ion at these high dilutions is to be attributed to the reaction

$$Ag^+ + SO_4^= \rightleftharpoons AgSO_4^-$$

which results in a decrease of the silver ion activity, an increase in the solubility of silver iodide, and an asymmetric location of the equivalence point; *i. e.*, the equivalence point no longer corresponds exactly to the maximum value of $\Delta E/\Delta V$.

We have also found that the titration can be carried out with the same degree of accuracy in dilute potassium bicarbonate medium (pH about 8.3) as in dilute nitric acid.

The titration may be simplified and made more convenient by simply titrating to the equivalence potential instead of recording the data of the entire titration curve.[3] The average value of the equivalence potential found was +0.097 ± 0.005 v. against the saturated calomel electrode, as shown by the data of Table II. This value is in excellent agreement with that found in the titration of ordinary amounts of silver.[1] We have found that the value of the equivalence potential is practically the same (within ±5 mv.) in dilute potassium bicarbonate medium as in dilute nitric acid, and it is evident from Table II that it is also practically independent of temperature, and the presence of large amounts of barium nitrate. Titrations to the equivalence potential gave identically the same results as by the ordinary method, and are more convenient because the constant attention of the operator is not required.

It is evident from these results that this titration should be a valuable analytical method of investigating the solubility and activity relations of slightly soluble silver salts. We are using the method in a study of the activity of silver chloride and silver iodate in various salt solutions. Obviously the method could also be applied to the determination of very small amounts of iodide by adding an excess of silver nitrate solution to the unknown iodide solution and back-titrating the excess silver.

Acknowledgment.—We wish to express our appreciation to the Graduate School of the University of Minnesota for financial assistance in this work.

Summary

1. The accuracy of the potentiometric iodide–silver titration at extreme dilutions has been investigated. Using a 500-ml. sample, a 10^{-5} N silver solution can be titrated with an accuracy of ±0.2%, a 10^{-6} N solution with an accuracy of 1–2% and a 5×10^{-7} N solution with an accuracy of about 3% at room temperature. Large amounts of barium nitrate have no influence on the results, but a large positive error was found in the presence of high concentrations of sulfate ions.

2. The titration is recommended as an analytical tool in investigations of the solubility and activity relations of slightly soluble silver salts.

MINNEAPOLIS, MINN. RECEIVED SEPTEMBER 28, 1936

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[3] I. M. Kolthoff, *Rec. trav. chim.*, **47**, 397 (1928); I. M. Kolthoff and J. J. Lingane, THIS JOURNAL, **57**, 2126 (1935).

[CONTRIBUTION FROM THE EASTMAN LABORATORY OF PHYSICS AND CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

The Structure of Crystalline Bromine

BY B. VONNEGUT AND B. E. WARREN

Introduction

There is very little crystallographic information available concerning crystalline bromine. The material melts at −7.3° and single crystals are readily obtained from the vapor. It would be expected that the crystalline structure of bromine should be very similar to that of orthorhombic iodine.[1] This has turned out to be the case, and the structure analysis has been considerably simplified by making comparison with the known structure of iodine.

Experimental

Bromine crystals were formed from the vapor on the surface of a round-bottomed flask filled with dry ice and placed over the mouth of a beaker containing liquid bromine. The crystals showed a pronounced elongation along the direction of the c-axis, and were thus readily oriented for rotation and oscillation patterns about c. They were mounted by being placed upon a smooth surface of dry ice, and cemented to a fine glass rod with a soft vaseline which froze upon cooling. The crystal was maintained at about −150°

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[1] Harris, Mack and Blake, THIS JOURNAL, **50**, 1583 (1928).

during the exposure by being placed in the exhaust stream from a liquid air container. Since the crystal is bathed completely in a stream of dry cold air, there is no trouble from water vapor freezing out upon the crystal. The vapor pressure of the bromine crystal was sufficiently reduced by the cooling, so that a single crystal would last through a twelve-hour oscillation exposure. The experimental arrangement is shown schematically in Fig. 1.

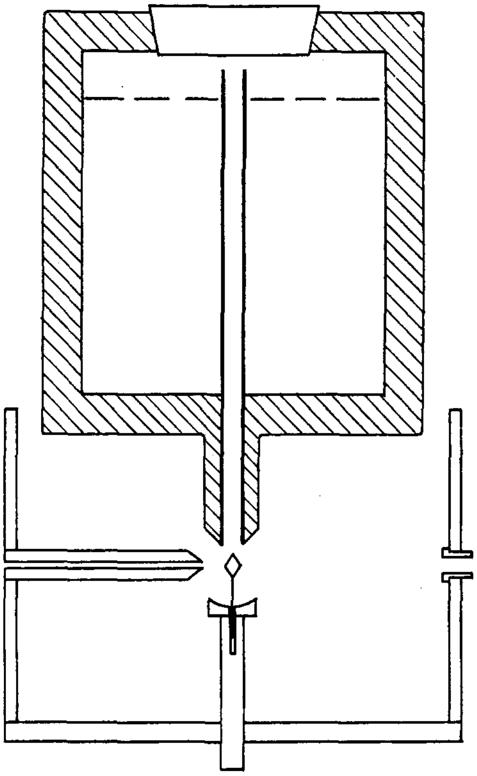

Fig. 1.—Method for producing low temperature x-ray diffraction patterns of bromine by placing crystal in liquid air exhaust.

Three 38° oscillation photographs were made in a cylindrical camera of radius 8.61 cm. The radiation used was Mo Kα with 0.30 mm. aluminum sheet in front of the film to reduce the blackening by fluorescent bromine radiation.

Unit Cell and Space Group.—From the layer line separations on the three oscillation patterns, the length of the c-axis was determined directly as 8.72 Å. By assuming that the axes of bromine would all stand in about the same ratio to the corresponding axes in iodine, tentative values of a and b were obtained which allowed a satisfactory indexing of all the spots on the oscillation patterns. Final values of the axes were then calculated from $h00$ and $0k0$ reflections; a = 4.48 Å., b = 6.67 Å.

All reflections hkl were missing except for $h + k$ = even. In addition, the reflections $0kl$ and $hk0$ were missing except for even indices. These vanishings are consistent with the space group *Ccma* (V_h^{18}) which is the space group found previously for orthorhombic iodine.[1]

Since the isomorphism of the bromine and iodine structures is completely established by the intensity comparisons which are given below, one can assume 8 atoms per unit cell as in iodine and calculate the density of bromine at about −150°.

$$\rho = \frac{8 \times 79.9}{0.606 \times 8.72 \times 6.67 \times 4.48} = 4.05$$

This is in satisfactory agreement with most of the values given in the literature; 4.107 (−194°),[2] 4.13 (−253°).[3] The value 3.4 for the density of crystalline bromine given in the "International Critical Tables" is much too low.

Atomic Arrangement.—The eight atoms in the bromine unit cell are in the 8-fold position f of V_h^{18}. The coördinates are

$$\begin{array}{llll} x,0,z & \bar{x},0,\bar{z} & x,\tfrac{1}{2},\tfrac{1}{2}-z & \bar{x},\tfrac{1}{2},\tfrac{1}{2}+z \\ \tfrac{1}{2}+x,\tfrac{1}{2},z & \tfrac{1}{2}-x,\tfrac{1}{2},\bar{z} & \tfrac{1}{2}+x,0,\tfrac{1}{2}-z & \tfrac{1}{2}-x,0,\tfrac{1}{2}+z \end{array}$$

Structure factors were calculated for several values of the parameters x and z. The best general agreement between calculated and observed intensities was given for the values x = 0.135, z = 0.110.

The intensities of the spots on the oscillation patterns are given roughly by the relation[4]

$$I \alpha F^2/\xi$$

No attempt was made to apply any correction for temperature motion or absorption in the crystal. By looking for close agreement only among spots in the same row line, the neglect of these factors is not serious. Table I gives a comparison of values of $F/\xi^{1/2}$ calculated for x = 0.135, z = 0.110 and the visually estimated intensities of the spots. The agreement is sufficiently good to substantiate the proposed structure. No serious attempt was made to deduce precise values of the parameters x and z as the absorption in the sample was large, and only low order reflections were present on the oscillation patterns.

Discussion of Structure.—The resulting structure for bromine is shown in Fig. 2, projected on

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[2] Sapper and Biltz, *Z. anorg. Chem.*, **198**, 184 (1931).

[3] W. Heuse, *Z. physik. Chem.*, **A147**, 273 (1930).

[4] ξ is a coördinate in the reciprocal lattice; J. D. Bernal, *Proc. Roy. Soc.* (London), **A113**, 117 (1926).

TABLE I

COMPARISON OF CALCULATED AND OBSERVED INTENSITIES

hkl	Obsd.	$F/\xi^{1/2}$	*hkl*	Obsd.	$F/\xi^{1/2}$	*hkl*	Obsd.	$F/\xi^{1/2}$
200	abs	67	020	vs	780	242	abs	8
201	m	344	022	vw	142	243	m	306
202	abs	13	024	s	640	244	abs	39
203	ms	457	220	abs	59	440	m	252
204	abs	56	221	ms	305	441	abs	40
400	ms	310	222	abs	11	442	abs	45
401	abs	46	223	ms	405	443	abs	53
402	abs	55	224	abs	50	444	w	226
403	abs	64	420	m	272	151	vw	178
404	m	277	421	abs	43	152	m	250
111	s	407	422	abs	51	153	abs	105
112	vs	556	423	abs	59	154	abs	91
113	wm	236	424	m	252	060	m	300
114	w	175	131	w	266	062	abs	54
311	ms	249	132	m	370	064	m	270
312	m	212	133	abs	156	260	abs	33
313	wm	148	134	abs	135	261	w	172
314	abs	78	040	s	680	262	abs	6
511	abs	87	042	abs	79	263	w	236
512	m	212	044	ms	380	264	abs	27
513	abs	54	240	abs	44	080	w	230
514	abs	78	241	m	230	082	abs	43

the 010 plane. Each atom has one nearest neighbor at a distance 2.27 Å., the other member of the Br_2 molecule. The x-ray crystal value of the Br–Br distance 2.27 Å. is to be compared with the band spectrum value[5] 2.28 Å. and the electron diffraction value[6] 2.28 Å. The close agreement is fortuitous as the x-ray value is probably uncertain by ±0.10 Å.

Each atom has three other close neighbors in the same reflection plane (plane of paper) at distances: 3.30, 3.30, 3.75. Eight more neighbors in the planes above and below are at slightly larger distances: 4.00, 4.00, 3.98, 4.10.

Crystalline bromine is definitely a molecular structure, the Br_2 molecule being easily recognized in the crystalline structure from consideration of the observed interatomic distances. The structure of orthorhombic bromine is isomorphous with that of iodine,[1] but apparently different from the structure of crystalline chlorine.[7] The structure of bromine forms one more example of the application of the 8-N law to the structures of the B sub-group elements in columns IV–VII.

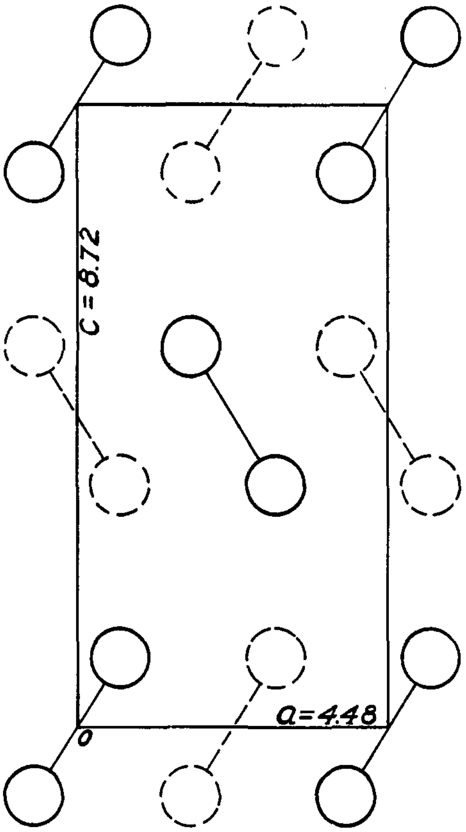

Fig. 2.—Structure of crystalline bromine projected upon the 010 plane. Full circles represent atoms in the plane of the paper, broken circles represent atoms above and below the plane of the paper by $b/2$. The Br_2 molecules are indicated by the connecting lines.

Summary

Oscillation patterns about the c-axis were made of a bromine crystal held at about −150°. The lattice is orthorhombic with axes: $a = 4.48$ Å., $b = 6.67$ Å., $c = 8.72$ Å. The 8 atoms are in the position $8f$ of the space group $Ccma$ (V_h^{18}), with $x = 0.135$ and $z = 0.110$. The structure is isomorphous with that of iodine, and shows a definite Br_2 molecule with Br–Br distance of 2.27 ± 0.10 Å. The x-ray density at about −150° is 4.05.

CAMBRIDGE, MASS. RECEIVED OCTOBER 15, 1936

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(5) L. Pauling and M. Huggins, *Z. Krist.*, **87**, 205 (1934).

(6) L. O. Brockway, *Rev. Modern Phys.*, **8**, 231 (1936).

(7) Keesom and Taconis, *Physica*, **3**, 237 (1936).