Only the best kind of litmus should be used, a diluted solution of which has a genuine blue color. It must be mentioned that the degree of blue produced by the sodium chloride is a shade less intense than that produced by adding potassium hydroxide to a neutral violet solution of litmus.

An adequate explanation of the *modus operandi* of the reaction between sodium chloride and litmus + mercuric chloride must account for the following facts.

1. The reaction takes place only if *first* the mercuric chloride has come in contact with the litmus.
2. The blue color produced by the sodium chloride is not lasting; in a few minutes the liquid assumes a violet color.
3. The blue color of the reaction is a shade less deep than the one produced by potassium hydroxide; the solution possesses a tint of lilac, which is not noticed if potassium hydroxide is used instead of sodium chloride.

9th Line, No. 34,
Leningrad, U. S. S. R.
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[Contribution from the Gates Chemical Laboratory, California Institute of Technology, Pasadena, California, No. 145]

# THE CRYSTAL STRUCTURES OF MERCURIC AND MERCUROUS IODIDES

By Maurice L. Huggins and Paul L. Magill

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## Introduction

Since the determinations of the crystal structures of the mercury iodides here described were completed (in the summer of 1925) other investigators, as shown below, have published x-ray analyses of these substances, their conclusions being substantially in accord with our own. It seems desirable, nevertheless, to publish in brief form our measurements and deductions as they afford an independent confirmation of the results obtained, as our methods of obtaining and utilizing the data differ from those employed by the others, and as our structure determinations are more nearly unique.

This research was carried on while the senior author was a National Research Fellow at the California Institute of Technology. Some of the apparatus used was bought with the aid of a grant to Dr. A. A. Noyes from the Carnegie Institution of Washington. We wish to express our thanks for this aid and also to thank Dr. R. G. Dickinson for the use of apparatus designed by him and for personal instruction in methods of crystal-structure analysis.

## A. MERCURIC IODIDE

The red modification of mercuric iodide, $HgI_2$, is said[1] to crystallize with ditetragonal bipyramidal ($D_4^h$) symmetry. The axial ratio[1] ($c/a$) has been determined as 2.008 and the density[2] as 6.283 g./cc. The crystals exhibit very perfect cleavage parallel to the (001) faces.

### Determination of the Structure from Spectral Photographs Alone

Spectral photographs were obtained, using the Mo K radiation with (1) the $c$ axis, (2) the crystallographers' $a$ axis, and (3) the other possible $a$ axis (making an angle of 45° with that chosen by the crystallographers), as the axis of rotation. All of the reflections observed (from 48 different forms) could be given integral indices on the basis of a unit having the dimensions $a_0$ = 4.34 Å. and $c_0$ = 12.34 Å., but not on the basis of any smaller unit. Larger units would leave many unaccounted for absences. These exact values were obtained by direct comparison of the (110) and (001) reflections with those from a cleavage face of calcite.

A unit of this size contains two Hg and four I atoms, the calculated density being 6.45 g./cc. The axial ratio is 2.84, which is just $\sqrt{2}$ times the crystallographers' value. The factor $\sqrt{2}$ arises from the fact that the

Table I

Data from Spectral Photograph $HgI_2$-4

| Form | Rel. inter-planar dist. | Obs. intens. | Rel. intens. calcd. for equal inter-planar dist. | Form | Rel. inter-planar dist. | Obs. intens. | Rel. intens. calcd. for equal inter-planar dist. |
|---|---|---|---|---|---|---|---|
| Left side of photograph | | | | Right side of photograph | | | |
| 011 | 0.944 | m | 0.185 | 123 | .404 | f | .185 |
| 012 | .818 | ms | .313 | 124 | .378 | 0 | .044 |
| 013 | .686 | m | .185 | 220 | .353 | ms | 1.000 |
| 014 | .580 | vf | .044 | 125 | .352 | vf | .185 |
| 020 | .500 | ms | 1.000 | 222 | .343 | vf | .105 |
| 015 | .495 | f | .185 | 126 | .325 | f | .231 |
| 022 | .472 | vf | .105 | 224 | .317 | 0 | .010 |
| 121 | .442 | f | .185 | 130 | .316 | 0 | .020 |
| 016 | .428 | f | .231 | 132 | .309 | vf | .288 |
| 122 | .427 | f | .313 | 127 | .301 | vf | .185 |
| 017 | .376 | vf | .185 | 134 | .289 | f | .992 |
| 026 | .344 | f | .541 | 226 | .283 | f | .541 |
| 028 | .290 | f | .714 | 128 | .278 | vf | .152 |
| Right side of photograph | | | | 231 | .276 | vf | .185 |
| 110 | 0.707 | 0 | .020 | 232 | .272 | f | .313 |
| 112 | .633 | m | .288 | 233 | .266 | vf | .185 |
| 114 | .502 | m | .922 | 234 | .258 | 0 | .044 |
| 121 | .442 | mf | .185 | 235 | .249 | vf | .185 |
| 122 | .427 | mf | .313 | 236 | .239 | vf | .231 |

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[1] Groth, "Chemische Krystallographie," Engelmann, Leipzig, **1906**, Vol. 1, p. 218.

[2] International Critical Tables, Vol. 1.

$a$ axes of the true (namely, the smallest) unit make 45° angles with the $a$ axes chosen by the crystallographers.

The considerations leading to the determination of the arrangement of atoms within the unit are as follows.

1. In each of the spectral photographs the half above the horizontal zone was an exact mirror image of that below this zone.

2. The "special positions" of the correct space group must include either two single non-equivalent positions or a pair of equivalent positions, for the mercury atoms.[3]

3. The reflections obtained included some from planes of each of the following classes: $(h + k + l)$ odd. $h = 0$; $k$ odd. $h = 0$; $l$ odd. $h = 0$; $(k + l)$ odd. $(h + k)$ odd.[4]

4. All odd order reflections from the (001) planes were absent, although even orders through (008) were obtained. Similarly, odd orders of (010) were absent, although in proper position for reflection.

5. The (110) reflection was absent or extremely weak on photographs showing moderately strong (220) reflections. Moreover, (004) reflections were absent or very faint on photographs showing fairly strong (006) reflections.

6. Certain structures would place the Hg atoms in layers 6.17 Å. apart, with the I atoms either all crowded together in the same planes as the Hg atoms or distributed between alternate layers of Hg atoms, the distance between Hg layers separated by I atoms being the same as between Hg layers having nothing between them. Such structures obviously could not be correct.

Only one tetragonal structure satisfies the requirements imposed by the above considerations. In that, which may be derived from either of the space groups $V_d^4$, $D_4^6$, or $D_{4h}^{15}$, the Hg atoms are at the positions $(0,0,0)$ and $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$, and the I atoms at $(0,\frac{1}{2},u)$, $(\frac{1}{2},0,\bar{u})$, $(\frac{1}{2},0,\frac{1}{2}-u)$ and $0,\frac{1}{2},u + \frac{1}{2})$.

To determine the value of the parameter $u$ it is necessary to use further intensity comparisons. Great care must be exercised in making use of such comparisons from rotation spectra, since the relative intensities of two spots on the photographic plate depend on a number of other factors besides the relative reflecting powers of the two sets of planes being compared. It would seem safe, however, to use comparisons between spots which are fairly close together on the plate and which differ considerably in intensity, provided the stronger reflection is that further

[3] The "equivalent positions" of the various space groups have been tabulated by Wyckoff, "The Analytical Expression of the Results of the Theory of Space Groups," Carnegie Inst. Pub. No. **318** (1922).

[4] Absences to be expected from the various structures have been tabulated by Astbury and Yardley, *Trans. Roy. Soc.* (*London*), **224A,** 221 (1924).

from the spot produced by the direct beam. A number of such comparisons are listed in Table II.

TABLE II

COMPARISONS FROM $HgI_2$-4

012 > 011. 015, 016, 017, 020, 026, 028 > 014. 026, 028 > 017. 026, 028 > 022, 024. 112, 114, 121, 122, 123, 125, 126, 127, 128, 220, 222, 226, 231, 232, 233, 234, 236, 132, 134 > 110. 220 > 112. 220 > 121, 122, 123. 125, 126, 127, 128, 226, 231, 232, 233 > 124. 226 > 125, 126, 127. 132, 134, 231, 232, 233, 235, 236 > 130. 134 > 132. 134, 226, 231, 232, 233, 235, 236 > 224. 232 > 231. 235, 236 > 234.

OTHER COMPARISONS (FROM OTHER SPECTRAL PHOTOGRAPHS)

012, 013, 026, 028, 015, 016 > 002. 006, 008, 013, 015, 016, 017, 018, 019, 026, 028 > 004. 020 > 011. 018, 019 > 014. 028 > 019.

On calculating and plotting the structure factors in the usual manner, it has been found that these comparisons are all satisfied only for the parameter range from $u = .131$ to $u = .150$, if the Hg and I atoms scatter in proportion to their atomic numbers, for a slightly smaller range if the ratio, $\overline{\text{Hg}}/\overline{\text{I}}$, of their scattering powers is somewhat less than that of their atomic numbers, and for a slightly larger range if the scattering power ratio is somewhat greater than the atomic number ratio. The relative intensities calculated for the planes listed in Table I, assuming $u = .140$ and that the reflecting powers are proportional to the atomic numbers and not correcting for different interplanar distances, are given in the last column of that table.

## Corroboration of the Structure with the Aid of Laue Photographs

This structure determination was checked by means of Laue photographs, the analysis being made in the usual way.

TABLE III

USEFUL DATA AND COMPARISONS FROM LAUE PHOTOGRAPH $HgI_2$-11

| Indices | Est. intens. | Interpl. dist., Å. | Wave length, Å. | Indices | Est. intens. | Interpl. dist., Å. | Wave length, Å. |
|---|---|---|---|---|---|---|---|
| 109 | 3.5 | 1.31 | 0.43 | $2,\bar{1},\overline{10}$ | 1.3 | 1.04 | 0.45 |
| 0,1,10 | 0.8 | 1.19 | .33 | $0,1,\overline{12}$ | 1.6 | 1.00 | .42 |
| $\bar{2}34$ | .3 | 1.12 | .36 | $1,0,\overline{12}$ | 2.0 | 1.00 | .43 |
| $\bar{2}3\bar{4}$ | .4 | 1.12 | .45 | $1,1,\overline{16}$ | 0.2 | 0.75 | .44 |
| 1,0,11 | .4 | 1.09 | .28 | 2,1,16 | .4 | .72 | .44 |
| $\bar{2}3\bar{5}$ | 1.3 | 1.06 | .42 | $\bar{2}58$ | .05 | .71 | .46 |
| $3\overline{25}$ | 1.6 | 1.08 | .43 | $5,\bar{2},\overline{11}$ | .1 | .65 | .46 |
| $\bar{1},2,\overline{10}$ | 1.3 | 1.04 | .44 | | | | |

Comparisons: 235 > 234. 0,1,12 > 235. 1,2,16 > 1,1,16. 1,2,10 > 234. 0,1,12 > 1,2,10. 2,5,11 > 258.

By means of intensity comparisons between planes reflecting the same wave length, it was found possible to limit the parameter to quite a small range, namely, between .136 and .142 if we assume reflecting powers proportional to the atomic numbers, between .138 and .142 if we assume the ratio ($\overline{Hg}/\overline{I}$) of reflecting powers to be 10% greater than that of their atomic numbers, and between .136 and .140 if we take $\overline{Hg}/\overline{I}$ as 10% less than the atomic number ratio. The uneliminated region disappears entirely if the ratio of scattering powers is assumed to be 22% greater or 28% less than that of the atomic numbers. In view of these results we believe $u$ = .140 ± .003 to be a conservative estimate of the parameter.

## Comparison with the Results of Other Investigators

Havighurst,[5] using powder photographs and ionization spectrometer measurements from single crystal faces, has determined the dimensions of the unit cell as $a_0$ = 4.356 Å. and $c_0$ = 12.34 Å. Bijvoet, Claasen and Karssen,[6] using powder photographs and rotation spectra, have obtained $a_0$ = 4.38 Å. and $c_0$ = 12.43 Å. and deduced the same type of arrangement as have we, with $u$ = .139 ± .007.

## Description and Discussion of the Structure

The structure (Figs. 1 and 2) may be described as consisting of "layer molecules." The smallest interatomic distance (Hg-I) within each layer, taking $u$ as .140, is 2.77 Å.; the shortest distance between atoms (I-I) in different layers is 4.10 Å. Within each layer each Hg atom is surrounded tetrahedrally by four equidistant I atoms and each I by two

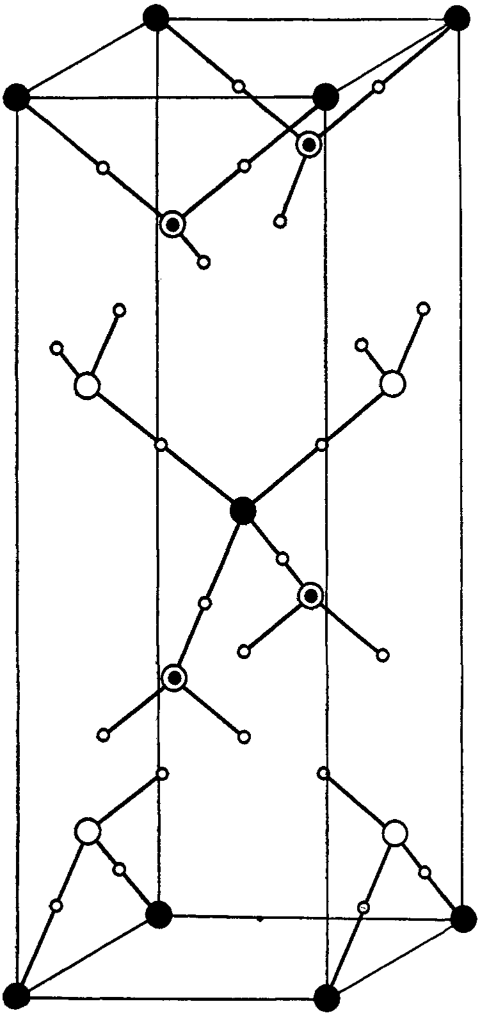

Fig. 1.—The unit cell of $HgI_2$. Large dots represent Hg centers and large circles and circled dots I centers. Small circles show the probable approximate "positions" of pairs of valence electrons.

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[5] Havighurst, *Am. J. Sci.*, **10**, 556 (1925).

[6] Bijvoet, Claasen and Karssen, *Proc. Acad. Sci. Amsterdam*, **29**, 529 (1926).

equidistant Hg atoms. These atoms we may assume to be held tightly together, while the forces between the layers are, relatively weak accounting for the fact that these crystals cleave so readily parallel to their (001) faces.

The most probable distribution of valence electrons[7] would seem to be that shown in the figures, both Hg and I kernels being tetrahedrally surrounded by electron pairs.

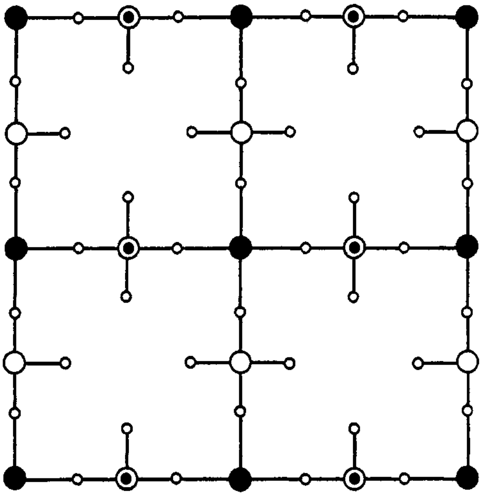
Fig. 2.—A small section of a layer in a crystal of $HgI_2$.

Assuming such a distribution and defining an atomic radius as the distance from nucleus to the center of a valence pair, it is evident that the distance between Hg and I centers equals the sum of their radii.

One of the authors[8] has calculated the Hg and I radii, in crystals such as HgS, CuI and AgI, to be about 1.50 Å. and 1.25 Å., respectively. The sum of these values (2.75 Å.) is closer to the observed Hg-I distance (2.77 Å.) than might have been expected, considering the inaccuracies of the calculations and the differences between the crystals involved.

## B. MERCUROUS IODIDE

Crystals of mercurous iodide, $Hg_2I_2$, are also tetragonal, with an axial ratio of 1.673 and a density of 7.70 g./cc. Cleavage again is parallel to the (001) planes.

### Determination of the Structure

The unit cell found to be in agreement with both the Laue and spectrum data contains four Hg and four I atoms, $a_0$ and $c_0$ being 4.92 Å. and 11.64 Å., respectively. The $a_0$ value was obtained by direct comparison of a (110) reflection spectrum with that from a calcite cleavage face; $c_0$ was calculated from $a_0$, assuming the axial ratio given above to be correct (except for the factor $\sqrt{2}$). This $c_0$ value was checked approximately

[7] Cf. Huggins, *Phys. Rev.*, **27**, 286 (1926).

[8] Huggins, *ibid.*, **28**, 1086 (1926). New and better data not then available (especially Barth and Lunde, *Norsk geol. tids.*, **8**, 281 (1925) and Zachariasen, *ibid.*, **8**, 302 (1925)) result in values for some of the radii which differ somewhat from those published. The newer values are used here.

by means of transmission spectra from the (001) planes. The calculated density is 7.68 g./cc.

In determining the type of arrangement within the unit the following observations were found useful:

1. Both spectrum and Laue photographs were symmetrical about lines passing through the central spot.
2. No $(h + k + l)$ odd reflections appeared.
3. Reflections were observed from planes of the following classes: $h = 0$; $k$ odd; $l$ odd. $h = \pm k$; $(2h + l)/4$ not integral. $h$ odd; $k$ odd; $l/4$ integral.
4. $l = 3$ reflections were all absent or extremely weak.
5. $l = 2$ and $l = 6$ reflections were all absent or too faint to be observed.
6. The reflection from (130) was stronger than that from (121).

Applying these data to all tetragonal structures and considering $\overline{Hg}/\overline{I}$

TABLE IV

DATA FROM SPECTRAL PHOTOGRAPH $Hg_2I_2$-5

| Form | Rel. interplanar dist. | Obs. intens. | Form | Rel. interplanar dist. | Obs. intens. |
|---|---|---|---|---|---|
| Left side of photograph | | | Right side of photograph | | |
| 110 | 0.707 | vs | 011 | 0.922 | mf |
| 112 | .607 | 0 | 013 | .619 | vf |
| 114 | .454 | s | 020 | .500 | ms |
| 121 | .439 | f | 022 | .460 | 0 |
| 123 | .389 | 0 | 121 | .439 | f |
| 220 | .354 | ms | 015 | .428 | ms |
| 116 | .344 | 0 | 024 | .382 | ms |
| 222 | .339 | 0 | 031 | .330 | vf |
| 125 | .325 | m | 017 | .320 | mf |
| 017 | .320 | mf | 130 | .316 | m |
| 224 | .303 | m | 026 | .309 | 0 |
| 130 | .316 | m | 033 | .307 | 0 |
| 133 | .293 | 0 | 132 | .305 | 0 |
| 134 | .279 | mf | 134 | .279 | mf |
| 231 | .276 | vf | 118 | .273 | m |
| 118 | .273 | m | 035 | .273 | mf |
| 127 | .270 | vf | 028 | .255 | mf |
| 233 | .262 | 0 | 040 | .250 | mf |
| 235 | .239 | mf | 042 | .244 | 0 |
| 330 | .236 | mf | 044 | .230 | mf |
| 332 | .231 | 0 | 145 | .216 | vf |
| 240 | .224 | mf | | | |
| 228 | .227 | f | | | |
| 242 | .220 | 0 | | | |
| 334 | .219 | mf | | | |
| 244 | .209 | f | | | |

Comparisons: $l = 0 > l = 1,2,3$. $1 > 2,3$. $4 > 1,2,3,6$. $5 > 1,2,3,6$. $7 > 2,3,6$. $8 > 1,2,3,6$.

for all values from 1.00 to 2.00, all but the following have been definitely ruled out:

1. $C_{4v}^9$ (aa,aa). Hg at $(0,0,0)(\frac{1}{2},\frac{1}{2},\frac{1}{2})(0,0,u)(\frac{1}{2},\frac{1}{2},u+\frac{1}{2})$. I at $(0,0,v)(\frac{1}{2},\frac{1}{2},v+\frac{1}{2})(0,0,w)(\frac{1}{2},\frac{1}{2},w+\frac{1}{2})$.

2. (e,e) of $V_d^9$, $V_d^{11}$, $D_4^9$ or $D_{4h}^{17}$; (f,f) of $V_d^9$. Hg at $(0,0,u)(0,0,\bar{u})(\frac{1}{2},\frac{1}{2},u+\frac{1}{2})(\frac{1}{2},\frac{1}{2},\frac{1}{2}-u)$; I at $(0,0,v)(0,0,\bar{v})(\frac{1}{2},\frac{1}{2},v+\frac{1}{2})(\frac{1}{2},\frac{1}{2},\frac{1}{2}-v)$. The second is a special case of the first, obtained by putting $w = u - v$ and shifting the origin.

The $C_{4v}^9$ structure cannot conclusively be eliminated without very tedious calculations. These we have not made, as they seemed unnecessary in view of the satisfactory agreement obtained otherwise and the absence of any crystallographic or other evidence of polarity.

Calculating structure factors for arrangement (2) for various values of $l$, $u$, $v$ and $\overline{\text{Hg}}/\overline{\text{I}}$, the best agreement with our data (Tables IV and V) was obtained for $u = .117$ and $v = .353$, with $\overline{\text{Hg}}/\overline{\text{I}} = 1.3$ times the ratio

TABLE V

SELECTED DATA FROM LAUE PHOTOGRAPHS

| Indices | Est. intens. | Interpl. dist., Å. | Wave length, Å. | Indices | Est. intens. | Interpl. dist., Å. | Wave length, Å. |
|---|---|---|---|---|---|---|---|
| | $Hg_2I_2$-12 | | | | $Hg_2I_2$-4 | | |
| 138 | 0.6 | 1.06 | 0.30 | $\bar{2}33$ | 0.2 | 1.29 | 0.41 |
| $2,\bar{1},11$ | .6 | 0.95 | .39 | $\bar{3}27$ | .4 | 1.05 | .43 |
| $3\bar{3}8$ | .2 | .91 | .30 | $2\bar{3}7$ | .4 | 1.05 | .45 |
| $1,0,\overline{13}$ | 1.6 | .88 | .30 | $\bar{2},1,11$ | .4 | 0.95 | .41 |
| $3,\bar{2},11$ | 0.2 | .84 | .39 | $1,\bar{2},11$ | .4 | .95 | .42 |
| $\bar{3},2,11$ | .2 | .84 | .44 | $5\bar{3}0$ | .6 | .84 | .40 |
| 1,1,14 | .5 | .81 | .33 | $\bar{3}50$ | .6 | .84 | .42 |
| $1,1,\overline{14}$ | 1.0 | .81 | .39 | 1,2,13 | 3.5 | .83 | .45 |
| $4\bar{3}9$ | 0.6 | .78 | .43 | 2,1,13 | 3.5 | .83 | .44 |
| 1,2,15 | .1 | .73 | .38 | $\bar{5}34$ | .4 | .81 | .41 |
| $1,2,\overline{15}$ | .05 | .73 | .43 | | | | |
| $1,1,\overline{16}$ | .1 | .71 | .30 | | $Hg_2I_2$-1 | | |
| $4,\bar{3},13$ | .1 | .66 | .30 | | | | |
| $\bar{4},3,13$ | .1 | .66 | .34 | $3\bar{2}3$ | 0.05 | 1.29 | 0.42 |
| $5\bar{4}9$ | .1 | .66 | .37 | $4,\bar{1},13$ | .4 | .72 | .42 |
| $\bar{5}49$ | .1 | .66 | .39 | $5\bar{2}9$ | .1 | .67 | .41 |
| 1,3,16 | .05 | .66 | .40 | | | | |
| 1,2,17 | .2 | .65 | .30 | | | | |
| $1,2,\overline{17}$ | .4 | .65 | .35 | | | | |
| $2,1,\overline{17}$ | .4 | .65 | .41 | | | | |
| 1,4,17 | .2 | .59 | .40 | | | | |
| $\bar{4},1,17$ | .1 | .59 | .43 | | | | |
| $4,\bar{1},17$ | .2 | .59 | .39 | | | | |

No $l$ = 2, 6 or 10 reflections in first order on any of above photographs.

Comparisons from $Hg_2I_2$-12: $l = 17 > l = 16$. $17 > 15$. $17 > 13$. $17 > 9$. $14 > 11$. $13 > 8$. $9 > 11$.

Comparisons from $Hg_2I_2$-4: $l = 13 > l = 7$. $4 > 3$. $0 > 11$.

Comparisons from $Hg_2I_2$-1: $l = 13 > l = 3$. $9 > 3$.

TABLE VI

RELATIVE VALUES OF THE STRUCTURE FACTOR FOR $Hg_2I_2$ CALCULATED FOR CERTAIN VALUES OF THE PARAMETERS AND OF $\overline{Hg}/\overline{I}$

| $l$ | $u$ = 0.117<br>$v$ = .353<br>$\overline{Hg}/\overline{I}$ = 1.96 | $u$ = 0.116<br>$v$ = .347<br>$\overline{Hg}/\overline{I}$ = 1.51 | $u$ = 0.116<br>$v$ = .347<br>$\overline{Hg}/\overline{I}$ = 1.96 |
|---|---|---|---|
| 0 | 2.96 | 2.51 | 2.96 |
| 1 | 0.85 | 0.55 | 0.89 |
| 2 | .08 | .17 | .12 |
| 3 | .23 | .10 | .17 |
| 4 | 2.77 | 2.23 | 2.68 |
| 5 | 1.59 | 1.42 | 1.81 |
| 6 | 0.15 | 0.37 | 0.22 |
| 7 | .16 | .33 | .16 |
| 8 | 2.25 | 1.52 | 1.93 |
| 9 | 2.30 | 2.17 | 2.60 |
| 11 | 0.29 | 0.27 | 0.09 |
| 13 | 2.79 | 2.50 | 2.96 |
| 14 | 0.33 | 0.45 | 0.77 |
| 15 | .22 | .18 | .16 |
| 16 | .76 | .02 | .27 |
| 17 | 2.96 | 2.29 | 2.74 |
|  | 7 < 3 | 3,5,16 too low<br>7 < 6<br>17 < 13 | 7,11 too low<br>17 < 13 |

TABLE VII

COMPARISON OF UNIT DISTANCES AND PARAMETERS OBTAINED BY DIFFERENT INVESTIGATORS

| $Hg_2Cl_2$ | $a_0$, Å. | $c_0$, Å. | $u$ | $v$ |
|---|---|---|---|---|
| Mauguin[9] | 4.45 | 10.90 | 0.125 | 0.375 |
| Hylleras[10] | 4.45 | 10.88 | .125 | .375 |
| Havighurst[11] | 4.47 | 10.89 | .110 | .360 |
| Havighurst[12] |  |  | .116 | .347 |
| $Hg_2Br_2$ |  |  |  |  |
| Hylleras[10] | 4.67 | 11.16 | .125 | .375 |
| Havighurst[11] | 4.65 | 11.10 | .108 | .358 |
| Havighurst[12] |  |  | .116 | .347 |
| $Hg_2I_2$ |  |  |  |  |
| Hylleras[10] | 4.91 | 11.57 | .125 | .375 |
| Havighurst[11] | 4.92 | 11.61 | .105 | .355 |
| Havighurst[12] |  |  | .116 | .347 |
| Huggins and Magill | 4.92 | 11.64 | .117 | .353 |

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[9] Mauguin, *Compt. rend.*, **178**, 1913 (1924). From powder photographs.

[10] Hylleras, *Physik. Z.*, **26**, 811 (1925). From powder photographs.

[11] Havighurst, *Am. J. Sci.*, **10**, 15 (1925). From powder photographs and ionization spectrometer measurements on $Hg_2Cl_2$. The parameter values were calculated on the assumptions that $v - u = .250$ and that the Hg-Hg distance = 2.40 Å. in each case.

[12] Havighurst, THIS JOURNAL, **48**, 2113 (1926). The parameter values were obtained from calculations of the density of scattering power for x-rays at points on the tetragonal axis. These are undoubtedly more accurate than the earlier values.

of the atomic numbers (see Table VI). Although the true values of the parameters may differ slightly from these, greater differences than 0.01 would seem to be very improbable.[13]

## Description and Discussion of the Structure

The arrangement of atomic centers within the unit cell is shown in Fig. 3. It is apparent that the structure can be considered as an aggregation of IHgHgI "molecules," so distributed as to surround each Hg atom by four I atoms in other molecules and *vice versa*. The shortest distances between atoms, calculated from our values of the unit distances and parameters, are as follows. Hg-Hg, 2.72 Å.; I-I, 3.42 Å.; Hg-I (on same tetragonal axis), 2.75 Å.; Hg-I (not on same tetragonal axis), 3.65 Å.

If there are two valence electrons per Hg atom and seven per I atom, there are just sufficient for a complete octet around each I kernel and a pair between each two adjacent Hg kernels. It would seem reasonable to assume that each I valence shell consists of four electron pairs tetrahedrally disposed, as in the case of $HgI_2$, but the orientation of these tetrahedra cannot at present be determined.

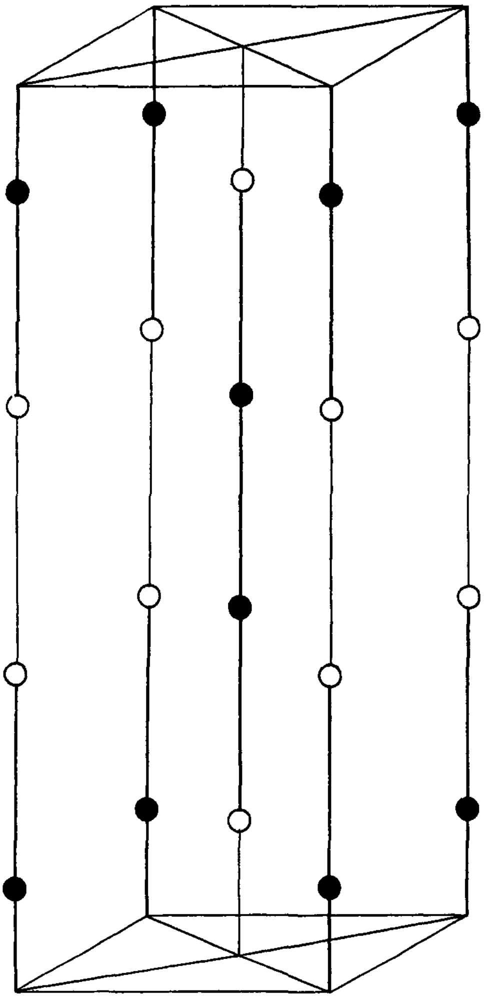

Fig. 3.—The unit cell of $Hg_2I_2$.

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[13] For no combination of parameters and ratio of reflecting powers was complete agreement obtained. For this reason we thought it advisable to postpone publication until our comparisons could be checked by new data, and others obtained. Although up to the present time it has not seemed feasible to do this, further delay in publication would appear to be unnecessary, in view of the agreement between our results and those published by others. Havighurst's 1926 parameter values give no better agreement than ours, no matter what ratio of $\overline{Hg}/\overline{I}$ is assumed (see Table VI). The reason for the disagreement is probably that the assumption that the atoms can be treated as point-scatterers is probably not valid when considering reflections from very complicated planes.

## Summary

The crystal structure of tetragonal $HgI_2$ has been determined, (a) using spectral photographic data alone, and (b) using data from Laue photographs, together with spectra from the (100), (110) and (001) planes. The unit (Fig. 1) has the dimensions $a_0$ = 4.34 Å. and $c_0$ = 12.34 Å. and contains Hg atoms at (0,0,0) and $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ and I atoms at $(0,\frac{1}{2},u)$, $(\frac{1}{2},0,\bar{u})$, $(\frac{1}{2},0,\frac{1}{2} - u)$ and $(0,\frac{1}{2},u + \frac{1}{2})$, with $u = .140 \pm .003$. The valence electrons are probably in pairs at tetrahedron corners around both Hg and I atoms, each Hg being bonded to four I atoms and each I to two Hg atoms. The structure may be said to consist of "layer molecules." The interatomic distance (Hg-I) within each layer is 2.77 Å. The shortest distance (I-I) between atoms in different layers is 4.10 Å.

The unit of $Hg_2I_2$ is a tetragonal prism having the dimensions $a_0$ = 4.92 Å. and $c_0$ = 11.64 Å. Hg atoms are at $(0,0,u)$, $(0,0,\bar{u})$, $(\frac{1}{2},\frac{1}{2},u + \frac{1}{2})$ and $(\frac{1}{2},\frac{1}{2},\frac{1}{2} - u)$; I atoms at $(0,0,v)$, $(0,0,\bar{v})$, $(\frac{1}{2},\frac{1}{2},v + \frac{1}{2})$ and $(\frac{1}{2},\frac{1}{2},\frac{1}{2} - v)$; $u$ and $v$ being approximately .117 and .353, respectively. The structure (Fig. 3) is thus built up of IHgHgI molecules, within which the Hg-Hg and Hg-I distances are approximately 2.72 Å. and 2.75 Å., respectively. These results are in good agreement with those obtained by others.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

# HYDROGEN GAS THERMOMETER COMPARED WITH THE OXYGEN AND HYDROGEN VAPOR-PRESSURE THERMOMETERS BY MEANS OF A COPPER-CONSTANTAN THERMOCOUPLE

BY W. F. GIAUQUE, H. L. JOHNSTON AND K. K. KELLEY[1]

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In connection with establishing a temperature scale for this Laboratory, a preceding paper[2] gives the results of comparison of copper-constantan thermocouples with the hydrogen gas thermometer from 15 to 283°K.

The present article presents results obtained by comparison of standard thermocouple W of Giauque, Buffington and Schulze (designated hereafter G., B. and S.) with the oxygen and hydrogen vapor-pressure thermometers.

The temperatures obtained from the oxygen vapor pressures as given by Cath[3] are in very satisfactory agreement with those obtained from the thermocouple of G., B. and S. On the other hand, the results obtained by means of the hydrogen vapor-pressure measurements have fortunately

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[1] National Research Fellow in Chemistry, University of California.

[2] Giauque, Buffington and Schulze, THIS JOURNAL, **49**, 2343 (1927).

[3] Cath, *Comm. Phys. Lab. Univ. Leiden*, 152d, **1918**.