The reaction between ceric and ferrous solutions is suitable for the potentiometric determination of either ion with a high order of accuracy. The reaction is sluggish near the equivalence point but this fact does not cause serious inconvenience. The reaction may be applied in the standardization of ceric solutions and in the potentiometric determination of cerium.

Ceric solutions may be standardized or determined by titration with standard oxalic acid. The ceric solution must be heated. The reverse titration is impractical because of the slow rate of reaction, even when the oxalic acid solution is heated.

A potentiometric study of the determination of cerium has been made. Oxidation by bismuthate or persulfate followed by potentiometric titration with ferrous sulfate is a very rapid and satisfactory mode of procedure.

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[CONTRIBUTION FROM THE GATES CHEMICAL LABORATORY OF THE CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 163]

THE CRYSTAL STRUCTURES OF BETA BENZENE HEXABROMIDE AND HEXACHLORIDE

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Introduction

In a previous investigation[1] β-benzene hexabromide,[2] $C_6H_6Br_6$, and β-benzene hexachloride, $C_6H_6Cl_6$, both crystallizing in the cubic system, were found to possess the space group symmetry T_h^6 with four molecules in the cubic unit of structure. The $C_6H_6X_6$ molecule was found to possess a three-fold rotation axis and a center of symmetry. Since all atoms of any one element are in equivalent positions, and since all atoms are in the general positions,[3] a completion of the structure determination requires the evaluation of three parameters for each element in each compound. In the case of the bromide, where the great majority of all electrons are in the bromine atoms, at least the predominant features of the intensities of x-ray reflection must be determined by the positions of the halogen atoms. Consequently a determination of the bromine

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[1] Hendricks and Bilicke, THIS JOURNAL, **48**, 3007 (1926).

[2] Since this paper confines itself to the beta isomers, the Greek prefix will be omitted.

[3] The coördinates of the general positions in T_h^6 are:

$$(xyz)(\tfrac{1}{2}+x, \tfrac{1}{2}-y, \bar{z})\ (\bar{x}, \tfrac{1}{2}+y, \tfrac{1}{2}-z)(\tfrac{1}{2}-x, \bar{y}, \tfrac{1}{2}+z)$$
$$(zxy)(\bar{z}, \tfrac{1}{2}+x, \tfrac{1}{2}-y)(\tfrac{1}{2}-z, \bar{x}, \tfrac{1}{2}+y)\ (\tfrac{1}{2}+z, \tfrac{1}{2}-x, \bar{y})$$
$$(yzx)(\tfrac{1}{2}-y, \bar{z}, \tfrac{1}{2}+x)(\tfrac{1}{2}+y, \tfrac{1}{2}-z, \bar{x})(\bar{y}, \tfrac{1}{2}+z, \tfrac{1}{2}-x)$$
$$(\overline{xyz})(\tfrac{1}{2}-x, \tfrac{1}{2}+y, z)(x, \tfrac{1}{2}-y, \tfrac{1}{2}+z)(\tfrac{1}{2}+x, y, \tfrac{1}{2}-z)$$
$$(\overline{zxy})(z, \tfrac{1}{2}-x, \tfrac{1}{2}+y)\ (\tfrac{1}{2}+z, x, \tfrac{1}{2}-y)(\tfrac{1}{2}-z, \tfrac{1}{2}+x, y)$$
$$(\overline{yzx})(\tfrac{1}{2}+y, z, \tfrac{1}{2}-x)(\tfrac{1}{2}-y, \tfrac{1}{2}+z, x)\ (y, \tfrac{1}{2}-z, \tfrac{1}{2}+x).$$

parameters seemed to offer an approach to these structures for it could be undertaken with the expectation of avoiding the complicating necessity of simultaneous consideration of more than three parameters.

Experimental Data

For the present purpose it was found desirable to obtain certain x-ray data not previously published. The crystals used were prepared as by Hendricks and Bilicke; from them were made spectral, Laue and powder photographs in the usual manner. Spectral photographs were obtained from (100) and (111) of $C_6H_6Br_6$; that from (111) was especially good and permitted a perhaps better determination of d_{100} than the previous powder data. This new value for the bromide is d_{100} = 10.49 Å., giving a calculated density 3.191 g./cc., while the density observed by Hendricks and Bilicke is 3.197 g./cc. The relative intensities of the spectral reflections are shown in Table I. New Laue photographic data for both compounds, obtained with the primary beam nearly perpendicular to (111) are given in Table II. The axes were so chosen (with respect to a permu-

Table I

Intensities of Reflection from $C_6H_6Br_6$

Order, n	1	2	3	4	5	6
Obs. rel. intensities for(100)	absent	weak	absent	medium	absent	strong
S_{Br} for (100)	0	2.1	0	5.9	0	15.7
Obs. rel. intensities for (111)	absent	very weak	absent	medium strong	strong	absent
S_{Br} for (111)	3.0	2.0	0.2	8.7	16.5	5.5

Table II

Laue Photographic Data from $C_6H_6Cl_6$ and from $C_6H_6Br_6$

Form (hkl)	$\frac{d_{hkl}}{d_{100}}$	Estimated intensities						S_{Br}	S_{Cl+C}
		$C_6H_6Br_6$			$C_6H_6Cl_6$				
		λ 0.35 Å.	λ 0.40 Å.	λ 0.45 Å.	λ 0.35 Å.	λ 0.40 Å.	λ 0.45 Å.		
279	0.086	0.1	0.1	..	0.15	0.15	..	7.32	9.60
972	.086	.05	.05	..	.0	.05	..	3.07	2.49
10.5.1	.089	..	.2	..	.25	.30	.35	12.30	12.48
5.10.1	.089	.0	.0	..	.0	.0	..	0.51	1.21
916	.092	..	.05	..	.0	.0	.0	4.34	4.06
196	.092	..	.0	.0	.0	..	.0	0.76	1.83
10.3.3	.092	..	.05	..	.0	.05	.1	4.94	5.6
477	.094	..	.1	.1	.05	.05	.1	5.88	7.18
576	.095	..	.05	.05	.0	.0	.0	3.45	2.81
756	.095	..	.0	.0	.0	.0	.0	1.1	2.1
294	.099	.0	.0	..	.08	.15	..	1.87	2.51
924	.099	.0	.0	..	.0	.0	..	1.60	1.91
168	.099	..	.0	..	..	.0	..	1.23	2.52
186	.099	..	.0	..	..	.0	..	1.63	1.17
367	.103	..	..	.4	.45	.6	..	11.84	12.33
763	.103	..	..	.0	.0	.0	..	2.32	2.23

Table II (*Concluded*)

Form (hkl)	$\frac{d_{hkl}}{d_{100}}$	Estimated intensities						S_{Br}	S_{Cl+C}
		$C_6H_6Br_6$			$C_6H_6Cl_6$				
		λ 0.35 Å.	λ 0.40 Å.	λ 0.45 Å.	λ 0.35 Å.	λ 0.40 Å.	λ 0.45 Å.		
267	.106	.0	.0	..	..	.0	.0	2.03	1.86
276	.106	.0	.0	.0	..	.0	.0	1.90	1.15
338	.110	.0	..	..	.0	..	..	0.23	1.34
832	.114	..	.05	..	.0	..	.25	2.18	3.88
823	.114	..	.0	..	.0	.0	.05	0.29	3.14
465	.114	..	..	.2	.4	.45	.5	5.19	6.27
564	.114	..	..	.1	..	.08	.17	3.95	3.90
751	.115	..	..	.2	..	.1	..	7.19	4.14
157	.115	..	..	.05	.0	.0	.0	2.05	1.02
147	.123	.1	.15	..	.1	.15	..	3.51	5.00
417	.123	.3	.4	..	.45	.6	.7	6.28	8.56
156	.127	.0	.0	..	..	.0	.0	1.51	2.03
165	.127	.0	.0	..	..	..	.08	1.80	1.74
723	.127	.05	.1	..	..	.15	.2	3.12	2.91
732	.127	.4	..	.4	.7	..	.9	6.22	9.20
155	.140	.8	..	..	.7	..	..	8.47	11.54
354	.141	..	.15	..	.1	..	.25	2.58	1.87
453	.141	..	.2	..	.25	..	.35	3.53	3.23
362	.143	.8	..	..	.6	..	..	10.82	8.74
263	.143	.0	..	..	.0	..	..	0.98	0.11
136	.147	..	..	.7	..	.7	..	8.42	9.02
163	.147	..	..	.05	..	.0	..	2.23	2.12
153	.169	.55	.7	..	..	..	.7	6.77	5.75
513	.169	.0	.0	..	.0	.0	.0	0.30	0.4
144	.174	1.0	1.2	..	..	1.0	1.0	7.28	6.78
423	.186	.15	.2	..	..	.15	..	1.81	2.10
432	.186	.9	1.0	..	..	1.1	..	5.33	6.42

tation of h and k) that planes ($hk0$) with k odd appeared in the first order, since the space group had already been shown to be T_h^6, requiring the absence of ($hk0$) with h odd. In Table III is given a remeasurement of

Table III

Powder Photographic Data from Benzene Hexabromide

Form	d_{hkl} Å., obs.	d_{hkl} Å., calcd.	Obs. intensity	Form	d_{hkl} Å., obs.	d_{hkl} Å., calcd.	Obs. intensity
221	3.49	3.498	10.0	423, 432, 250	1.955	1.950	1.5
230	2.905	2.912	11.0	441, 522	1.83	1.827	0.5
321, 312	2.805	2.806	3.0	442, 600	1.748	1.749	2.0
411	2.47	2.473	6.0	611, 523, 532	1.707	1.703	4.0
402, 420	2.35	2.348	1.5	612, 621	1.64	1.64	2.0
421, 412	2.28	2.29	4.0	443, 450			

the previous powder photograph[4] with a General Electric Company ruler.[5] The measurements were obtained by setting the line due to (221) at 3.49 = $10.49/\sqrt{9}$ Å. Some changes in the assignment of indices to the more com-

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[4] Ref. 1, Table I, p. 3008.

[5] Davey, *Gen. Elec. Rev.*, 29, 128 (1926).

plicated lines will be noticed. In Table IV are given powder photographic data for $C_6H_6Cl_6$. All powder data were obtained with Mo $K\alpha$ radiation.

TABLE IV

POWDER PHOTOGRAPHIC DATA FROM BENZENE HEXACHLORIDE

Form	d_{hkl} Å., obs.	d_{hkl} Å., calcd.	Obs. intensity	Form	d_{hkl} Å., obs.	d_{hkl} Å., calcd.	Obs. intensity
200	5.00	5.04	0.5	421, 412	2.20	2.20	4.0
210	4.50	4.57	1.5	422	2.056	2.056	0.3
211	4.11	4.11	7.0	430	2.00	2.015	0.3
220	3.56	3.563	0.8	431, 413	1.98	1.975	0.3
221	3.35	3.36	10.0	333, 511	1.932	1.94	1.0
311	3.04	3.04	2.0	432, 423, 250	1.87	1.87	1.5
230	2.79	2.79	7.0	512, 521	1.838	1.84	0.8
321, 312	2.70	2.69	6.0	441, 522	1.76	1.754	1.2
400	2.53	2.52	2.0	442, 600	1.67	1.68	1.5
322, 410	2.44	2.44	1.0	611, 532, 523	1.635	1.635	4.0
411	2.38	2.375	6.0	621, 612 504, 443	1.58	1.574	1.3
420, 402	2.25	2.25	2.0	541, 514	1.56	1.555	1.0

The Bromine Parameters

A systematic determination of the bromine parameters did not seem practicable; consequently values were sought by trial. Since the usefulness of a result obtained in this way depends solely on its adequacy to account for experimental material, we shall confine ourselves largely to a discussion of the results finally obtained. It may be said, however, that the trials were made without reference to consideration of interatomic distance. The general course pursued was to neglect the effect of the carbon and hydrogen atoms and to find a set of parameter values which would make the structure factor S for the sixth order for (100) greater than that for the fourth, and that for the fourth greater than that for the second. Many sets of values satisfying these conditions were, of course, found which did not then satisfy the conditions imposed by the (111) reflections, namely, that the fifth order should be greater than the fourth and both of these much greater than the first, second and third. Use was also made of the observation from a (100) spectral photograph that (411) is stronger than (311) and (211) all in the first order. Further elimination and refinement of the parameter values was then made with the Laue data. It is interesting that when the values had been sufficiently refined to account for a small portion of the Laue data, considerably more data were then accounted for without the necessity of further change. The values finally obtained[6] are $x = 0.39$; $y = 0.22$; $z = 0.085$.

In Table I are included values of the structure factor S_{Br} for the bromine atoms alone computed with the above parameters. Except in the case of

[6] An equivalent set of parameters is $x = -0.11$, $y = 0.28$, $z = -0.085$, which gives directly the coördinates of an atom nearest the origin.

the first order from (111), the agreement with the observations is good; neglect of the carbon atoms is most likely to cause error in such cases of weak reflections with large values of d/n.

In the Laue data of Table II are included only reflections from planes with interplanar distances down to 0.90 Å.; below this the assignment of indices became somewhat uncertain. Intensities have been estimated at three different wave lengths by short interpolations, when necessary, on plots of intensity against wave length. Whenever, at a given wave length, a plane reflects more strongly than one with a larger interplanar distance, it is found to have the larger structure factor. This agreement affords an extensive test of the parameter values.

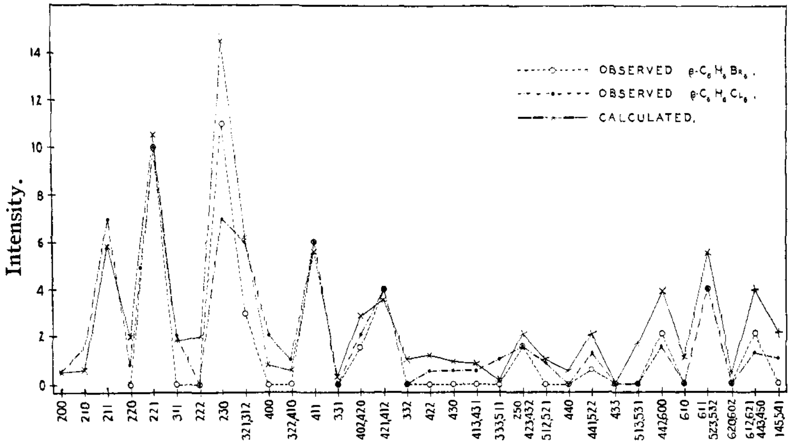

Fig. 1.—Observed powder photographic intensities from $C_6H_6Cl_6$ and $C_6H_6Br_6$ and intensities calculated for the halogen alone.

Comparison of the Laue data for benzene hexachloride with that for benzene hexabromide shows for the most part a parallelism in the intensities even for complicated reflections. From this it seems that the halogen parameters cannot be more than slightly different in the two compounds.

In Fig. 1 is given a graphical representation of the observed powder photographic intensities together with a set of calculated intensities whose relative values were obtained from the empirical[7] formula $I \propto S^2(d/n)^{2.35}$, using for the structure factors S the values obtained for the halogen alone, placing as before, $x = 0.39$, $y = 0.22$ and $z = 0.085$. Since the powder data include many reflections not employed in obtaining the parameters, the general correspondence between the observed and calculated values gives considerable confirmation of the approximate correctness of the parameter values.

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[7] Wyckoff, "The Structure of Crystals," Chemical Catalog Company, New York, 1924, pp. 99–107, 199–201.

Discussion of the Structure

The parameter values given are such that each bromine atom is surrounded by eight others; two of these are at a distance of 3.40 Å., while the other six are at distances of 3.74 to 3.97 Å. These latter distances, at least, appear reasonable when compared with 4.21 Å., the distance[8] between iodine atoms in stannic iodide and in cadmium iodide. Again, the distance between bromine atoms in lithium bromide is 3.88 Å.

Since there are four $C_6H_6X_6$ molecules in the unit of structure, their centers must be at points equivalent to (0,0,0) or at points equivalent to $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$. The arrangement of the six bromine atoms nearest to (0,0,0) is shown in Fig. 2a. That of the six nearest to $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ is shown in Fig. 2b; the latter form approximately a regular octahedron. But more information than the parameter values of the halogen atoms alone is needed to enable us to decide which of these two configurations represents the six bromine atoms belonging to a single molecule. Stereochemical considerations decidedly favor considering the group shown in Fig. 2a as belonging to a single molecule. If a cyclohexane ring be constructed of carbon atoms 1.54 Å. apart (the distance between carbon atoms in diamond) and with the lines connecting the center of one atom to the centers of the adjacent two making the angle 109° 28′ (the tetrahedral angle), we may inquire whether it is possible to orient such a ring in either of the bromine configurations in such a way that a bromine atom will lie in a third tetrahedral direction from each carbon atom. With the configuration of Fig. 2b this cannot be accomplished even approximately; but if the cyclohexane ring be placed with its center at (0,0,0) in the manner shown in Fig. 2c, the bromine atoms fall very closely in tetrahedral directions from the carbon atoms. Moreover, their distance from the carbon atoms, 1.94 Å., appears to be a reasonable one.[9]

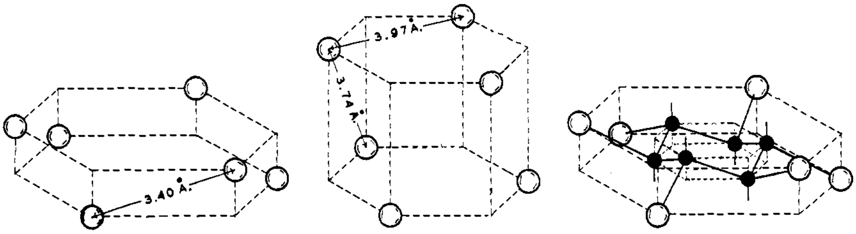

Fig. 2a. Fig. 2b. Fig. 2c.

Fig. 2.—(a) Arrangement of bromine atoms about (000); (b) arrangement of bromine atoms about $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$; (c) suggested arrangement of carbon and bromine atoms in the $C_6H_6Br_6$ molecule.

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[8] The various interatomic distances used here have been computed from data from the International Critical Tables, Vol. I, 340 ff.

[9] Some idea of what should be a reasonable C-Br distance may be obtained from the

A consequence of the conclusion that a molecule center is at (0,0,0) is that the shortest Br to Br distance, 3.40 Å., occurs within a single molecule, while the other distances of from 3.74 to 3.97 Å. are between bromine atoms of separate molecules.

The calculated carbon parameters corresponding to this arrangement are $x = -0.076$, $y = +0.099$, and $z = -0.065$ for the bromide, and $x = -0.079$, $y = +0.103$, and $z = -0.068$ for the chloride. In the last column of Table II are given structure factors for the chloride calculated using these parameters for carbon, placing the reflecting power of carbon one-fourth of that for chlorine and using the same parameters for chlorine as found for bromine. The effect of introducing the carbon atoms is in most cases small, but a few cases may be seen where it is important; the agreement with the observations is, on the whole, somewhat improved. The x-ray data appear, then, to be compatible with a molecular model involving the usual cyclohexane ring.

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Summary

New x-ray data from spectral and Laue photographs of benzene hexabromide and from Laue and powder photographs of benzene hexachloride are presented. It is shown that by assigning to the bromine atoms the parameter values $x = 0.39$, $y = 0.22$, and $z = 0.085$ in the general positions of T_h^6, the data for benzene hexabromide are qualitatively accounted for in a satisfactory manner. The intensity data for the chloride are very similar to, but not always identical with, those for the bromide. It is pointed out that these parameter values lead to reasonable interatomic distances and are in agreement with a molecule containing a cyclohexane ring of "tetrahedral" carbon atoms.

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following computation. In SnI_4 the distance Sn to I is 2.63 Å. The difference between the radii of tin and carbon may be taken from the structures of gray tin and diamond. In the former the distance Sn to Sn is 2.80 Å.; in the latter the distance C to C is 1.54 Å. whence we obtain $r_{Sn} - r_C = \frac{1}{2}(2.80 - 1.54) = 0.63$. The difference between the radii of iodine and bromine may be taken from the structures of the cuprous halides in which the copper is surrounded tetrahedrally by halogens. The distance Cu to I is 2.63 Å. and the distance Cu to Br is 2.49 Å.; whence $r_I - r_{Br} = 2.63 - 2.49 = 0.14$, and finally the estimate of the distance C to Br becomes $2.63 - 0.63 - 0.14 = 1.86$ Å.