lying the formation of coördinated structures in complex crystals. The proposed structure, shown in Fig. 4, may be represented by formulas such as $H_4[SiO_4 \cdot W_{12}O_{18}(OH)_{36}]$. It correlates the characteristic differences between the properties of the 12-molybdo- and tungsto-acids and those of the $[MoO_4]^{--}$ and $[WO_4]^{--}$ ions with the existence of molybdenum and tungsten atoms with coördination numbers 6 and 4, respectively, in these two types of compounds. It leads to a number of replaceable hydrogen atoms in agreement with experiment, and accounts for the large water content of the acids and their salts. The cubic point-group symmetry of the suggested structure for the complex anions explains the tendency of these compounds to form cubic or pseudocubic crystals.

The iso-12-tungstosilicate and iso-12-tungstoborate ions are ascribed the structure shown in Fig. 5, in which two 12-anions are combined through the formation of oxygen bonds.

A structure for one class of unsaturated acids, corresponding to formulas such as $H_6[(PO_4)_2 \cdot W_{18}O_{30}(OH)_{48}]$, is also suggested, involving the combination of two 12-anions as shown in Fig. 6. Possible structures for other unsaturated acids are indicated.

Among the predictions made on the basis of the proposed structure and susceptible to experimental investigation are the following: that the normal 12-anions have the point-group symmetry $T_d$, and the iso-12-anions and the 9-anions the symmetry $D_{3d}$ or $D_{3h}$; that the normal 12-acids have a molecular weight corresponding to one $RO_4$ group per complex, and the iso-12-acids and 9-acids to two; and that the constituent atoms in the complexes occupy certain positions relative to each other, such that each tungsten or molybdenum atom has a first coördination shell of six oxygen atoms none of which is part of the central $RO_4$ group.

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

# THE CRYSTAL STRUCTURE OF META-IODOBENZOIC ACID[1]

BY HAROLD P. KLUG, EDWARD MACK, JR., AND F. C. BLAKE

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We have been led to an x-ray examination of the crystals of a number of benzene derivatives in connection with a study of vapor pressures and heats of vaporization. It seems worth while at this time to report the crystal structure which we have found for *m*-iodobenzoic acid, especially since the solution obtained seems to be unique, and very few unambiguous solutions have been reported for organic compounds crystallizing in the

[1] An abstract of a thesis presented by H. P. Klug in partial fulfilment of the requirements for the degree of Doctor of Philosophy at the Ohio State University in June, 1928.

monoclinic system. *m*-Iodobenzoic acid is a particularly interesting case because of the fact that it is so nearly orthorhombic, the angle $\beta$ being 91° 29.5′. When $\beta$ is so slightly different from a right angle, it is difficult to identify the reflections from certain sets of planes, namely, the pyramids and orthodomes.

*m*-Iodobenzoic acid was prepared by the method of O. Grothe,[2] which consists of the hot diazotization of a strong solution of *m*-aminobenzoic acid in dilute sulfuric acid mixed with a concentrated solution of potassium iodide in excess. The yield was very poor (less than 5%). The crude product was purified by two vacuum sublimations; this gave a product with a melting point of 186.6–186.8°. Crystals grown from ether were well-formed, flat needles, showing the (0 0 1) face.

Groth[3] gives the following data on the crystal: $a : b : c = 1.3450 : 1 : 5.6247$; $\beta = 91° 29.5'$; m. p. 185°; sp. gr. 2.171.

**Preparation of X-Ray Photographs and Their Analysis for Data.**—Data for the analysis of this crystal were obtained by means of the powder, Laue and oscillated crystal methods. Photographs were taken and the usual measurements and calculations made.

In the powder method sodium chloride was used as a comparison standard. The *m*-iodobenzoic acid was powdered to pass through a 200-mesh sieve and the glass capillary tube was oscillated through an angle of 15° during exposure to the molybdenum $K_\alpha$ doublet from a water-cooled Coolidge tube. The exposure was for twenty-six hours at 35 kilovolts with a current of 18 milliamperes. Distances on the film could be measured to within 0.002 cm. Blake's[4] correction constant, $3 \cot \theta \, d\theta$, for powder films was used in all the calculations. Using the crystallographer's orientation and notation, Wyckoff's quadratic[5] form of the equation for the monoclinic unit becomes, when squared and solved for $\sin^2 \theta$

$$\sin^2 \theta = \frac{\lambda^2}{b_0^2}\left\{\frac{h^2}{4a^2 \sin^2 \beta} + \frac{l^2}{4c^2 \sin^2 \beta} \pm \frac{hl \cos \beta}{2ac \sin^2 \beta} + \frac{k^2}{4}\right\}$$

If we designate the bracketed term by $L$, then

$$L = \frac{\sin^2 \theta \, b_0^2}{\lambda^2}$$

The thirteen lines measurable on the powder photographs could all be accounted for only on the assumption of a 4-molecule cell.

The agreement between the observed and calculated values of $L$ is excellent.

Laue photographs were taken perpendicular to the (0 0 1) face and at small angles to the perpendicular, with the general radiation from a tung-

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[2] O. Grothe, *J. prakt. Chem.*, [2] **18,** 324 (1878).

[3] Groth, "Chemische Kristallographie," Engelmann, Leipzig, **1906,** Vol. 4, p. 466.

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

[5] Wyckoff, "Structure of Crystals," Chemical Catalog Co., Easton, Pa., **1924,** p. 98.

TABLE I

DATA FROM A *m*-IODOBENZOIC ACID POWDER PHOTOGRAPH

| Indices $h\ k\ l$ | $L$ obs. | $L^a$ calcd. | Indices $h\ k\ l$ | $L$ obs. | $L^a$ calcd. |
|---|---|---|---|---|---|
| 0 0 4 | 0.1302 | 0.1284 | $\bar{1}$ 1 3 | 0.4587 | 0.4595 |
| 1 0 1 | .1521 | .1523 | 1 1 4 | .5255 | .5279 |
| 1 0 3 | .2240 | .2201 | $\bar{1}$ 0 7 | | .5236 |
| 0 0 6 | .2914 | .2890 | $\bar{1}$ 0 9 | .7744 | .7770 |
| $\bar{1}$ 0 5 | .3314 | .3344 | $\bar{1}$ 1 7 | | .7736 |
| 1 0 5 | .3515 | .3520 | 2 1 1 | .8376 | .8313 |
| 1 1 0 | .3934 | .3925 | $\bar{2}$ 1 2 | | .8449 |
| 1 1 2 | .4271 | .4281 | 2 1 3 | .9097 | .9027 |

[a] The calculated values of $L$ are purely theoretical values obtained by substituting the crystallographic data in the bracketed term of the above equation. The observed values of $L$ are obtained from the values of $\theta$ from measurements of the powder photographs.

sten target at 54–55 kilovolts, 14 milliamperes and for two and one-fifth hours. The crystal to film distance was 5 cm. for all photographs.

The oscillated crystal photographs were taken with the $K_\alpha$ doublet from a molybdenum target at 55 kilovolts, 19 milliamperes, for twenty-four to twenty-six hours. In addition to the usual method of calculating angle $\theta$ for each reflection, the indices of the planes reflecting were checked by means of Bernal[6] diagrams. The analysis shows unequivocally that the cell contains four molecules. The large number of reflections gives the data necessary for space-group determination.

**Correction of the Axial Ratio.**—On some of the oscillated crystal photographs where the reflections were unusually sharp and distinct, and therefore capable of quite accurate measurement, the agreement between the two values of $L$ was not what it should have been. This might have been due to a slight inaccuracy in the axial ratio. Since there could be no doubt about the correctness of the various orders of (0 0 1) found on one of the films, and also of the various reflections of (0 1 $l$) in the first layer line above and below, it was decided to use them as a basis for correcting the axial ratio. The new axial ratio, then, assuming that $\beta$ is correct as given, is

$$a : b : c = 1.3252 : 1 : 5.5824$$

The size of unit cell is

$$a_0 = 6.206,\ b_0 = 4.683,\ c_0 = 26.14\ \text{Å}.$$

All of the data for the oscillated crystal and powder photographs were recalculated on the basis of this new axial ratio; the agreement between the theoretical and observed values was remarkably good for all except a few lines out of several hundred.

**Absorption in the Crystal and a New Use of Filters in Laue Photograph Technique.**—The critical absorption limit for the strongly absorbing iodine falls at 0.37 Å. It might be expected that the iodine would absorb

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[6] Bernal, *Proc. Roy. Soc. London,* **113A,** 117 (1927).

most or all of the wave lengths below its critical absorption limit. Then the calculated values of $n\lambda$ for the Laue photographs would show no values below 0.37 Å. for the correct cell. Inspection of the data showed this to be the case for a four molecule cell.

Some method was then needed to determine whether the assumption that the iodine absorbed all wave lengths below 0.37 Å. was justified. The critical absorption limit for tin lies just above that for iodine, being at 0.42 Å. If a filter of tin of sufficient thickness to cut out all wave lengths below its critical absorption limit were used, a Laue photograph might be taken without the absorption of the iodine being a factor. Since the lower wave length limit would be known accurately, there would be no doubt as to the true size of the unit cell. The thickness of pure tin foil necessary to absorb nine-tenths of the radiation in those wave lengths below 0.37 Å. was calculated with the Wyckoff[7] and Compton[8] modifications of the absorption equation. In the former case the calculated thickness was 0.0082 cm., in the latter 0.0087 cm. The filter actually used was 0.0085 cm. in thickness. It was assumed that if the absorptive power of the iodine approached the value it was supposed to have, it would absorb the other tenth of the radiation below 0.37 Å.

To check the efficiency of this filter, reflection photographs from the (1 0 0) face of rock salt were taken, with and without the filter. The salt crystal was oscillated through an angle of 40° during the exposure. The $\alpha_1$, $\beta_1$, $\beta_2$, $\beta_3$, $\beta_4$, $\gamma_1$, $\gamma_2$ and $\gamma_3$ lines of the $L$ spectrum of tungsten appeared on the photograph taken without the filter. These lines were used for calibration of the camera. The tube was working under the same voltage and current as during the taking of the Laue photographs. The photograph without the filter showed the low wave length limit to be at 0.31 Å. instead of 0.25 Å. This probably indicates a peak in the transformer curve. The silver absorption edge was found at 0.47 Å., the bromine edge at 0.91 Å. and the weaker second-order silver edge at 0.96 Å. The photograph taken with the filter showed a very faint radiation up to the absorption edge for tin at 0.41 Å. The second-order tin absorption edge was found to correspond with 0.83 Å.

Inspection of the photograph taken without the filter confirmed the assumption that the iodine atoms might completely absorb the radiation below 0.37 Å., for the radiation is comparatively weak below this. A Laue photograph was taken using the filter. It was analyzed in the same manner as the others, and proved that the unit cell contained four molecules, there being no values of $n\lambda$ below 0.42 Å.

Wyckoff[9] discusses the use of filters to obtain a more desirable distribu-

[7] Wyckoff, ref. 5, p. 83.

[8] Compton, "Bulletin of the National Research Council," No. 4, 1920.

[9] Wyckoff, *Am. J. Sci.*, [4] **50**, 339 (1920).

tion of wave lengths for Laue photographs, and concludes that their use is not desirable. Their use in the manner just described, however, seems a valuable addition to Laue photograph technique.

**Determination of the Space-Group.**—Inspection of the data showed that all types of planes were present except $(h\ 0\ l)$ when $(h + l)$ is odd. Since these are the only abnormalities, the basic lattice is the simple $\Gamma_m$ lattice of Bravais and not $\Gamma'_m$. Astbury and Yardley[10] have tabulated the data for the examination of the 230 space-groups by x-rays. In the monoclinic sphenoidal class there are only two space-groups, $C_2^1$ and $C_2^2$, based on the $\Gamma_m$ lattice. The first of these has no abnormal spacings and the latter only (0 1 0) halved. The class, therefore, cannot be sphenoidal, as given by Groth. The molecules of *m*-iodobenzoic acid are most certainly asymmetric, and there are four of them in the unit cell. Thus the class cannot be domatic. This leaves the two space-groups $C_{2h}^4$ and $C_{2h}^5$ in the prismatic class as the only possibilities. These two groups are the same except that the symmetry axis is a screw axis in $C_{2h}^5$ and therefore (0 1 0) is also halved in this space-group. Examination of the powder photograph showed that (0 1 0), which should have fallen between (1 0 3) and (0 0 6), was missing. Therefore, (0 1 0) is halved and the space-group is $C_{2h}^5$. $C_s^2$ does not have (0 1 0) halved, and this is further proof that the class cannot be domatic.

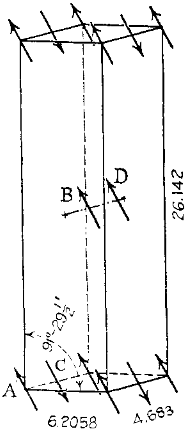

Fig. 1.

**Determination of Parameters.**—The space-group $C_{2h}^5$ contains a plane of symmetry and a screw axis of symmetry. This means that if one of the molecules is placed at the corners of the lattice, the second molecule is obtained from it by reflection in a plane perpendicular to the *b* axis, plus possible translations parallel to the *a* and *c* axes. The other two molecules are obtained by rotating these two through 180°, plus a translation along the *b* axis.

The coördinates of the equivalent points of the four molecules in the unit cell, relative to the crystallographic axes, are $(0\ 0\ 0)$, $(^1/_2\ v\ ^1/_2)$, $(u\ ^1/_2\ w)$, $(u + ^1/_2,\ v + ^1/_2,\ w + ^1/_2)$. These are equivalent to the positions given by Wyckoff,[11] for in his notation the *b* and *c* axes have been interchanged. Also the *a* and *c* axes in the monoclinic system are interchangeable.

The determination of the variable parameters *u*, *v* and *w* can be accomplished with a fair degree of accuracy from the data on the oscillated crystal photographs. The presence on one of the photographs of extremely strong reflections for (1 0 1), (1 0 3), (1 0 5), (1 0 7), (1 0 9), (1 0 11), and for

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[10] Astbury and Yardley, *Phil. Trans. Roy. Soc. London*, **224A**, 221–257 (1924).

[11] Wyckoff, "The Analytical Expression of the Results of the Theory of Space-Groups," Carnegie Institute Publication No. 318, Washington, **1922**, p. 151.

the corresponding planes where $l$ is negative, make it extremely probable that $u$ and $w$ are equal to 0. The coördinates then become: (0 0 0), ($^1/_2$ $v$ $^1/_2$), (0 $^1/_2$ 0), ($^1/_2$ $v$ + $^1/_2$ $^1/_2$).

The positions of the molecules within the cell are shown in Fig. 1. The B molecule is obtained from the A molecule by reflection and translations parallel to the $a$ and $c$ axes. The C and D molecules are obtained from A and B, respectively, by rotation through 180° and a translation along the $b$ axis.

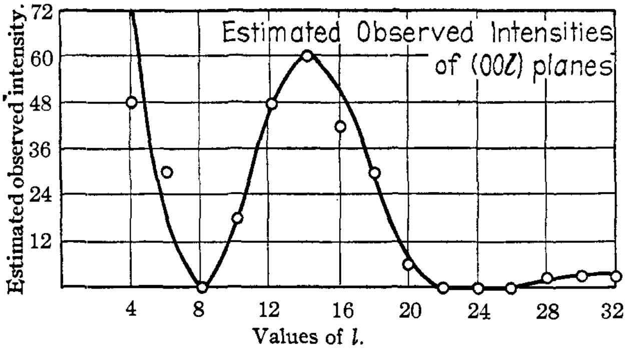

Fig. 2.—Estimated observed intensities of (0 0 $l$) planes.

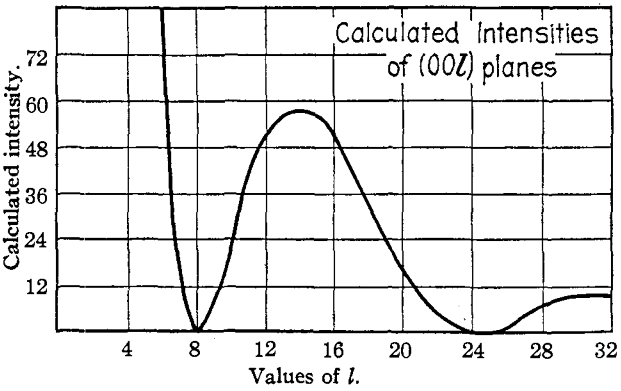

Fig. 3.—Calculated intensity of (0 0 $l$) planes.

The test of the correctness of these positions is whether the theoretically calculated values of the intensities of reflection check the actual intensities on the photographs. Wyckoff[12] gives the following expression for the intensity of x-ray reflection

$$I \alpha \left(\frac{d_{hkl}}{n}\right)^{2.35} \left\{ [\sum_{s} \overline{N}_s \cos 2\pi n\,(hx_s + ky_s + lz_s)]^2 + [\sum_{s} \overline{N}_s \sin 2\pi n\,(hx_s + ky_s + lz_s)]^2 \right\}$$

It would be hopeless to attempt to compare in this manner the intensities for each of the several hundred reflections appearing on the films, but it

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[12] Wyckoff, ref. 5, p. 107.

may be done for a few important sets of planes. In Fig. 2 is shown a graph of the estimated intensities of the various orders of (0 0 1) plane from one of the oscillated crystal photographs. It will be seen that the curve shows a minimum point at (0 0 8) and a maximum at (0 0 14). This would indicate that there must be another molecule or a periodicity along the *c* direction at a distance of approximately $^1/_{14}$ to $^1/_{16}$. The structure factors, $(A^2 + B^2)$, for the even-order (0 0 *l*) planes were calculated, and from these the theoretical intensities were determined. It was assumed in these calculations that the molecule, as a whole, reflected from its center of gravity. Also the factor $\overline{N}_s$ was dropped since it is a constant throughout the calculations. The theoretical curve of the intensities is given in Fig. 3. The assumption has been made that this *z* parameter is $^1/_{16}$. The agreement between the two curves is good. The data for these curves are given in Table II.

TABLE II

INTENSITY DATA FOR (0 0 *l*) PLANES FROM OSCILLATED CRYSTAL PHOTOGRAPH NUMBER 3

| Plane | Estimated obs. intens. | Calculated intensity | Plane | Estimated obs. intens. | Calculated intensity |
|---|---|---|---|---|---|
| 0 0 2 | [a] | 5758 | 0 0 1 8 | 30 | 33 |
| 0 0 4 | 48 | 661 | 0 0 2 0 | 6 | 15 |
| 0 0 6 | 30 | 75 | 0 0 2 2 | 0 | 4 |
| 0 0 8 | 0 | 0 | 0 0 2 4 | 0 | 0 |
| 0 0 1 0 | 18 | 23 | 0 0 2 6 | 0 | 2 |
| 0 0 1 2 | 48 | 51 | 0 0 2 8 | 3 | 7 |
| 0 0 1 4 | 60 | 59 | 0 0 3 0 | 3 | 10 |
| 0 0 1 6 | 42 | 51 | 0 0 3 2 | 3 | 10 |

[a] 0 0 2 is missing from the film because of a hole in the back of the camera where the undeviated beam passed out. 0 0 4 is probably underestimated in intensity on account of blackening near undeviated beam.

Thus a periodicity along the *c* axis equal to approximately $^1/_{16}$ of its length is reasonably certain. W. H. Bragg[13] has recently been able to explain the observed intensities of the reflections from the various planes of naphthalene, on the basis of a periodicity within the molecule. An examination of a model of the molecule of *m*-iodobenzoic acid reveals some interesting things in this respect. The model, embodying the "puckered" benzene ring, may be approximately represented (to scale) by the drawing in Fig. 4. The center of gravity of the ring and the rest of the molecule is approximately at M. Since their weights are so nearly the same (I = 127) and the rest of the ring = 121, the center of gravity of the whole molecule will be approximately at P on the line joining the centers of gravity of the two parts. If it is assumed that the carboxyl group is disposed approximately as shown in Fig. 4, and that the distance between the centers of the carbon and iodine atoms is approximately 1.54/2 + 2.788/2 Å.,[14] and that

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[13] W. H. Bragg, *Z. Krist.*, **66**, 22 (1927).

[14] Harris, Mack and Blake, THIS JOURNAL, **50**, 1595 (1928).

the molecule is located with respect to the *c*-axis as shown, then the projected distance along the *c* axis between P and M or between P and I is very nearly 1.65 Å., which is about $^1/_{16}$ of the length of the cell. The general pattern of the reflections occurring is probably set up by the molecule as a whole, and may be thought of as originating from the center of gravity, P. The points M and I would also set up reflections which will be in phase with each other but will be completely out of phase with those from P for (0 0 8). Since their sum is equivalent to the reflection from P, (0 0 8) will be missing. In the neighborhood of (0 0 16) they will be in phase with P and make these reflections unusually strong. Thus the intensities for the (0 0 *l*) planes may be readily explained.

To determine the value of the parameter *v* along the *b* axis the (0 1 *l*) and (0 $\bar{1}$ *l*) reflections on film Number 3 were taken. Examination of the film shows that in general those reflections are weaker where *l* is even. This would indicate that the value of *v* must be nearly $^1/_2$. The structure factors for this set of planes were calculated and the intensities determined. The periodicity along the *c* axis had to be taken into account here, too, and with respect to this set of planes it is approximately $^1/_{12}$. Table III gives the observed and calculated intensities of this set of planes. It will be seen that the observed intensities agree only roughly with the calculated intensities. This is because the C molecule falls half way along the *b* axis. It is not equivalent to the A and B molecules in its effect on the x-ray beam. If it were equivalent the first order of (0 1 1) would be missing completely, whereas it is present but greatly reduced in intensity. (0 1 2) has its intensity increased considerably because of the C molecule. (0 1 3) is reduced in intensity for the same reason as (0 1 1). Beyond this the effect of the C molecule is still noticeable but not quite so great. We are not able to take it into account quantitatively in the determination of the theoretical

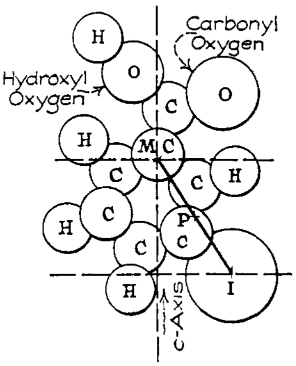

Fig. 4.

TABLE III

INTENSITY DATA FOR (0 1 *l*) PLANES FROM OSCILLATED CRYSTAL PHOTOGRAPH NUMBER 3

| Plane | Estimated obs. intens. | Calculated intensity | Plane | Estimated obs. intens. | Calculated intensity |
|---|---|---|---|---|---|
| 0 1 1 | 6 | 482 | 0 1 8 | 8 | 4 |
| 0 1 2 | 16 | 37 | 0 1 9 | 10 | 60 |
| 0 1 3 | 12 | 197 | 0 1 10 | 4 | 8 |
| 0 1 4 | 10 | 9 | 0 1 11 | 10 | 77 |
| 0 1 5 | 15 | 17 | 0 1 12 | 4 | 8 |
| 0 1 6 | 0 | 0 | 0 1 13 | 6 | 57 |
| 0 1 7 | 12 | 12 | 0 1 14 | 4 | 4 |

intensities. The best value for the parameter $v$ is approximately $^4/_{10}$. The data on these planes are given in Table III.

**Model of the Unit Cell.**—A model was made by constructing molecules to scale from wooden balls as shown in Fig. 4. These were then placed at the positions of the four lattice points. The junctions along the $a$ direction are across hydrogen atoms. The large number of orders of (0 0 1) planes reflecting indicates a concentration of the atoms in the (0 0 1) planes. The model shows this, and also explains the very complete cleavage parallel to this plane. The other cleavage (1 0 1) is likely from the model.

## Summary

*m*-Iodobenzoic acid belongs to the monoclinic prismatic class instead of monoclinic sphenoidal. Its axial ratio is $a : b : c = 1.3252 : 1 : 5.5824$; $\beta = 91° 29.5'$. The unit cell contains four molecules and has the following dimensions: $a_0 = 6.206$ Å.; $b_0 = 4.683$ Å.; $c_0 = 26.14$ Å. The space-group is $C_{2h}^5$. The molecules are located within the cell at the positions (0 0 0), $(^1/_2\ v\ ^1/_2)$, $(u\ ^1/_2\ w)$, $(u + {}^1/_2, v + {}^1/_2, w + {}^1/_2)$, where $u$ and $w$ are approximately equal to 0, and $v$ equals very nearly $^4/_{10}$. Model molecules, built up of wooden balls, embodying the "puckered" benzene ring fit into the cell defined above very well. The model accounts for the cleavage of the crystal.

An addition to Laue photograph technique through the use of filters has been described.

COLUMBUS, OHIO

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

# THE MEASUREMENT OF THE HYDROGEN-ION CONCENTRATION IN UNBUFFERED SOLUTIONS. I. THE ADSORBENT PROPERTIES OF PLATINIZED PLATINUM

BY I. M. KOLTHOFF AND TOHRU KAMEDA

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It is a well-known fact that the measurement of the hydrogen-ion concentration in a solution with an extremely small buffer capacity is a very hard problem. If a platinized electrode is used, it takes a long time before the potential is constant and it is hardly possible to find reproducible results; moreover, it is doubtful whether the final reading of the electromotive force corresponds to the $P_H$ of the original solution. It was our intention to make a careful study of the hydrolysis of solutions of pure zinc salts and we used a platinized platinum spiral for the measurement of the $P_H$.[1] However, we met with many difficulties; the e.m.f. measured always corresponded to a higher hydrogen-ion concentration than was

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[1] For electrode cell, *cf.* I. M. Kolthoff and W. Bosch, *Rec. trav. chim.*, **46,** 430 (1927).