapor pressure of the common volatile constituent from the two separated liquid phases if the rotation is continued long enough. After equilibrium has been established the two solutions are separately available for analysis and for any other use that may be desired.

The design and mounting of the equilibrator will be clear from the figure, which shows the plan or top view, end elevation, side elevation and mounting in the thermostat. The essential features are two tubes (A) and (B) which make an angle of about 14 circular degrees with each other in a vertical direction and which are connected at each end by glass tubes (C) and (D) each provided with a ground glass stopper (I) and (J). The stoppers may be replaced at the end of the run by delivery tubes of the type (L) shown in the figure which are ground to fit the same openings. The connecting tubes permit free circulation of the vapor but prevent mixing of the solutions. They are bent inward and upward as shown so that