

I.

A STUDY OF THE ALLOTROPES OF SELENIUM

As a part of his oral examination as a candidate for the degree of Doctor of Philosophy, J. D. McCullough will defend the following propositions:

- I. Selenium and iodine form a compound having the formula Se_2I_2 .
- II. Dynamic allotropy in the various forms of solid selenium as suggested by G. Briegleb (Zeit. phys. Chem. A-144--321,340 (1929)) does not exist.
- III. Of the three known crystalline forms of elementary selenium, the hexagonal (metallic) form is the most stable at 25°C . Of the remaining forms, both of which are monoclinic, the alpha variety is the more stable at 25° .
- IV. The Allison Magneto-optic Method of Analysis is a reliable means of determining the number of isotopes of the positive constituent of ionic compounds.

ACKNOWLEDGMENTS

To Doctor Arnold O. Beckman I am indebted for suggesting the work on selenium. For his very able guidance throughout my work at the Institute, and for his friendship, I wish to express my deep appreciation. Professor Linus Pauling and Doctor James H. Sturdivant have been very kind in making their most excellent X-ray equipment available for identification work and for structure analysis. I am also greatly indebted to Professor William C. Morgan and other members of the Chemistry Staff at the University of California at Los Angeles for their kind cooperation in making my attendance at the Institute possible.

- I. A STUDY OF THE ALLOTROPES OF SELENIUM
- II. EVIDENCE FOR EXISTENCE OF A SELENIUM-IODINE COMPOUND
- III. AN ATTEMPT TO REPRODUCE THE ALLISON MAGNETO-OPTIC EFFECT
- IV. THE CRYSTAL STRUCTURE OF POTASSIUM
CHLOROSMATE AND POTASSIUM BROMOSMATE

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A THESIS

By

James Douglas McCullough

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IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR
THE DEGREE OF DOCTOR OF PHILOSOPHY,

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CALIFORNIA INSTITUTE OF TECHNOLOGY

Pasadena, California

1936

ABSTRACT

I.

A new vacuum-vaporization method for determination of transition temperatures, due to Dr. A. O. Beckman, has been tested and proven to be all right by means of the mercuric iodide transition at 127°.

This method shows an apparent transition between a red micro-crystalline form of selenium and the hexagonal form at a temperature of 74-75°C.

The relative stability of the three crystalline forms of selenium at 25° has been definitely established as:

- (1.) hexagonal selenium (most stable),
- (2.) α - monoclinic selenium,
- (3.) β - monoclinic selenium (least stable).

II.

Evidence quoted in the literature which supposedly disproves compound formation between iodine and selenium in no case prohibits the possibility of a highly dissociated compound.

Absorption spectra were photographed which give strong evidence favoring a selenium-iodine compound in solution.

Quantitative measurements on the equilibrium between selenium and iodine in ethylene bromide and carbon tetrachloride indicate a compound of formula Se_2I_2 , and possibly SeI_4 also.

III.

The Magneto-optic Apparatus was set up according to the directions given by Allison in his numerous publications. The broad minima attributed to the solvent could be located as described, but no minima of the sharp type due to isotopes of the positive ions were observed.

IV.

With the aid of Laue and oscillation photographs, potassium chlorosmate and potassium bromosmate have been shown to have the ammonium chloroplatinate structure. The edge of the unit cube was found to be $9.729 \pm 0.02 \text{ \AA}$ for potassium chlorosmate and $10.30 \pm 0.03 \text{ \AA}$ for potassium bromosmate. The halogen parameters were found to be 0.243 ± 0.002 and 0.244 ± 0.001 respectively. These values give an osmium-chlorine separation of $2.36 \pm 0.02 \text{ \AA}$ and an osmium-bromine separation of $2.51 \pm 0.01 \text{ \AA}$ in the complexes. Subtracting the normal electron-pair bond radius for the halogen in each case, the octahedral electron-pair bond radius for quadrivalent osmium is found to be $1.37 \pm 0.02 \text{ \AA}$ in K_2OsCl_6 and $1.37 \pm 0.01 \text{ \AA}$ in K_2OsBr_6 .

INTRODUCTION

The principal objective of this study has been an attempt to determine such transition temperatures as exist among the three known crystalline forms of elementary selenium. The main portion of the work involved the use of a new method for determining solid-solid transition temperatures due to Dr. A. O. Beckman of this Institute.

The selenium allotropes have been the subject of considerable discussion since the discovery of the element. The range of stability of the various modifications and their relationship to each other have not been well known. The crystalline forms of the element so far established are:

(1) Hexagonal Selenium, the so-called metallic variety. Grey metallic luster, not soluble to any appreciable extent in solvents which dissolve other forms of the element.

Density 4.86

Lattice Constants⁽¹⁾

$$a = 4.34\text{\AA}; c = 4.95\text{\AA}$$

(2) Alpha Monoclinic Selenium, dark red in color, semi-metallic luster.

Density 4.46

Lattice Constants⁽²⁾ (for 32 atom cell)

$$a = 8.992\text{\AA}; b = 8.973\text{\AA}; c = 11.52\text{\AA}$$

$$\beta = 91^{\circ} 34'$$

(3) Beta Monoclinic Selenium, also red in color. First identified by Muthmann⁽³⁾ by optical methods.

2.

Density⁽²⁾ 4.42Lattice Constants⁽²⁾ (for 32 atom cell)

$$a = 12.74\text{\AA}; b = 8.04\text{\AA}; c = 9.25\text{\AA}$$

$$\beta = 93^{\circ} 4'$$

The alpha and beta forms are both moderately soluble in methylene iodide and carbon bisulfide, yielding red-amber colored solutions.

Some investigators⁽⁴⁾ have failed to recognize the existence of two monoclinic forms of selenium. During the present study crystals of both monoclinic forms were obtained. Klug⁽²⁾ made use of these crystals in his x-ray study of selenium and was able to prove the existence of two distinct varieties. The usual habit of these crystals is in the form of pseudo-hexagonal plates, which are practically impossible to identify by means of the petrographic microscope. The angles (100) : (110) are $57^{\circ} 46'$ and $57^{\circ} 59'$ respectively for the alpha and beta varieties.

It is likely that the workers who have not been aware of the existence of the beta form have worked with mixtures of the alpha and beta modifications. The errors due to this oversight, however, may not be serious due to the fact that most preparations of monoclinic selenium are nearly pure alpha and because of the similarities of the two forms. X-ray examination of several preparations made in this laboratory by evaporation of solutions of the element in carbon bisulfide and by modifications of the continuous method described by Halla Bosch and Mehl⁽⁵⁾ show only lines due to the alpha modification, the positions for the strong-

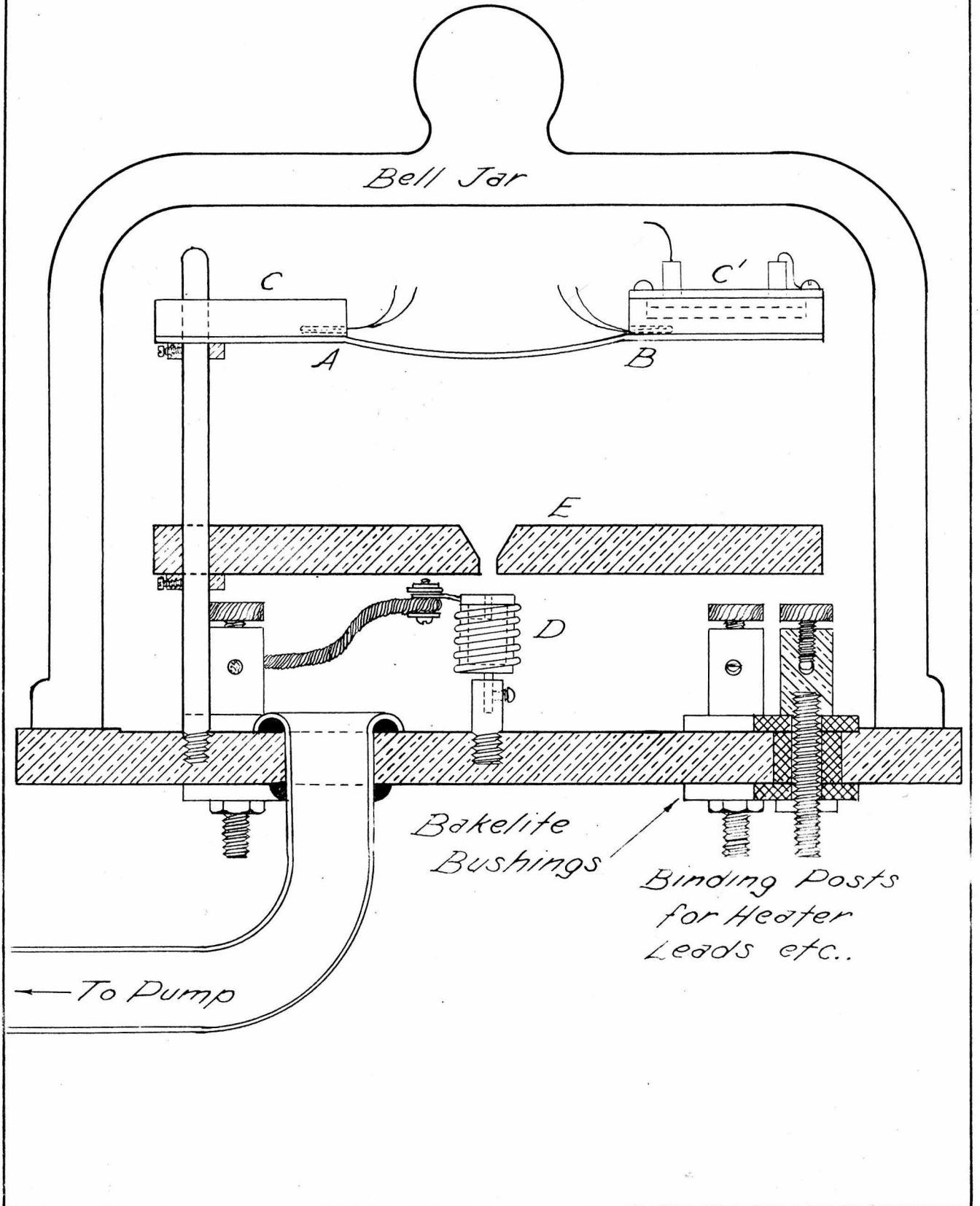
est reflections from the beta form being blank.

DESCRIPTION OF METHOD AND APPARATUS

The new method for determining solid-solid transition temperatures consists of the slow vaporization of the substance under investigation in a vacuum and its subsequent deposition on a surface of known temperature. This surface usually consists of a brass bar heated at one end, so that a range of temperature is covered at a single run. One form of the apparatus is shown in Figure 1. The material to be vaporized is placed in the graphite crucible D which is surrounded by a chromel or tungsten wire heater. The bar C - C' receives the deposit. C' is a hollow copper block which contains a heating element and a thermocouple well at B. The copper block C is not heated but has a thermocouple well at A. When the temperature of the block C' is maintained at 75°, the block C reaches equilibrium at about 55°. The heavy brass shield E serves to protect the bar from heat radiated from the crucible heater. The pressure in the bell jar is not measured accurately but is tested from time to time by applying a potential of about 25 K. V. to a spark gap of about 10 centimeters length in the vacuum. The vacuum was maintained sufficiently good to prevent a glow across the gap.

The thermocouples were Chromel X-Copel junctions and were calibrated at 0°, 99.4° and 217.0° in melting ice, condensing steam and condensing naphthalene respectively.

VACUUM VAPORIZATION APPARATUS

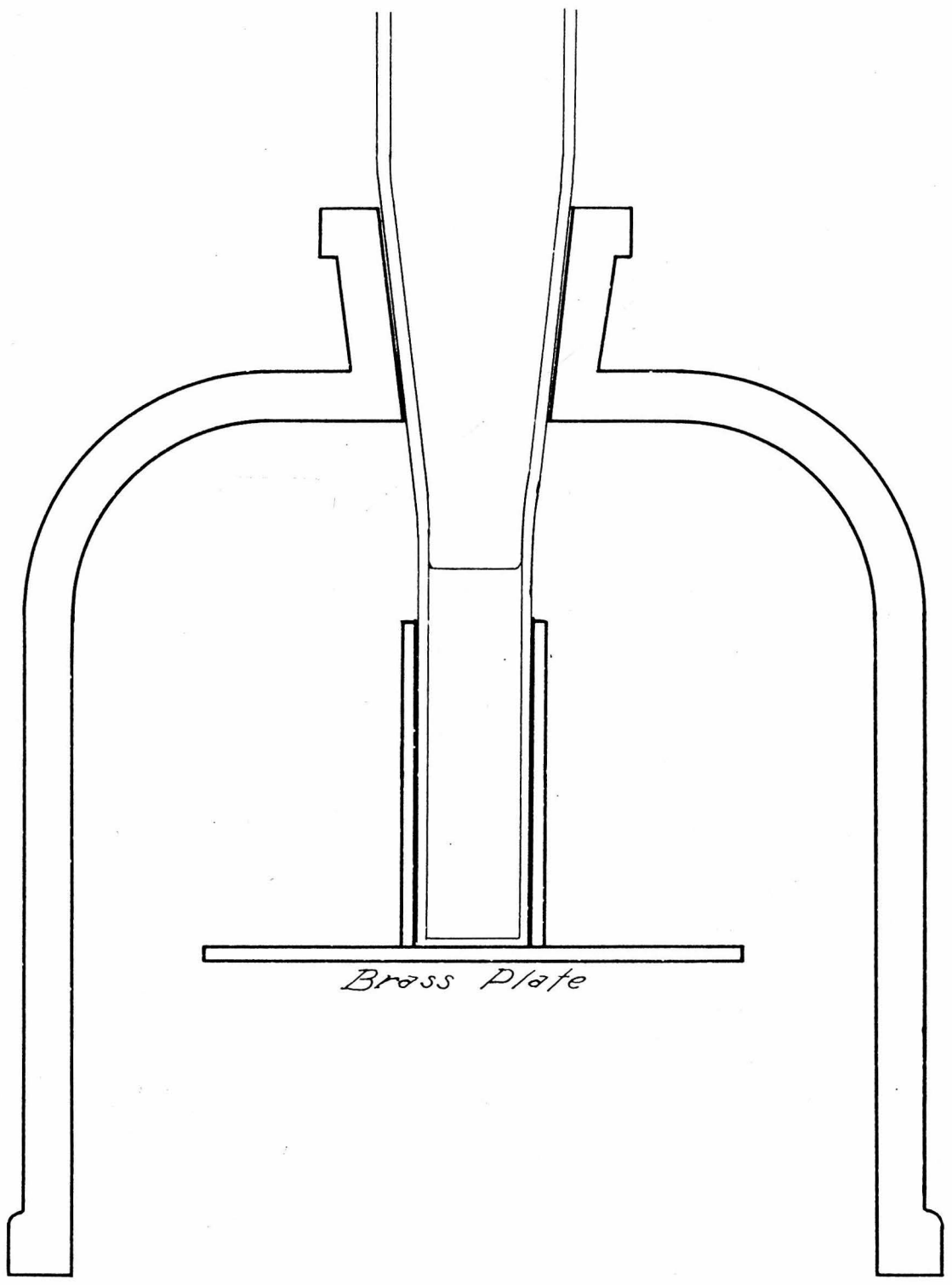


The method is not confined to work above room temperature but by use of liquid air, solid carbon dioxide, etc. on one end of the bar, the range below room temperature may be investigated. In order to facilitate working at low temperatures a modified form of apparatus was made, the diagram of which is shown in Figure 2. The inner tube, A, is of pyrex which is fitted into the bell jar by means of a ground glass joint. The deposit is received in this case on a brass plate, P, soldered to the end of a snug fitting brass tube, B.

EXPERIMENTAL TEST OF THE METHOD

In order to test the method, the transition between the red (tetragonal) and yellow (orthorhombic) forms of HgI_2 was checked. Since the vapor pressure of HgI_2 at the transition temperature ($127-128^\circ$) is about 0.1 mm. it was necessary to modify the usual procedure. The bell jar was evacuated as usual, then the stop-cock to the pumps was closed. The vaporization was then started by very gradually heating the crucible. In order to protect the brass bar from the corrosive action of HgI_2 at the high temperature, it was given a very thin coating of Duco Cement thinned with ethyl acetate. A heavy coating is to be avoided since it would hinder the transfer of heat from the condensing vapor to the bar. The necessity of good heat transfer is borne out by the fact that red HgI_2 deposits on metals at

BELL JAR FOR USE AT LOW TEMPERATURES



Brass Plate

room temperature while the yellow form appears on glass at this same temperature, the red form being stable. A gold plated block has also been used in order to secure freedom from corrosion, and yet have a good conducting surface.

Several test runs were made using HgI_2 . In one run the temperature of the warmer end of the bar was 129° , while the other end took a temperature of 103° . The transition occurred at a place 1-2 mm. from the warmer block, the length of the bar being 58 mm. On the assumption of a uniform temperature gradient this gives a transition temperature of $128-128.5^\circ\text{C}$. Using the form of the apparatus shown in Figure 2, iso-amyl alcohol was boiled in the glass tube, A, by means of an electric heater, the top of the tube being equipped with a reflux condenser. A thermometer dipping in the boiling liquid showed a temperature of 129° . The yellow form of HgI_2 deposited inside a circle at the center of the block where it was fastened to the glass tube, while red crystals deposited outside this zone. This would indicate a transition just under 129° , the exact difference not being known since no means of measuring the temperature of the block directly was provided in this case.

PURIFICATION OF SELENIUM

The selenium used in this work was the so-called metallic powder obtained from the General Chemical Co. Since it was found to contain considerable non-volatile material, it was carefully purified in the following way.

The powder was dissolved in 6N HNO_3 , using no more of the acid than necessary. The resulting solution was filtered thru sintered glass, then evaporated to dryness. The SeO_2 was then sublimed and dissolved in 12N HCl . TeO_2 being much less volatile than SeO_2 is left behind in the sublimation. Selenium is precipitated from 12N HCl by SO_2 , while tellurium is not. The selenium is filtered out of the solution, washed and put thru the same process again. The product was then washed with water and alcohol and dried over CaCl_2 .

For use in the vaporization experiments some of the dried selenium was fused and then cooled down to 150° where it was kept for several hours. This treatment yields a product which is pure hexagonal selenium as shown by the x-ray diagram and its failure to dissolve in the common solvents. A sample of this product has been kept in a sealed tube with CS_2 for three years without a trace of color showing in the solvent.

VACUUM VAPORIZATION OF SELENIUM

Using the method already outlined, selenium was very slowly vaporized, the average time required was about two hours for 0.1-0.2 g. of selenium. The pressure was kept sufficiently low to prevent a glow across the spark gap when the potential was applied. The sound of the fore pump was a good means of telling whether the pressure was above or below the range in which a discharge would occur.

The results of these experiments are shown in Table I. Figure 3 is a photograph of the brass bar showing the deposit of selenium resulting in Experiment 5. A sharp line between two forms of the deposit shows at the left. The curvature of the line near the edge of the bar indicates that the effect is really due to temperature difference, since the edges of the bar would be expected to be cooler than the middle portion. The line at the right is a reflection from the curved surface of the bar. The transition temperature is indicated by these experiments to be between 74 and 75°.

In some cases there was a slight drift in the temperature of the bar during the deposition. Fluctuation in temperature was greatly reduced by using a separate storage battery for the heater circuit.

Attempts were made to narrow down this range by using a heavier bar with a correspondingly smaller temperature gradient, but this simply made the boundary less distinct with no resulting increase in accuracy.

The selenium which deposited in the region above 75° was grey in color and appeared metallic. X-ray powder photos showed it to be definitely of the hexagonal "metallic" variety. The deposit below 74° in each case was red and semi-transparent. It was birefringent when observed between crossed nicols on a petrographic microscope, but no X-ray diagram could be obtained under the same conditions where good photographs of the hexagonal variety resulted.

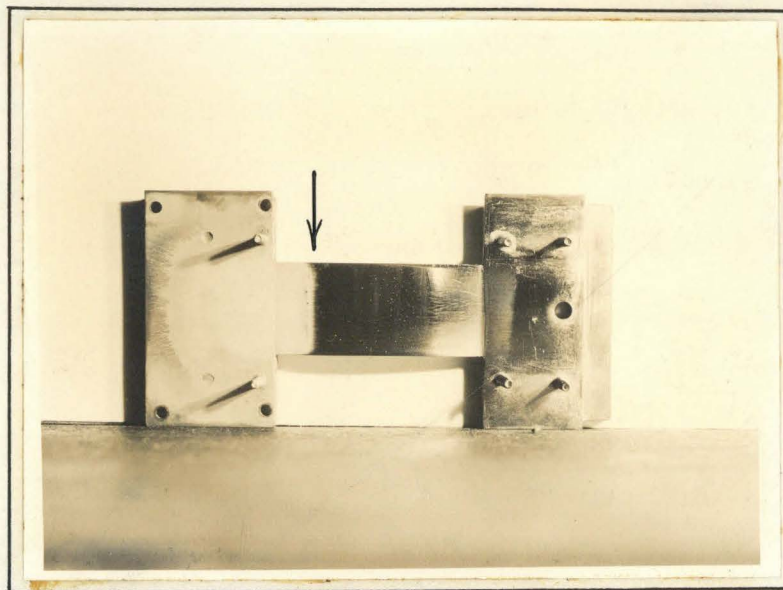


FIGURE 3

Photograph of bar showing deposit of selenium in Experiment 5. The arrow indicates the line along which the transition occurred.

TABLE I

Expt.	Temperature Warmer End °C	Temperature Cooler End °C	d mm.	Transition on Temperature °C
1	74	58	All Red	Above 74°
2	80 - 81	60 - 62	19	74 - 74.5
3	76	55	0 - 10	73 - 76
4	75 - 75.5	54	2	74.5 - 75
5	77.5	56	10	74
6	75	54	0	75
7*	76.5	55	5	74
8**	75	53	3	74

* Vitreous Selenium Vaporized.

** Monoclinic Selenium Vaporized.

Samples of this red form and the hexagonal form from the bar were placed in sealed glass tubes with some carbon bisulfide. The red form dissolved in sufficient quantity to impart a decided amber color to the liquid, while the hexagonal did not impart the slightest trace of color to it. These tubes were placed in a thermostat at 70° . The red form blackened after a few hours and after two days the solution became colorless. X-ray photographs showed that the selenium had been converted to the hexagonal form. The hexagonal selenium remained unchanged.

When the red deposit is allowed to stand in CS_2 at room temperature it changes in a few hours to the α -monoclinic form as shown by X-ray powder photos. Furthermore, when the α -monoclinic crystals are placed in quinoline or in a solution of iodine in CS_2 they are converted to the hexagonal variety, again this is proven by means of the X-ray photographs.

These facts indicate that the hexagonal crystals are more stable than the red deposit both at 70° and at room temperature, making it appear doubtful that the phenomenon observed at $74-75^{\circ}$ is actually a transition in the usual meaning of the term.

The phenomenon is apparently the same as the one observed by Goetz and Dodd⁽⁶⁾ in studying bismuth and selenium deposited on water cooled pyrex surfaces in a vacuum. They contend that there is a definite temperature below which the vapor will not deposit in macro-crystalline form,

but rather is micro-crystalline. They were unable to measure these temperatures with the apparatus used. The first thin layer deposited is micro-crystalline and acts as a poor conductor for the heat liberated by the condensing substance. This causes a gradual rise in the temperature of the surface upon which deposition takes place until the critical temperature is reached at which the macro-crystalline deposit starts. After removing from the glass surface, the two layers easily separate and show a different structure. They were not examined by means of X-rays.

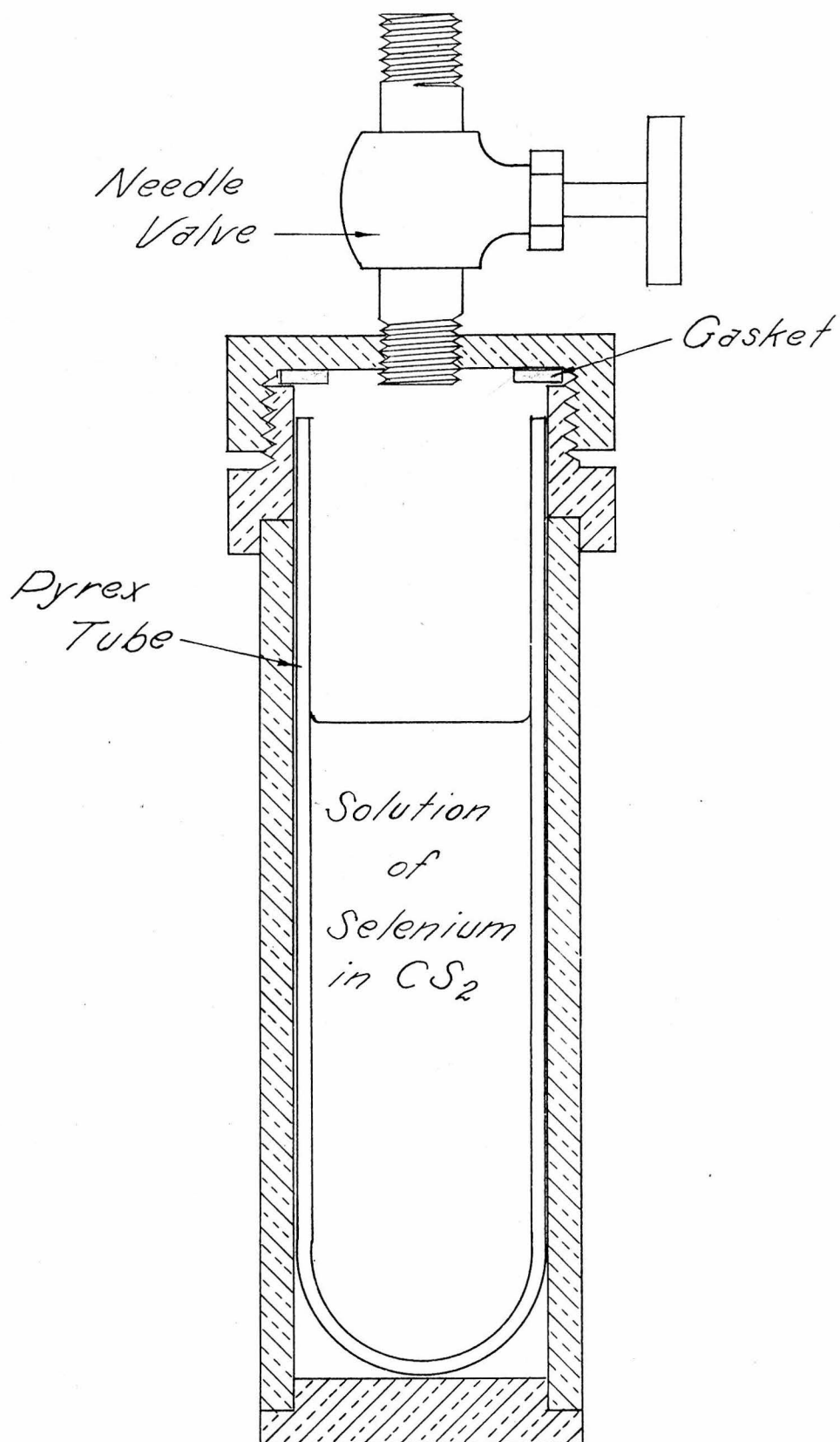
Kapitza⁽⁷⁾ found that bismuth would deposit from its vapor in a vacuum as a glassy amorphous layer at room temperature, but deposited as crystals at 200°C. The two forms were found to have different specific resistances but were not examined by means of X-rays.

The writer has found also that arsenic and antimony yield amorphous layers when deposited on a surface at room temperature in vacuo. X-ray powder photographs serve to prove the lack of a crystalline structure. Comparison samples were photographed simultaneously, using the crystalline elements. These gave the customary patterns.

CONSTANT TEMPERATURE CRYSTALLIZATION FROM SOLUTION

In another series of experiments, selenium was crystallized from solutions of the element in carbon bisulfide, at constant temperatures ranging from 25° up to 100° by allowing the solvent to slowly vaporize. The rate of evaporation was controlled by placing the solution in the container shown in Figure 4. A pyrex tube serves to hold the solution. This is placed inside the brass cylinder and the cap screwed in place. An asbestos filled copper gasket makes the joint gas tight. The needle valve permits adjustment of the rate of evaporation of the solvent, which may be condensed in order to check on this rate. About 50 cc of solution, saturated with amorphous selenium at room temperature was used in each vaporization which required from three to five days. The brass cylinder was placed in a thermostated oil bath during the crystallization.

In one respect these experiments checked the vacuum vaporization method, namely that hexagonal crystals were always obtained at temperatures above 75°. Below 72° red crystals were obtained which always showed the X-ray powder diagram for α -monoclinic selenium. Between 72° and 75°, the products varied somewhat. In one vaporization carried out at 74.5° a single red crystal appeared along with many smaller ones of the hexagonal variety. Because of the difference in appearance of this crystal from red crystals which had been obtained from CS₂ at room temperature, H. P. Klug became interested in it and succeeded in identifying it as the β variety by means of Laue and Oscillation photographs.

fig. 4

Later attempts to grow more β crystals at this and neighboring temperatures failed.

Powder photographs of the crystals obtained below 72° are identical to those obtained by photographing the powder resulting from grinding a single α crystal. The crystals obtained between 72° and 75° are mostly of the form, but the photographs show some of the principal lines of the hexagonal variety. Some of these photographs are shown in Figure 6.

DILATOMETRIC MEASUREMENTS

Crystals of α monoclinic selenium were prepared by a continuous method similar to that described by Halla, Bosch and Mehl⁽⁵⁾. X-ray photographs of the product show lines of the α variety only. Two grams of these crystals were placed in a dilatometer having a bulb volume of about 1 cc. and a capillary of about 0.5 mm. inside diameter. The capillary was provided with a millimeter scale. The liquid used in this case was dibutyl phthalate which has a slight solvent power on selenium.

From the density of the α crystals, 4.46, the volume of 2 grams would be 0.448 cc. The corresponding volume for the β variety is 0.453 cc. and for the hexagonal form 0.411 cc. This means an increase in volume of 0.005 cc. or a rise of 8 mm. of the liquid in the capillary for complete change to the β form. For complete transformation to the

hexagonal form there would be a decrease in volume of 0.037 cc. or a fall of 5 cm. in the meniscus.

When kept at 25° no change in the scale reading could be observed in two weeks. The temperature was raised by five degree intervals and kept constant at each step for two or three days. At 45° the scale reading decreased 0.03 cm. per day. At 70° the rate of fall became 0.13 cm. per day. Except for this gradual fall in scale reading, no irregularity occurred in the volume-temperature curve obtained. On going back to 25° there was no indication of a rise in the capillary, which at this time was 1.56 cm. lower than the 25° reading at the start. The above process was repeated with similar results. On standing at room temperature, the reading when placed in a 25° thermostat showed a decrease of 0.40 cm. from the 25° reading made a year earlier. This latter fact indicates the instability of α -monoclinic selenium at room temperature. An X-ray examination of the selenium after removal from the dilatometer showed both the hexagonal and the α -monoclinic phases to be present.

MISCELLANEOUS EXPERIMENTS

In order to better establish the stability relationships existing between the three crystalline forms of the element, a series of rather simple experiments was made. In all cases where statements are made regarding the modification being worked with or produced, this has been

definitely established by means of some kind of X-ray photograph. Examples of these photographs are shown in Figure 6. In addition, some crystals were further identified by making measurements on several interfacial angles by means of an optical goniometer.

(1.) Amorphous red selenium, the variety precipitated by means of sulfur dioxide or hydrazine in aqueous solution, was placed in quinoline at 25°. The red powder turned dark in a few hours, and after two days the transformation to the hexagonal form was complete. The resulting product showed no trace of color when placed in carbon bisulfide. This is in agreement with the work of A. P. Saunders⁽⁸⁾ who showed that the density of amorphous selenium increased to 4.8, the value for the hexagonal form, when placed in quinoline.

Saunders confined his experiments in quinoline to the amorphous form of the element. It was considered of interest to try the effect of that liquid on other forms of selenium. These effects were as follows: The red form of selenium obtained by the vacuum vaporization process changed in a few hours to the α modification, then more slowly to the hexagonal form. Fairly large α crystals which could be identified were the intermediate product. The α and β crystals undergo a slow change in quinoline to the hexagonal form. The change takes place in a few hours when the crystals are powdered first. Hexagonal selenium undergoes no change in three years. The effect of quinoline on selenium seems

to be due to its ability to open the Se_8 ring, allowing the atoms to arrange themselves in the more stable spirals.

(2.) When benzene is slowly added to a saturated solution of selenium in carbon bisulfide, small α -monoclinic crystals are precipitated. When acetone is used as the precipitating liquid, small, dark red needles result which were shown to be of the hexagonal variety.

(3.) β -monoclinic crystals will dissolve when placed at 25° or at 50° in a saturated solution of the α variety in carbon bisulfide containing excess of the solid. This experiment has been repeated several times with proven crystals. This is in keeping with the fact that β crystals are never found in products which are very slowly crystallized from solution, but only result in the comparatively rapid evaporation or cooling of saturated solutions of selenium in such solvents as carbon bisulfide or methylene iodide. The one exception to this already noted on page 11 may have been an accident brought about by the failure of any α nuclei to form. It has been found impractical to test the relative stability of the α and β crystals above 50° due to their great tendency to transform to the hexagonal form.

(4.) Various statements are found in the literature regarding the effect of light on selenium. Red amorphous selenium powder was placed in a quartz tube in direct sunlight on a warm, clear day. In half an hour the powder had sintered to a grey mass which proved to be hexagonal selenium. When

the tube was placed under water, still in the direct sunlight, the red powder remained unchanged for hours.

and α crystals have been kept for three years exposed to the light of the laboratory without change. Radiation from a quartz mercury arc also seems to be without effect. The effect of light seems, therefore, to be only that due to the heat produced.

(5.) Solutions of selenium in carbon bisulfide were sealed in pyrex tubes, both with and without hexagonal crystals. These tubes remained unchanged for three years at room temperature. On placing in an oven at 120° , the solution in contact with the crystals slowly deposits selenium, while the tubes containing no crystals showed no change in three days.

(6.) Crystals of α -monoclinic selenium will keep indefinitely at room temperature either alone or in contact with a saturated solution in carbon bisulfide. When held at 50° under either of the above conditions a slow change sets in and the crystals darken.

DISCUSSION

The present work has definitely established the relative stability of the various crystalline forms of selenium at 25°C . The hexagonal form is the most stable, with the α crystals next, the β crystals being least stable.

This is contrary to the belief of Saunders⁽⁸⁾ who placed the β crystals above the α form in stability.

The direct change of the hexagonal form to any other form of the element below its melting point (217°) has never been observed. By direct change here is meant any change which does not involve chemical combination.

The α and β crystals have never been obtained in any way other than from solution. Hexagonal crystals may be obtained from solutions under certain conditions, by slowly cooling molten selenium or by slow sublimation, provided the surface upon which deposition takes place is above 75°.

G. Briegleb⁽⁴⁾ postulated a dynamic equilibrium $\text{Se}_2 = 2\text{Se}$ in all solid forms of selenium. This is not in keeping with the known structure⁽⁹⁾ of hexagonal selenium which consists of infinite chains of selenium atoms in the form of spirals with a three-fold screw axis. Also, since both monoclinic forms of selenium contain 32 atoms in the unit cell,⁽²⁾ and since these crystals yield Se_8 molecules⁽¹⁰⁾ in solution, it is reasonable to believe that the monoclinic crystals are built up of Se_8 molecules. These molecules are probably of the same form as those found for S_8 in orthorhombic sulfur by Warren and Burwell⁽¹¹⁾ in which the atoms form an eight membered staggered ring in two parallel planes. Briegleb based most of his reasoning on the apparent molecular formula $\text{Se}_{1.33}$ to $\text{Se}_{1.88}$ found for selenium in molten iodine. These low values are probably due to compound forma-

tion as shown in Part II. of this thesis.

No satisfactory theory has been found which will explain the sharp line obtained between the red and hexagonal grey forms of selenium deposited on the brass bar in the vacuum vaporization experiments, other than that of a transition. That it is a transition in the ordinary sense seems improbable since the red deposit changes to the hexagonal form when placed in quinoline at room temperature or in carbon bisulfide at 70° . The effect is not due to the material from which the bar is made since the same results are obtained when it is given a thin coating of Duco cement. No reaction takes place between the selenium and the brass bar even at 100° as shown by the X-ray photographs of the deposit and by the fact that the brass maintains its shiny surface. If one considers the possibility of the selenium depositing in the red micro-crystalline form, followed by a change to the hexagonal form on that part of the bar where the temperature is above 75° , one would not expect a sharp line to result, but rather a more gradual change from the red to the grey form.

SUMMARY

A new vacuum-vaporization method for determination of transition temperatures, due to Dr. A. O. Beckman, has been tested and proven to be all right by means of the mercuric iodide transition at 127° .

This method shows an apparent transition between a red micro-crystalline form of selenium and the hexagonal form at a temperature of $74-75^{\circ}\text{C}$.

The relative stability of the three crystalline forms of selenium at 25° has been definitely established as:

- (1.) hexagonal selenium (most stable),
- (2.) α - monoclinic selenium,
- (3.) β - monoclinic selenium (least stable).

BIBLIOGRAPHY

- (1.) A. J. Bradley, *Phil. Mag.*, 48, 477, (1924).
- (2.) H. P. Klug, *Zeit. Krist.*, (A), 88, 128, (1934).
- (3.) Muthmann, *Ibid.*, 17, 353, (1890).
- (4.) E. Peterson, *Zeit. physik. Chem.*, 8, 601, (1891).
M. Coste, *Compt. Rend.*, 149, 674, (1909).
P. Mondain Monval, *Bull. Soc. Chim.*, 39, 1349, (1926).
G. Briegleb, *Zeit. physik. Chem.*, (A), 144, 321 and
340, (1929).
- (5.) Halla, Bosch and Mehl, *Ibid.*, (B), 11, 455, (1931).
- (6.) Goetz and Dodd, *Phys. Rev.*, 48, 165, (1935).
- (7.) P. Kapitza, *Proc. Roy. Soc.*, (A), 119, 428, (1928).
- (8.) A. P. Saunders, *Jour. Phys. Chem.*, 4, 423, (1900).
- (9.) R. W. G. Wyckoff, "Structure of Crystals", 2nd Edition.
- (10.) See references 1-5, Part II., This Thesis.
- (11.) Warren and Burwell, *J. Chem. Phys.*, 3, 6, (1935).

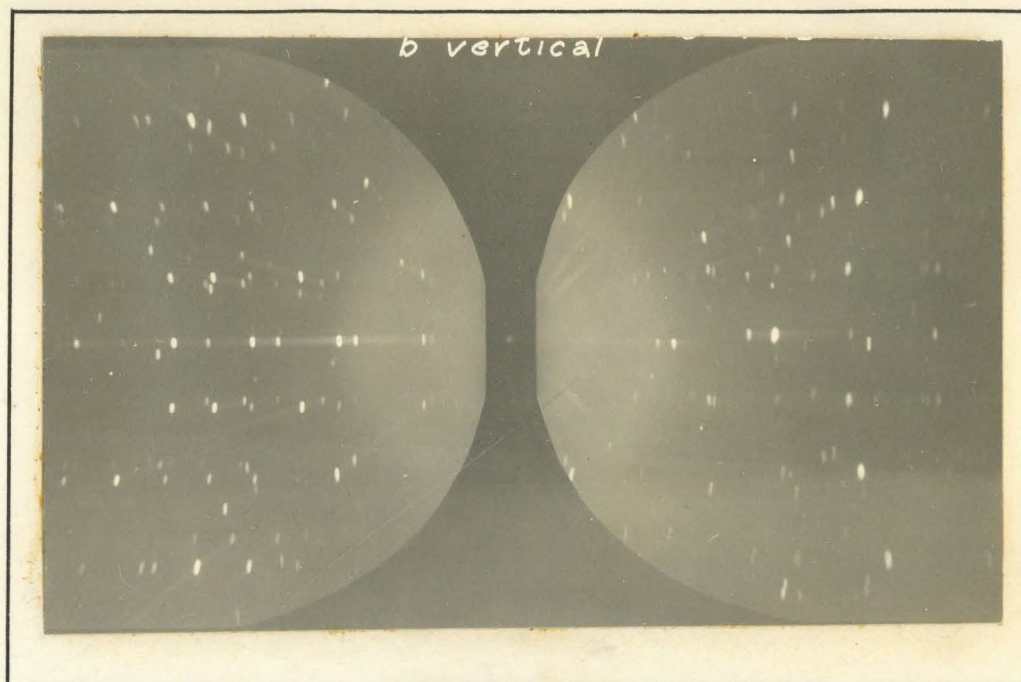


FIGURE 6a

Alpha Monoclinic Selenium

30° Oscillation photograph with unfiltered copper radiation glancing (001) of the 64 atom cell or (101) of the true 32 atom unit. A small crystal fragment is responsible for reflections which do not conform to the horizontal plane of symmetry which normally results for oscillations about the b axis.

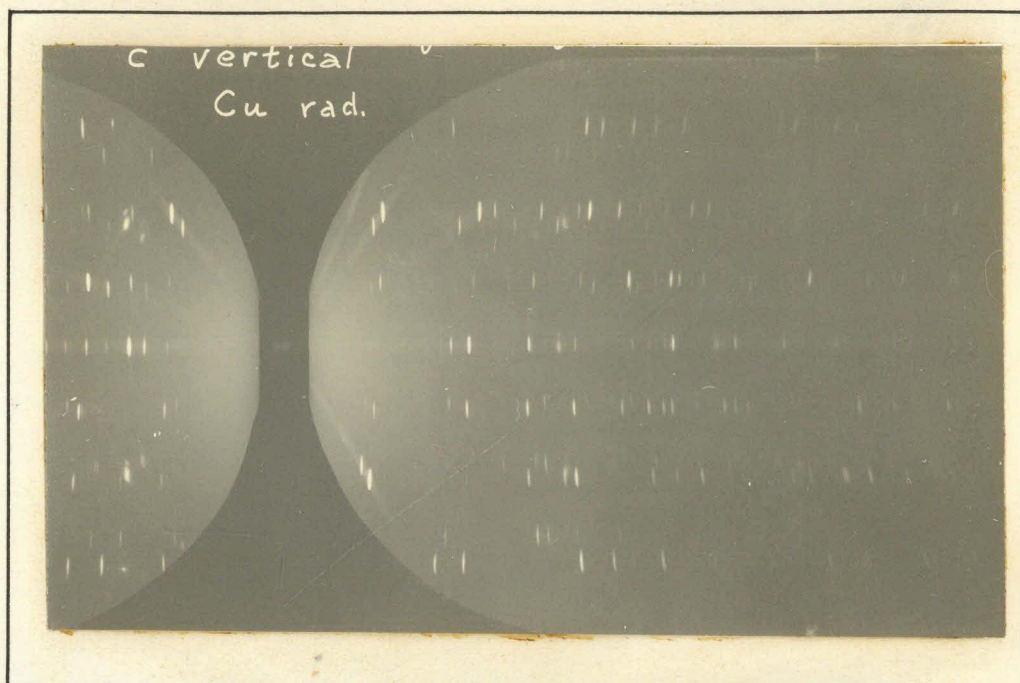


FIGURE 6b

Beta Monoclinic Selenium

30° Oscillation photograph with unfiltered copper radiation glancing (100) of the 32 atom unit. The oscillation was about the c axis which was placed vertically, hence no plane of symmetry.

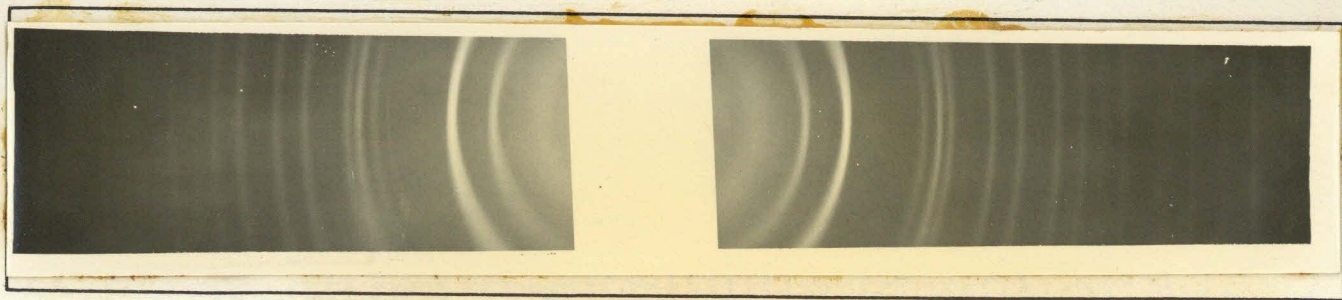


FIGURE 6c -- Powder photograph of hexagonal selenium deposited in vacuum on brass surface above 75°C.



FIGURE 6d -- Powder photograph of crystals (a mixture of α - monoclinic and hexagonal selenium) obtained by evaporation of a solution of selenium in carbon bisulfide at 74°C.



FIGURE 6e -- Powder photograph of α - monoclinic selenium, obtained from powder resulting from a single crystal.

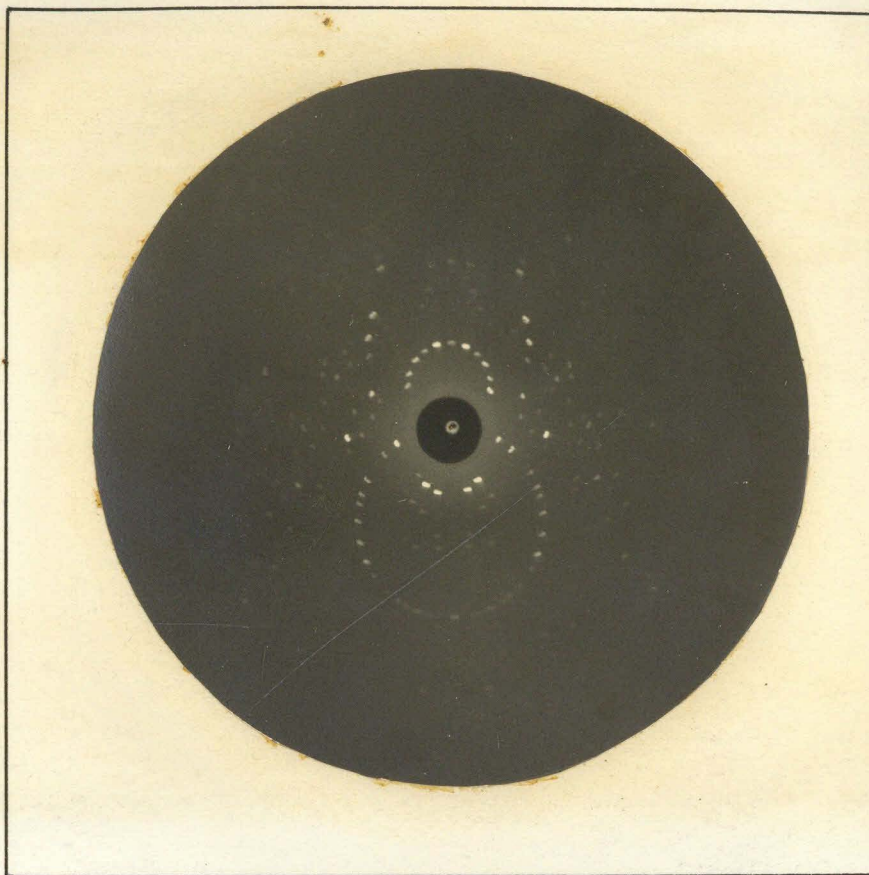


FIGURE 6f

Laue photograph of α - monoclinic selenium with X-ray beam normal to (101) of the 32 atom unit.

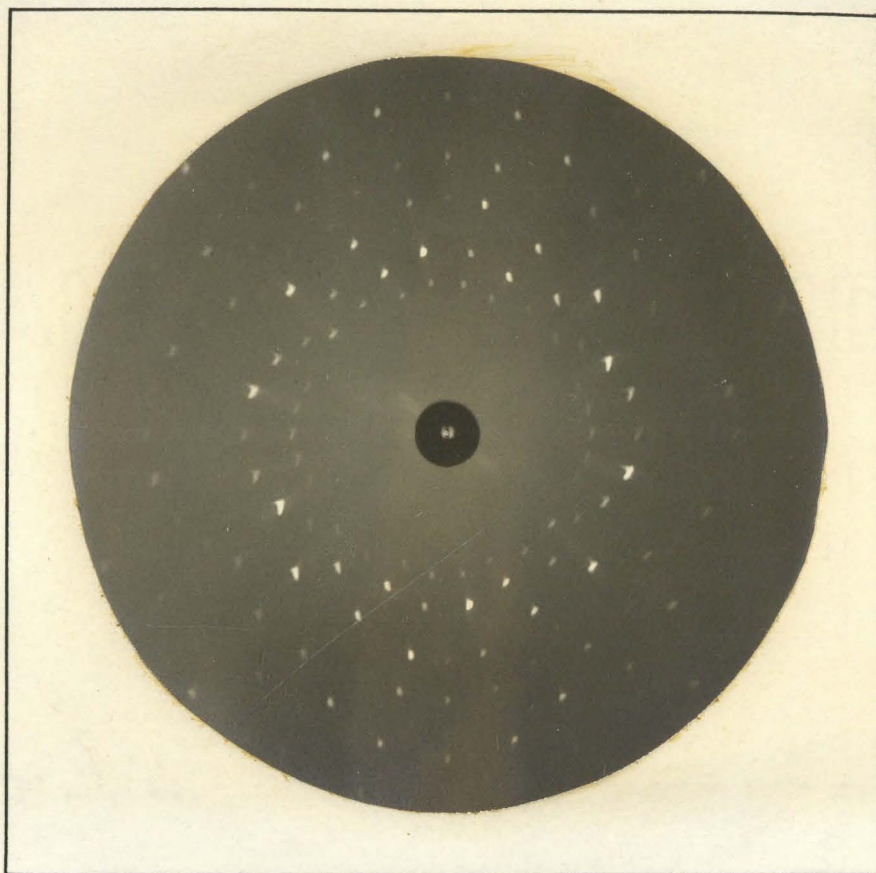


FIGURE 6g

Laue photograph of hexagonal
selenium with X-ray beam normal to $(10\cdot0)$.

II.

EVIDENCE FOR EXISTENCE OF A SELENIUM-IODINE COMPOUND

EVIDENCE FOR EXISTENCE OF A SELENIUM-IODINE COMPOUND

INTRODUCTION

Determinations of the molecular weight of selenium in iodine as a solvent, both cryoscopic and ebullioscopic, yield values which are abnormally low.⁽¹⁾⁽²⁾⁽³⁾ By the method of freezing point lowering, values ranging from 1.33 to 1.78 atoms to the molecule are found, while in boiling iodine the values range from 1.36 to 1.88. In such solvents as methylene iodide,⁽⁴⁾ phosphorus,⁽⁵⁾ diphenyl,⁽²⁾ and anthraquinone,⁽²⁾ at temperatures ranging from 4° to 277°C, the molecular weights found correspond to Se_8 . Further, the molecular weight of sulfur in iodine is found to be normal, that is, the molecule is S_8 .⁽²⁾

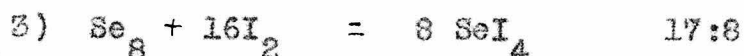
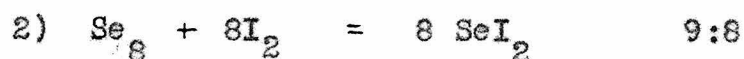
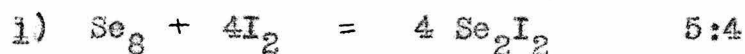
In order to account for this anomalous behavior of selenium toward iodine, various attempts have been made to find a selenium iodide. These attempts have all ended in negative or doubtful conclusions.

Pellini and Pedrina⁽⁶⁾ determined the freezing point-composition diagram for the two elements and found it to be of the normal V type with a eutectic at a point corresponding to about 50 atom percent of each element. The freezing points cannot be accurately determined, however, due to great tendency toward formation of undercooled liquids, especially for points in the central part of the diagram. This work was repeated by Beckmann and Grunthal⁽⁷⁾ with about the same results. This

2.

eliminates the possibility of a stable compound but does not eliminate the possibility of a dissociated one.

Using molten sulfur as a solvent, Beckmann and Platzmann⁽³⁾ also attempted to detect compound formation between selenium and iodine. The procedure consisted in the determination of the effect of selenium and of iodine separately and together on the freezing point of the sulfur. No compound formation was indicated. A similar set of experiments was made by Beckmann and Faust⁽⁴⁾ using methylene iodide as the solvent. Again no abnormal effect was found. However, it should be pointed out that neither of these methods would be sensitive enough to detect a highly dissociated compound. Three reactions which might be proposed are:



The ratios of the number of molecules used up to the number of molecules formed are given at the right. Reactions (1) and (2) would be difficult to detect unless they went well toward completion.

Wright⁽⁸⁾ measured the vapor pressure of iodine in the fusion products with selenium, sulfur and tellurium at various temperatures. In each case the vapor pressure was found to be the same as that for pure iodine at the same temperature. On passing a current of nitrogen over the

fusion products at 150°C, he found that the iodine was removed completely from sulfur and selenium, but that tellurium held back a quantity corresponding to TeI_4 . On this last fact he draws his conclusions that tellurium forms an iodide, while sulfur and selenium do not. The vapor pressure measurements do not exclude compound formation (even a stable compound) while the fact that selenium gives up all its iodine at 150° does not at all disprove the existence of a dissociated compound.

Beckmann and Faust⁽⁴⁾ measured the specific volume of selenium iodine mixtures and found that they could be calculated on the basis of an additive relationship, from the specific volumes of selenium and iodine, that is:

$$V_{(\text{mix})} = N_{\text{I}} V_{\text{I}} + N_{\text{Se}} V_{\text{Se}}$$

where the Vs refer to the specific volumes and the Ns are the atomic percentages. For Te -I mixtures they found deviations up to 1.5% from additivity, a compound being formed in this case. This evidence makes a selenium iodide seem improbable, but does not necessarily disprove the existence of one.

None of the work quoted definitely disproves the formation of a dissociated compound between selenium and iodine. The purpose of the present work has been to find evidence for the existence of a dissociated compound and to determine such facts about it as time permits.

PURIFICATION OF MATERIALS

The selenium was purified according to the method already outlined under the discussion of the selenium allotropes.

Iodine was purified by sublimation from an intimate mixture of about four parts of iodine to one part of potassium iodide. This product was then resublimed without the addition of potassium iodide.

The carbon bisulfide was shaken with mercury and allowed to stand over the metal for several days. It was then dried with CaCl_2 , filtered and distilled using a two foot column.

A good grade of carbon tetrachloride was dried with K_2CO_3 and CaCl_2 , then distilled without further purification. This was also the case with chloroform.

Ethylene bromide was fractionated from a student preparation by careful distillation. The distillate was then placed in a refrigerator and frozen. On removing from the refrigerator, the bottle was inverted and the solid permitted to melt about one third. This liquid was rejected and the remaining solid (F. P. 9.8°) was used.

ABSORPTION SPECTRUM STUDIES

F. Olivari⁽¹⁾ observed that a color change occurred when selenium was shaken with solutions of iodine in carbon bisulfide, but said that he believed this color to be the same as that resulting when white light passes

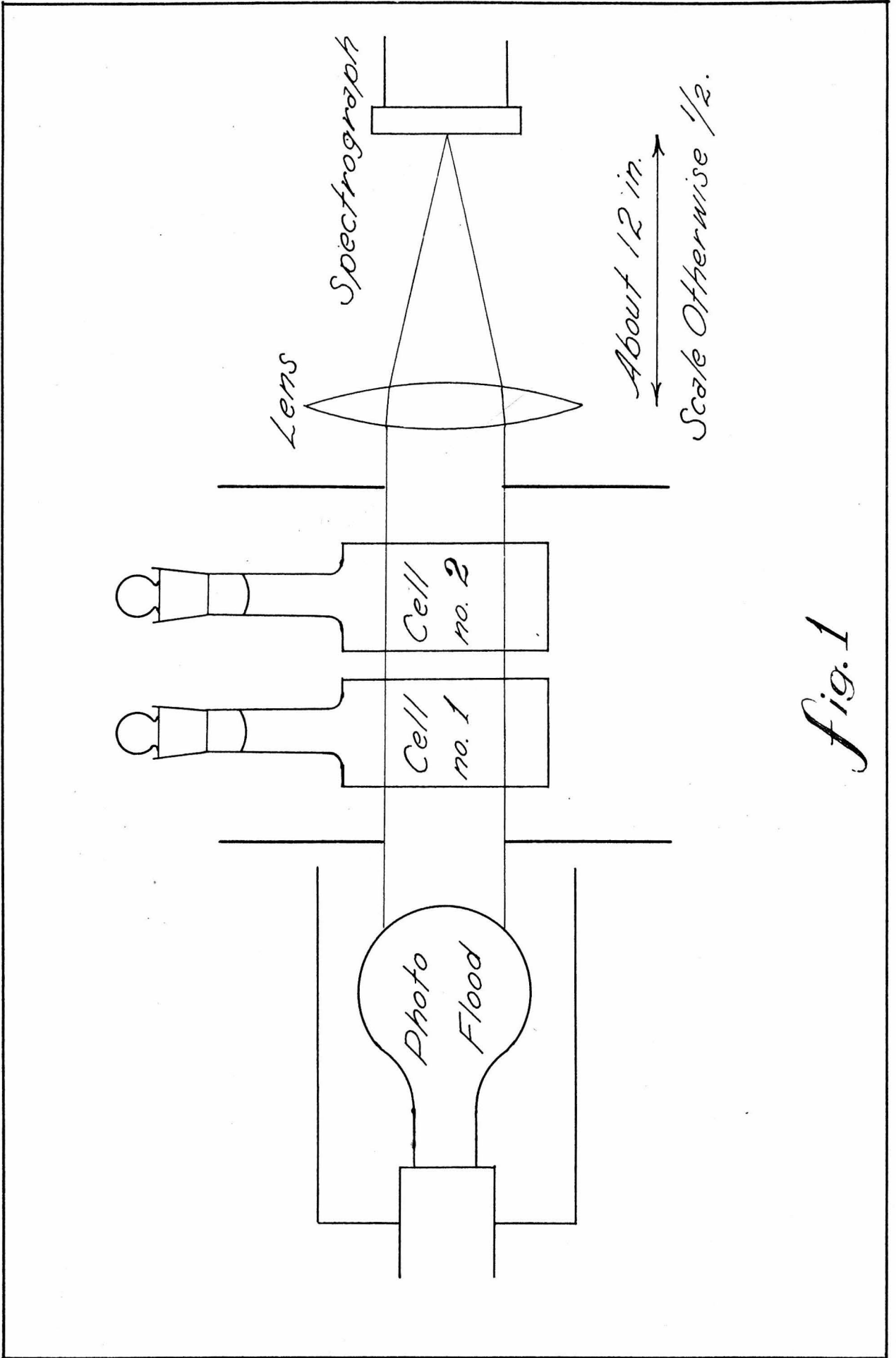


Fig. 1

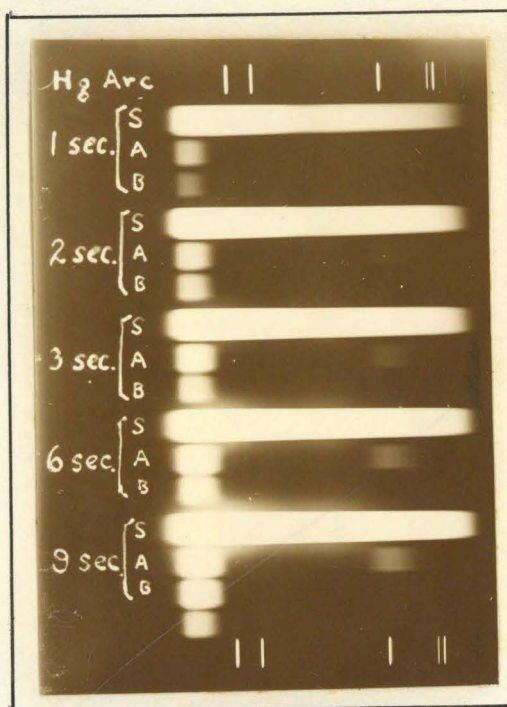
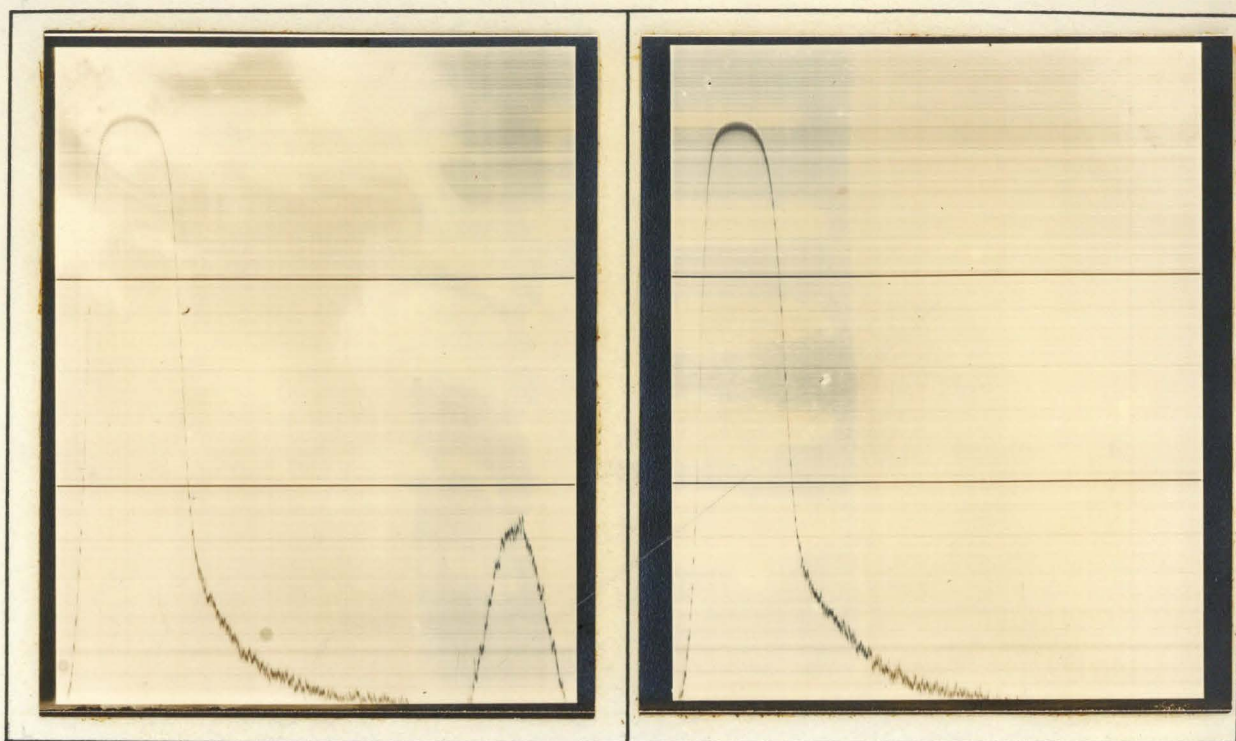


FIGURE 2

Absorption spectra showing evidence of compound formation between selenium and iodine. The spectra marked S are of the source photographed through both cells filled with pure carbon bisulfide. Those marked A are with the carbon bisulfide solutions of selenium and of iodine in separate cells, while the spectra marked B are with the two solutions mixed.



A

FIGURE 3

B

Microphotometer records of absorption spectra A and B with six second exposures. The new region of absorption on mixing the two solutions is clearly shown at the right of the records.

in succession thru first a solution of selenium in carbon bisulfide, then thru a solution of iodine in that solvent. Visual comparisons made by the author did not seem to agree with this conclusion. Beckmann and Grunthal⁽⁷⁾ also comment on this color change. They state that no color change is observed when the so called metallic selenium is shaken with a solution of iodine in carbon bisulfide in the cold, but that on heating, a color change did appear which they attribute to a conversion of the hexagonal selenium to the amorphous or soluble form. This is wrong on two counts. The hexagonal selenium will dissolve (as shown later) in solutions of iodine in any solvent in the cold and heating will not change the stable hexagonal selenium to the amorphous form, but rather the change goes in the opposite direction. (See preceding discussion on selenium allotropes in this thesis.)

In order to definitely establish the nature of the color change occurring on mixing a solution of selenium in carbon bisulfide with a solution of iodine in that solvent, absorption spectra were photographed. The experimental set-up is shown in Figure 1. The procedure was as follows:

The source was photographed first, the light passing thru both cells filled with pure carbon bisulfide. In the photograph, Figure 2, these spectra are marked "S". Next, Cell #1 was filled with a solution containing 0.885 g. of iodine per 1000 g. CS₂ and Cell #2 was filled with a solu-

tion containing 0.195 g. of selenium per 1000 g. CS_2 . The spectra photographed with this arrangement are marked "A". Finally these two solutions were emptied out, mixed and both cells refilled with the resulting solution. These spectra are designated "B". Examination of the spectra shows a definite increase in absorption especially in the violet, which region is absorbed practically completely by the mixed solutions. This lends very strong evidence in favor of a compound between the elements in solution. Great care was taken to see that the iodine was free of other halogens since they are known to react with selenium.

Microphotometer records were made of the spectra under A and B with the six second exposures. The records show more clearly the additional region of absorption. These are shown in Figure 3.

THE EQUILIBRIUM BETWEEN IODINE AND SELENIUM IN SOLUTION

In order to get some idea as to the stability of, or degree of dissociation of the compound, and in order to determine its formula, some experiments were carried out at 25° . The main purpose here was the determination of the relation between the concentrations of the dissolved selenium and the iodine.

First it was determined qualitatively that hexagonal (insoluble) selenium did actually dissolve in dilute solutions of iodine in such solvents as carbon tetrachloride, carbon bisulfide, chloroform and ethylene bromide. It was found that if the resulting mixture was filtered thru a

fine sintered glass filter, a good test for selenium could be obtained in the filtrate. When the pure solvents themselves are shaken with hexagonal selenium, or allowed to stand for very long periods, the filtrate shows no test for selenium. The selenium test was made in each case by shaking the filtrate with aqueous sulfur dioxide solution.

The experimental procedure used in the quantitative experiments was as follows:

Weighed quantities of pure iodine and solvent were placed in glass stoppered bottles. These were rotated overnight or longer in the thermostat at 25°. The solutions were then allowed to settle in the bath for ten minutes or longer, after which the samples were removed by slowly forcing the solution thru a small sintered glass filter by means of water free air saturated with the solvent. The sample was collected in a weighed, glass stoppered flask, the size of sample being determined by weighing.

In most of the experiments a gravimetric method of selenium analysis was used. The weighed sample was transferred to a separatory funnel and the flask was rinsed out with about 100 cc. of 3N NaOH solution, which was then poured into the funnel. The sample was shaken with the base solution for several minutes, then the two layers were separated. By this process, the selenium and iodine are transferred to the aqueous layer, the selenium being converted mainly to selenite, but partially to selenate. The aqueous layer is filtered thru

8.

sintered glass and saturated with sulfur dioxide. An equal volume of concentrated HCl is then added and more sulfur dioxide bubbled into the solution. This precipitates the selenite. The selenate is finally precipitated by the addition of hydrazine hydrochloride after the sulfur dioxide has been boiled off. In order to convert the colloidal selenium to a form in which it will be retained by the filter, the solution must be heated several hours. It is then collected in a sintered glass crucible, washed with water, then with alcohol and finally dried at 105° .

In some of the later experiments a quicker and more reliable volumetric method was developed. The details of the method will be published later. It will suffice here to say that in 6N HCl, selenium in any lower valence state is converted quantitatively by iodate to selenite, the iodate going to ICl as usual. An equilibrium mixture of selenium and iodine can be analyzed by titration with standard thiosulfate to get the total iodine, then with standard iodate to get the sum of iodine plus selenium. The selenium is found by difference. In the thiosulfate titration, the selenium precipitates, but this causes no trouble in the starch end point, since the selenium is wet by the organic solvent and does not enter the aqueous phase.

Data for the equilibrium in ethylene bromide are given in Table I and for carbon tetrachloride in Table II.

9.

TABLE I

Selenium - Iodine Equilibrium in Ethylene Bromide

(1) Moles of I ₂ per 1000 g. C ₂ H ₄ Br ₂	(2) Gram-atoms of Se per 1000 g. C ₂ H ₄ Br ₂	Ratio (1) / (2)
0.0445	0.00200	22.3
0.0756	0.00328	22.9
0.102	0.00452	22.6
0.169	0.00777	21.7
0.308	0.0152	20.2
0.397	0.0209	19.0
0.452	0.0252	17.9

TABLE II

Selenium - Iodine Equilibrium in Carbontetrachloride

(1) Moles of I ₂ per 1000 g. CCl ₄	(2) Gram-atoms of Se per 1000 g. CCl ₄	Ratio (1) / (2)
0.04236	0.001064	39.81
0.05622	0.001401	40.13
0.07620	0.001910	39.90

Fig. 2

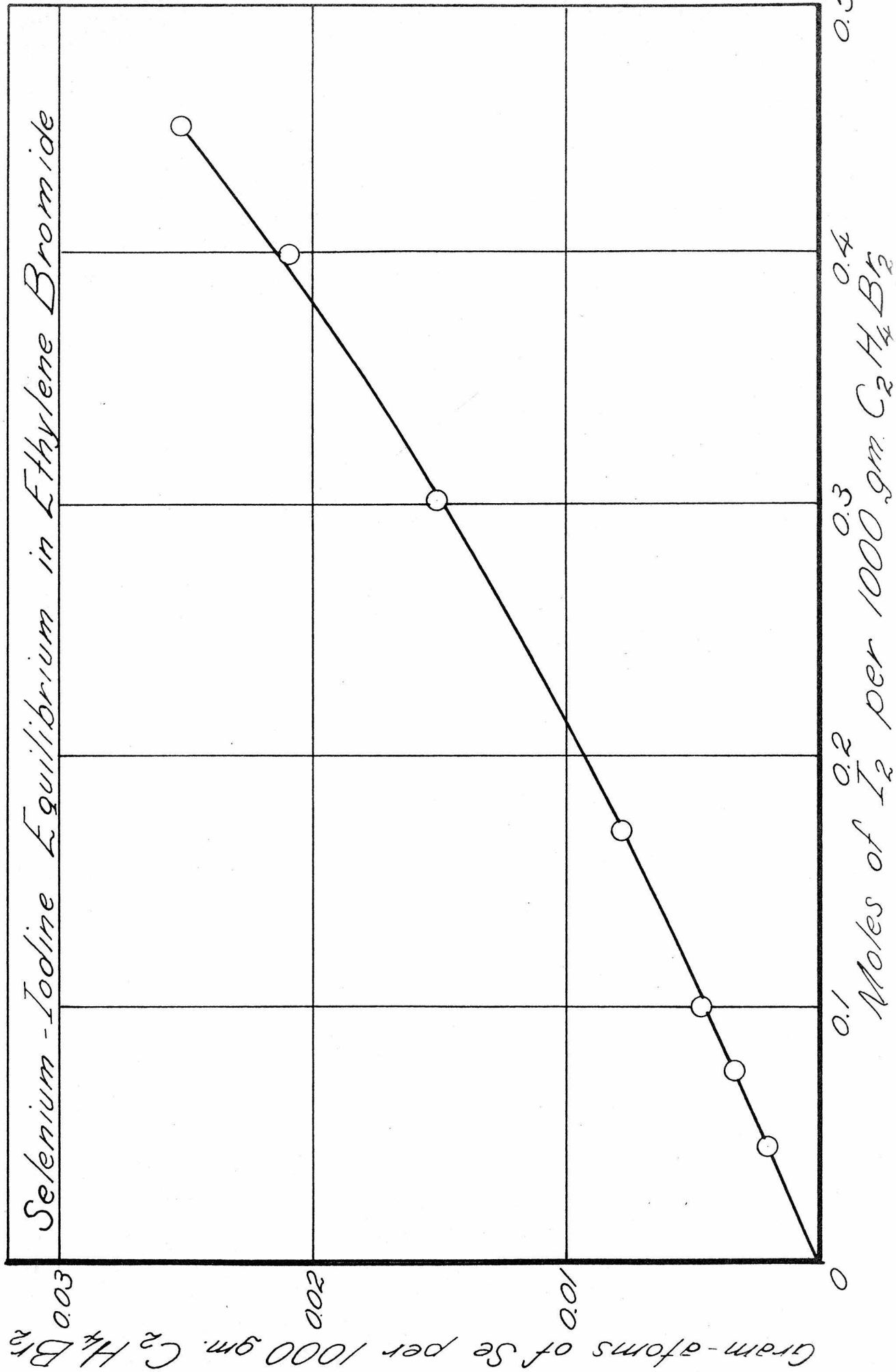
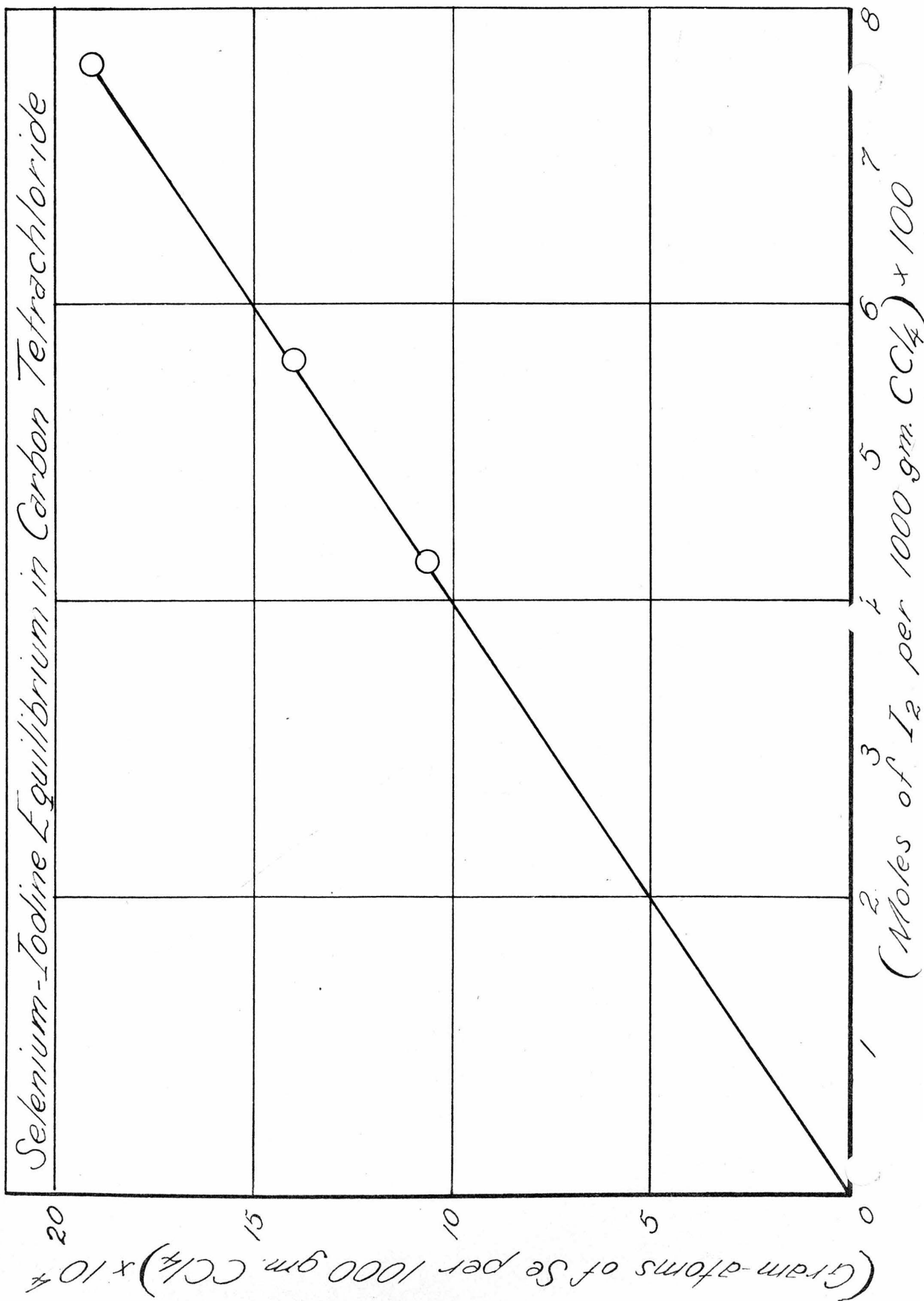
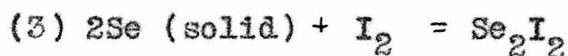
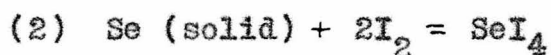
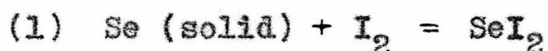


Fig. 3



These results are plotted in Figures 4 and 5 respectively. The curve for ethylene bromide shows a departure from a straight line, while that for carbon tetrachloride is remarkably straight. Over the same concentration range, however, no departure in the case of ethylene bromide is evident.

The following reactions are considered as possibilities, keeping in mind the known halogen compounds of the sixth group elements:



Using an excess of solid hexagonal selenium, the corresponding mass-action constants are:

$$K_1 = \frac{(\text{SeI}_2)}{(\text{I}_2)}$$

$$K_2 = \frac{(\text{SeI}_4)}{(\text{I}_2)^2}$$

$$K_3 = \frac{(\text{Se}_2\text{I}_2)}{(\text{I}_2)}$$

Neglecting activity effects for the time being we see that reactions (1) and (3) require a linear dependence of the dissolved selenium on the iodine concentration while

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in reaction (2) this yields a quadratic dependence,

$$\text{Se (dissolved)} = K_2(\text{I}_2)^2 .$$

Obviously, reaction (2) can play no more than a very small part in the carbon tetrachloride equilibrium. It probably does play a part in the ethylene bromide solutions, however. This shows up even more if we consider activity effects. G. Ferraro⁽⁹⁾ found that the distribution coefficient for iodine between ethylene bromide and water increased as the iodine concentration increased. The variation in the coefficient was from 650 to 696 as the iodine concentration in the aqueous phase varied from 0.03 to 0.183 g. per liter. If the usual assumption is made regarding the activity coefficient in the aqueous phase, namely that it is unity, this means that the activity coefficient of the iodine in ethylene bromide decreases with an increase in concentration. If the activity coefficient actually falls off with increasing iodine concentration, reaction (2) must be called upon to explain the increase in slope.

The effect of selenium on the solubility of iodine in the two solvents was also determined. The apparent solubility of iodine in ethylene bromide is the same (within a very small experimental error) whether or not selenium is present. In the case of carbon tetrachloride, however, the solubility of iodine is measurably increased when selenium is present. The quantity of this increase, together with the

12.

quantity of selenium in solution, enables one to write a formula for the compound. In so doing it is assumed that the small concentration of the selenium iodide present does not in itself affect the solubility of iodine in the solvent. This assumption seems reasonable since the concentration of the compound is only one-fortieth or one-eightieth that of the iodine.

The experimental procedure here was the same as already described. The solubilities of iodine in the solvents were also determined and found to be in good agreement with values given by Hildebrand⁽¹⁰⁾. The data are given in Table III. The solubility of hexagonal selenium in the solvents is immeasurably small. The increase in the solubility of iodine in carbon tetrachloride due to selenium is 0.215 g. or 0.00170 gram-atoms per 1000 g. of CCl_4 . The increase in solubility of selenium due to iodine is 0.1535 grams or 0.00195 gram-atoms per 1000 g. CCl_4 . This indicates 1.15 gram-atoms of selenium per gram-atom of iodine and that the compound predominating is Se_2I_2 since the linear dependence of the selenium concentration on that for iodine requires two atoms of iodine in the molecule.

The high value (1.15) obtained above must be due to a decrease in solubility of iodine in the solvent brought about by the compound, an effect which is to be expected. Since the above result was brought about by taking the small difference between two relatively large numbers, a very small decrease in the solubility of iodine brought about by the

15.

TABLE III

Solubilities - (Grams of Solute per 1000 g. pure Solvent
at 25°C.)

Iodine in $C_2H_4Br_2$	Iodine in $C_2H_4Br_2$ Sat'd. with Selenium	Selenium in $C_2H_4Br_2$ Sat'd. with Iodine
115.0	114.7	1.984
114.8	115.0	1.993
114.9 Ave.	114.9	1.989

Iodine in CCl_4	Iodine in CCl_4 Sat'd. with Selenium	Selenium in CCl_4 Sat'd. with Iodine
19.12	19.34	0.154
19.13	19.34	0.153
19.125 Ave.	19.340	0.1535

presence of the compound would cause a relatively large error in the difference of the two solubilities. By coincidence, the compound seems to increase the activity of I_2 in the ethylene bromide to the point where its apparent solubility is unchanged. By apparent solubility here is meant the total iodine in solution per 1000 g. solvent. Greater deviation might be expected in the case of ethylene bromide since the concentration of iodine is about five times and of the compound about ten times as great as in carbon tetrachloride.

The formation of SeI_4 also seems somewhat probable. It has already been pointed out that this would account for the increase in slope found in Figure II. Going back to the measurements on the molecular weight of selenium in iodine as the solvent (See page 1) it is recalled that values ranging from those corresponding to $Se_{1.33}$ to those corresponding to $Se_{1.88}$ were obtained, the lower values being obtained in the more dilute solutions and at the lower temperature. These measurements can also be explained on the assumption of a mixture of SeI_4 and Se_2I_2 in solution. At low selenium concentrations, relatively more SeI_4 would be expected, bringing about a lower apparent molecular weight for selenium. The lower molecular weights for selenium at the lower temperature cannot be explained by means of a dissociation of the type $Se_n = nSe$, since an increase in temperature would favor dissociation. This behavior can, however, be represented in terms of Se_2I_2 and SeI_4 , if we say that increased temperature shifts the equilibria in such a way as to increase the

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ratio of Se_2I_2 to SeI_4 .

In carbon tetrachloride, the equilibrium constant has the value:

$$K_1 = \frac{(\text{Se}_2\text{I}_2)}{(\text{I}_2)} = 0.0127.$$

In the ethylene bromide solutions, the data follow closely the empirical equation:

$$\text{Se (dissolved)} = 0.0400(\text{I}_2) + 0.0353(\text{I}_2)^2.$$

This leads to the following equilibrium constants in this solvent:

$$K_1 = \frac{(\text{Se}_2\text{I}_2)}{(\text{I}_2)} = 0.0208$$

$$K_2 = \frac{(\text{SeI}_4)}{(\text{I}_2)^2} = 0.0409 .$$

SUMMARY

Evidence quoted in the literature which supposedly disproves compound formation between iodine and selenium in no case prohibits the possibility of a highly dissociated compound.

Absorption spectra were photographed which give strong evidence favoring a selenium-iodine compound in solution.

Quantitative measurements on the equilibrium between selenium and iodine in ethylene bromide and carbon tetrachloride indicate a compound of formula Se_2I_2 , and possibly SeI_4 also.

BIBLIOGRAPHY

- (1) F. Olivari, Chem. Zentr. I, 83 (1910)
- (2) Beckmann and Hanslian, Zeit. anorg. Chem. 80, 221 (1913)
- (3) Beckmann and Platzmann, Ibid. 102, 215 (1918)
- (4) Beckmann and Faust, Ibid. 84, 103 (1913)
- (5) Helff, Zeit. phys. Chem. 12, 220 (1893)
- (6) Pellini and Pedrina, International Critical Tables, Vol. IV
Page 24
- (7) Beckmann and Grunthal, Zeit. anorg. Chem. 84, 97 (1913)
- (8) R. Wright, Jour. Chem. Soc. 107, 1527 (1915)
- (9) G. Herraro, British Abstracts, 773 (1933)
- (10) J. H. Hildebrand, J. A. C. S. 57, 866 (1935)

III.

AN ATTEMPT TO REPRODUCE THE
ALLISON MAGNETO- OPTIC EFFECT

AN ATTEMPT TO REPRODUCE THE ALLISON MAGNETO-OPTIC EFFECT

INTRODUCTION

The Magneto-optic Method of Analysis has been described by Allison in numerous articles since its discovery in the year 1927. The method if valid, would prove of great interest to chemists and physicists from both experimental and theoretical standpoints. The effect commands much interest, first, because of the very small concentrations (10^{-12} formal) at which it is claimed to be observed and second, because of the lack of any theoretical explanation for it.

As a means of analysis, it is claimed that not only can an element or radical be detected in solution in very minute quantities, but also that the various isotopes of the positive constituents show up separately, enabling one to determine the number of isotopes possessed by a metallic element. No means has been found for detecting isotopes of the negative elements or radicals by this method.

Two outstanding facts aroused the author's interest in the subject.

(1) In 1927 Aston⁽¹⁾, using a newly built mass spectrograph found a weight for the hydrogen nucleus which was in good agreement with the chemical atomic weight. This lead him to believe that hydrogen was therefore a pure element with atoms of only one mass. This calculation was made on the assumption that oxygen was also "pure", which later proved to be in error.

In October, 1930, Allison and Murphy⁽²⁾ in discussing isotopes, and believing that hydrogen atoms were all of one mass made the statement: "Hydrochloric, nitric and sulfuric acids each produce two minima, for which we are unable to account." (It should be noted that each isotope supposedly produces a minimum.) In other words, they were at a loss to explain the appearance of an extra minimum in the case of hydrogen. This would lead one to believe, in the light of the later discovery of H^2 in 1932 by Urey, Brickwedde and Murphy⁽³⁾ that the Magneto-optic Method is really all right.

(2) W. M. Latimer and H. A. Young⁽⁴⁾ reported that they not only checked various of Allison's results but that when HCl was dissolved in solutions containing heavy water they were able to detect still a third isotope of hydrogen. The isotope H^3 was later discovered by Lozier, Smith and Bleakney⁽⁵⁾ by means of the mass spectrograph. Since Latimer has the reputation of being a good scientific worker, his report caused many people to accept the Magneto-optic Method of Analysis as valid.

In view of the above facts, it was considered worth while to set up the apparatus so that the method might be given a further check and so that data might be obtained which would be of help in establishing some theoretical basis for the effect. Professor W. V. Houston of this Institute was interested in the latter aspect of the problem.

APPARATUS

All apparatus used was as nearly identical to that described by Allison as was practical at the time. The optical set-up was mounted on an optical bench so that exact alignment was facilitated. A rectifying tube was used, but due to the lack of a filament transformer, an auto-transformer was employed, which introduced a ground in the circuit at this point. Otherwise the electrical circuit was unaltered. The trolley wire was considerably larger (#12 hard-drawn copper wire) than the #18 used by Allison. This wire was also used in winding the helices into which the cells fit. A rather large Nicol prism was used as a polarizer while the analyzer and circle was borrowed from the laboratory polarimeter. The movable trolley was operated by means of a drum mounted in front of the observer.

The apparatus was first set up in the second sub-basement of the Astro-physics Laboratory, but this proved later to be too damp, so the equipment was moved to an old barracks on the campus. This was quite dry in summer.

EXPERIMENTAL

The zero point of the scale was located as directed by Allison, the minimum in this case, with carbon bisulfide in both cells being quite sharp. When the second cell was filled with a dilute aqueous solution of HCl, SnCl₂, KCl, etc., a rather broad minimum could be located, but the sharp

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minima, which have been attributed to the various isotopes of the positive ions, could not be observed.

Various methods of observation were employed. The room was kept in complete darkness during observation and the trolley position could not be seen. In the earlier work, a study of Allison's scale readings was purposely avoided so that observations would not be influenced in this way. In order to reduce eye fatigue, a method was sometimes employed which consisted of alternately looking into the eyepiece for a few seconds, then away for about the same length of time. Small changes in the trolley setting were usually made during every third or fourth rest period.

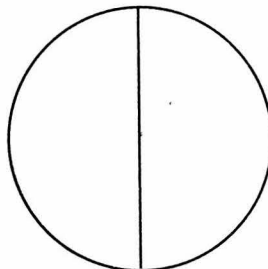
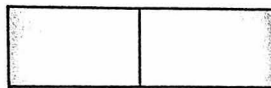
Many hours of observation with various solutions in the second cell at concentrations running from 0.1 to 10^{-10} formal were made. The water used in making up these solutions was redistilled from alkaline permanganate in an all glass still. Changes were made from time to time in the variables of the electric circuit such as the capacity of the condenser, length of spark gap, primary voltage, etc. A sodium vapor lab-arc was tried as a light source with even less success, in spite of it being steadier than the spark. This might be expected, since the Verdet Constants become smaller at longer wavelengths, with correspondingly smaller rotations of the plane of polarization. The spark remained in the circuit in this case of course, its light being shielded.

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The minima consist of a decrease of about 3 to 5% in the intensity of a very weak light source which is subject to flicker since it comes from a spark, and subject further to changes in line voltage which may amount to several percent.

In the latter part of the work a new idea was incorporated in the apparatus with the purpose in mind of getting a split field of vision, one-half of which would undergo minima while the other half would produce simultaneous maxima. If the two halves of the field are matched to start, then at the scale setting of one of Allison's minima, they should go out of match, one side getting weaker, while the other side grows stronger. Flickering of the light source should affect both halves alike, giving no relative change in intensity.

In order to bring about the above conditions, a quartz disc was made up, one half of which was cut from a left handed crystal, while the other half was cut from a right handed one. The two halves were cemented together as shown.



This disc was ground to such a thickness that the plane of polarization of light of 4481 from the magnesium spark experienced a resultant rotation of about 2° in each half or a separation of about 4° in the planes of polarization in the two halves of the field.

Since the minima are supposedly produced by differential rotations of the plane of polarized monochromatic light observed thru a Nicol prism, if the above described disc is placed somewhere in the light path between the two Nicol prisms, then the effect desired should be produced. On trying it out, this proved to be the case for the broad minima already described, yet no sharp minima could be located.

As a final resort, and not until then, a study was made of Allison's reported scale readings, which were then used in looking for minima. Again no sharp minima due to the isotopes were to be found.

DISCUSSION

Unfortunately, the failure to obtain sharp minima of the type described by Allison does not necessarily disprove the validity of the method. One thing, however, appears to be certain, namely, that the method, even though it may work in some cases, is extremely tedious in its operation and subject to unknown disturbances which cause it to be inoperative. At the present writing, the validity of the method is still unsettled. Numerous papers on both sides

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have appeared, none of which offer any unquestionable proof one way or the other.

BIBLIOGRAPHY

- Beams and Allison, Phys. Rev. 29, 161 (1927)
F. Allison, Phys. Rev. 30, 66 (1927)
F. Allison, Phys. Rev. 31, 313 (1928)
Allison and Murphy, Phys. Rev. 35, 124 (1930)
Allison and Murphy, Phys. Rev. 36, 1097 (1930)
Allison and Murphy, J. A. C. S., 52, 3796 (1930)
Allison, Murphy, Bishop and Sommer, Phys. Rev. 37, 1178 (1931)
Allison, Christensen and Waldo, Phys. Rev. 37, 1003 (1931)
F. Allison, Ind. Eng. Chem. 4, 9 (1932) (Anal. Ed.)
F. Allison, Jour. Chem. Educ. (1933) 10, 71

For a more complete bibliography see the paper by
F. G. Slack, Jour. Franklin Inst., 218, 445 (1934)

IV.

THE CRYSTAL STRUCTURE OF POTASSIUM
CHLOROSMATE AND POTASSIUM BROMOSMATE

(Contribution from Gates Chemical Laboratory, California Institute of Technology,
No. 532).

The Crystal Structure of Potassium Chlorosmate, K_2OsCl_6 , and of Potassium Bromosmate, K_2OsBr_6 .

By James D. McCullough in Pasadena (Calif.).

Potassium chlorosmate and potassium bromosmate are both included, along with potassium chlorostannate and ammonium chloroplatinate, in a rather long list of substances of the type R_2MX_6 given by Groth¹⁾ which crystallize in octahedra belonging to the cubic system and indicated as probably being isomorphous. Since the crystals of potassium chlorosmate were found to belong to the cubic system, and since potassium bromosmate had already been shown by Sachs²⁾ to give cubic crystals, it was believed quite probable that these two salts would have the ammonium chloroplatinate³⁾ (potassium chlorostannate⁴⁾) structure. It has been the purpose of the present study to confirm this hypothesis and by a careful determination of the halogen parameter in each case to obtain an accurate value for the octahedral electron-pair bond radius of quadrivalent osmium. The crystals used were octahedra about 0.2—0.5 mm. on an edge with some cube faces developed. For these crystals the author is indebted to Dr. Wm. R. Crowell and Mr. Harlan Baumbach of the University of California at Los Angeles, who obtained them in a recent study of osmium.

Oscillation photographs were prepared by reflecting MoK_α radiation from a (111) face. Laue photographs were prepared using tungsten radiation, the beam being in some cases normal to (111) and in other cases making a small angle with the normal to (111). A powder photograph was also prepared of K_2OsBr_6 using MoK_α radiation.

The Unit Cell and Space Group of K_2OsCl_6 .

Data from the oscillation photograph are recorded in table I. These data lead to the spacing $d_{111}/n = 5.617 \pm 0.01 \text{ \AA}$. Two Laue photographs were completely indexed and no value of $n\lambda$ calculated was found to be less than 0.24 \AA , the short wave length limit, when the value $a_0 = 9.729 \pm 0.02 \text{ \AA}$ was used.

1) Groth, R., »Chemische Krystallographie« I, 468.

2) Sachs, Z. Kristallogr. 34 (1901) 165.

3) Wyckoff, R. W. G., J. Amer. chem. Soc. 43 (1921) 2292.

4) Dickinson, R. G., Ibid. 44 (1922) 276.

Table I. Oscillation data for (111) of K_2OsCl_6 .

Plane	Line	Sin θ	d/n (Å)
(111)	α	0.0631	5.626
(222)	α	0.1626	5.626
(333)	α	0.1899	5.608
(444)	α_1	0.2521	5.612
	α_2	0.2537	5.614

From a roughly measured value of the density, 3.50, the unit cell was found to contain four "molecules".

The Laue photographs normal to (111) show a three-fold axis and three planes of symmetry, indicating a point group symmetry of T_d , O or O_h . A face-centered lattice is indicated by the observation of only odd indices for all first order reflections on the two Laue photographs. The space groups consistent with these observations are T_d^2 , T_d^5 , O^3 , O^4 , O_h^5 , O_h^6 , O_h^7 and O_h^8 . Reflections observed from such planes as (797) at $n\lambda = 0.33$ eliminate T_d^5 , O_h^6 and O_h^8 . O_h^7 is eliminated by the pure second order reflection from planes such as (305) at $n\lambda = 0.70$. The observation of reflection from (200) on the oscillation photograph eliminates O^4 . This leaves only T_d^2 , O^3 and O_h^5 to be considered, all without special criteria.

The Atomic Arrangement.

Four molecules in the unit cell require the placing of 8 K , 4 Os and 24 Cl . O^3 and O_h^5 furnish the same possibilities in this case, consisting of only two non-equivalent arrangements, both of which are also obtainable from T_d^2 . One of these arrangements is eliminated by observation on the Laue photographs of many first order reflections which are more intense than others coming from planes with larger spacings. The eliminated arrangement yields the same structure factor ($4f_{Os}$) for all first order reflections. This observation also serves to eliminate other non-equivalent arrangements based on T_d^2 . The remaining arrangement, that for the ammonium chloroplatinate structure, obtainable from O^3 , O_h^5 and T_d^2 is:

- 8 K in 8e, Face-centered arrangement starting in $\pm (1/4, 1/4, 1/4)$;
 4 Os in 4b, Face-centered arrangement starting in (0, 0, 0);
 24 Cl in 24a, Face-centered arrangement starting in $\pm (u, 0, 0$;
 $0, u, 0; 0, 0, u)$.

The above arrangement with $u = 0.243 \pm 0.002$ gives complete qualitative, and for those reflections to which a detailed treatment was given, quantitative agreement between observed and calculated intensities.

Evaluation of the Chlorine Parameter.

Oscillation photographs for use in making intensity comparisons were prepared by reflecting MoK_{α} radiation from a (111) face. Orders of (111) only were used in making the comparisons, the intensity for reflection from ($n n n$) being calculated by means of the following formula:

$$\sqrt{I_{nnn}} = \text{Constant} \cdot \left(\frac{1 + \cos^2 2\theta}{2 \sin 2\theta} \right)^{\frac{1}{2}} \cdot \sqrt{n} \cdot F.$$

The structure factor F was calculated from the f -values given by Pauling and Sherman¹). No temperature factor was introduced. The only intensity inequalities used were those for which a plane with a given spacing was observed to reflect more strongly than a plane with a larger spacing.

The visually estimated intensities for the various orders of (111) are:

(111)	40	(222)	1.0	(333)	3.0
(444)	40	(555)	2.5	(666)	0.3
(777)	0.5				

In figure 1, the square root of the calculated intensity for ($n n n$), $\sqrt{I_{nnn}}$, is plotted against the chlorine parameter u . The arrows under the plot serve to indicate those regions eliminated by the specified intensity inequality. In this way u is restricted to values between 0.244 and 0.250.

The parameter is further restricted by means of the Laue photographs. For this purpose, a series of timed exposures were prepared with the same crystal orientation. The exposure times were four, eight, twenty and forty hours respectively. Observations on these photographs are given in table II.

Table II. Intensity relations for Laue reflections of K_2OsCl_6 .

Plane	$n\lambda$	d_{hkl}	Exposure	Comparison	Plane	$n\lambda$	d_{hkl}	Exposure
($\bar{5}$ 19)	.440	0.935	20	>	($\bar{7}$ 37)	.449	0.935	40
($\bar{7}$ 37)	.449	0.935	40	>	($\bar{5}$ 19)	.440	0.935	8
(15.1.5)	.310	0.610	40	>	(9.1.13)	.309	0.610	4
(9.1.13)	.309	0.610	20	>	(15.1.5)	.310	0.610	40

These observations lead to the conclusions:

$$5(\bar{7}37) > (\bar{5}19) > 2(\bar{7}37) \quad 5(15.1.5) > (9.1.13) > 2(15.1.5).$$

1) Pauling and Sherman, J., Z. Kristallogr. 81 (1932) 1.

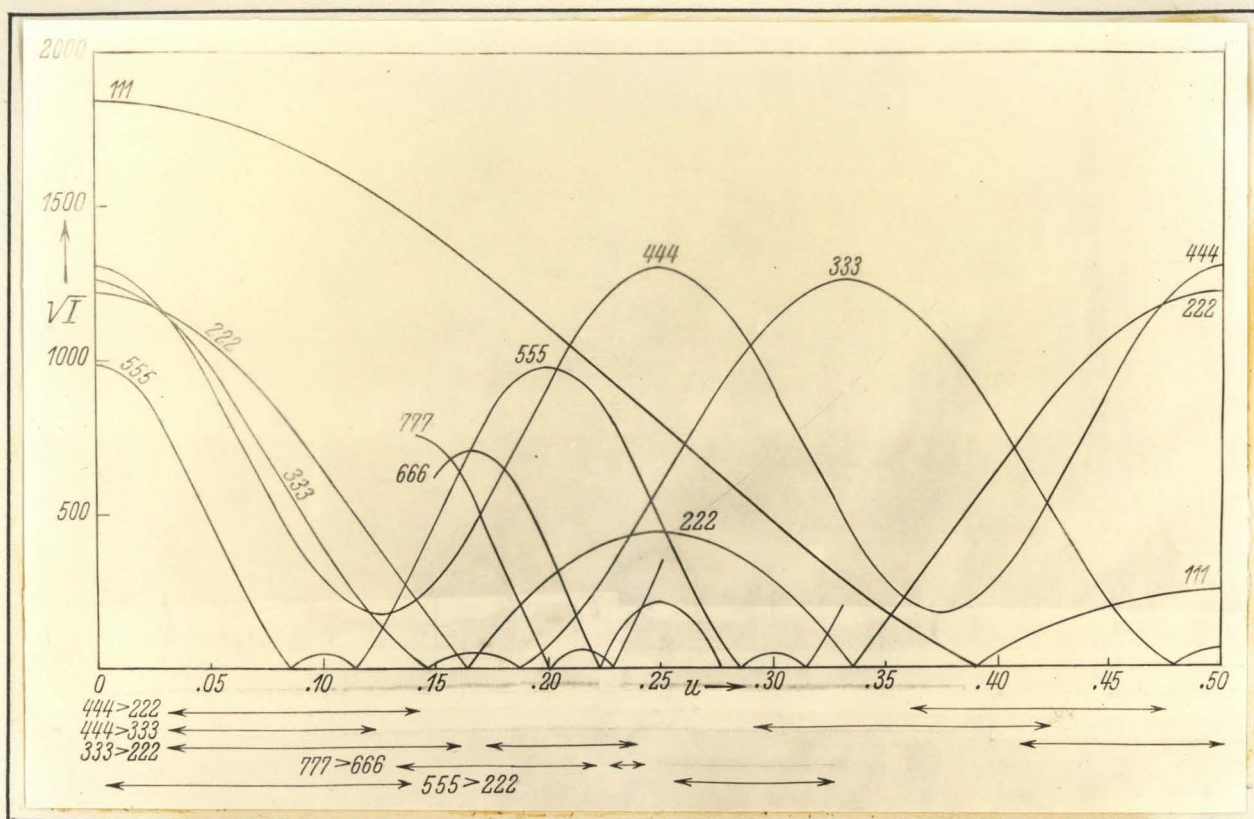


FIGURE 1

Plot showing the square root of the calculated intensities for various orders of (111) as functions of the chlorine parameter, u . The arrows show the regions eliminated by the indicated comparisons.

The calculated intensities for these planes as functions of the parameter u are shown in figure 2. In calculating these intensities, the factors $\left(\frac{1 + \cos^2 2\theta}{2 \sin 2\theta}\right)^{\frac{1}{2}}$ and \sqrt{n} have been omitted. The regions eliminated are again indicated by means of arrows under the plot.

The value $u = 0.243 \pm 0.002$ appears to be the most reasonable in keeping with the data. The corresponding value for the osmium-chlorine separation is $2.36 \pm 0.02 \text{ \AA}$. Subtracting from this the normal electron-pair bond radius for chlorine, 0.99 \AA^1 , the value $1.37 \pm 0.02 \text{ \AA}$ is obtained for the octahedral electron-pair bond radius of quadrivalent osmium.

The Size of the Unit Cell of Potassium Bromosmate.

By the same procedure, potassium bromosmate was found to have the ammonium chloroplatinate structure. The size of the unit was determined from measurements on a powder photograph prepared using MoK_{α} radiation. The data are listed in table III.

Table III. Data from powder photograph of K_2OsBr_6 .

hkl	$\sin \theta$	d_{hkl}	a_0
(111)	0.0595	5.965	10.33
(200)	0.0685	5.181	10.36
(220)	0.0977	3.633	10.28
(113)	0.1142	3.108	10.31
(222)	0.1197	2.965	10.28
(400)	0.1383	2.567	10.27
(240)	0.1541	2.303	10.30
(115), (333)	0.1794	1.978	10.28
(440)	0.1954	1.816	10.28
(244), (600)	0.2060	1.723	10.34
(226)	0.2281	1.556	10.33
(444)	0.2387	1.486	10.30
(117), (155)	0.2464	1.440	10.29
(228), (660)	0.2925	1.213	10.30
(248)	0.3214	1.104	10.30
			Average 10.30

Using $a_0 = 10.30 \pm 0.03 \text{ \AA}$, no value calculated for $n\lambda$ on two completely indexed Laue photographs was found to be less than the short wavelength limit of the X-rays.

1) Pauling, Linus, Proc. Nat. Acad. Sci. 18 (1932) 293.

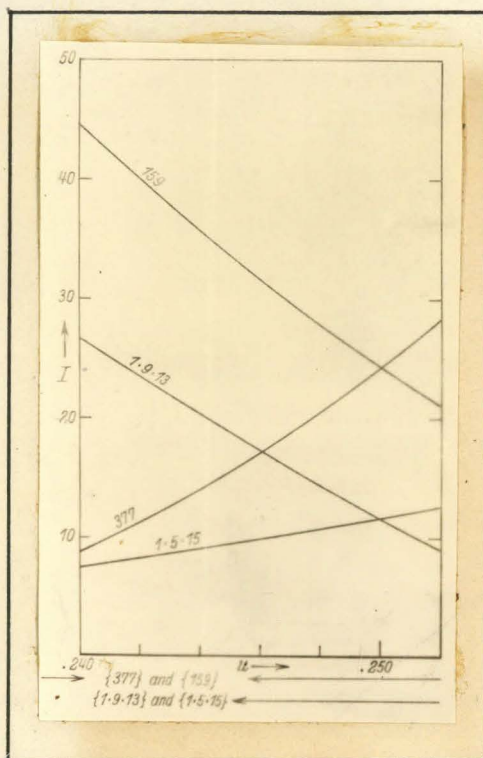


FIGURE 2

Calculated intensities
of selected Laue
reflections of K_2OsCl_6
as functions of the
chlorine parameter, u .

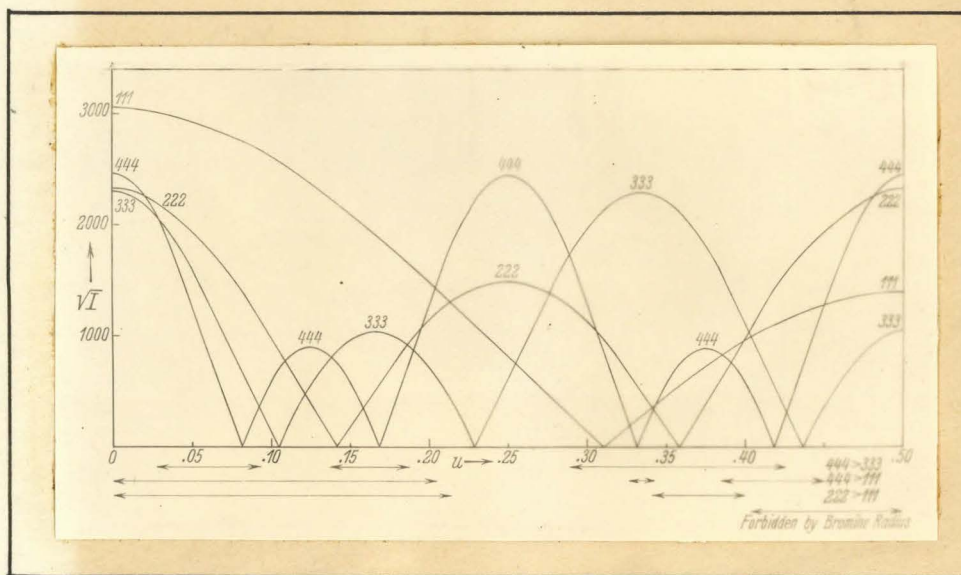


FIGURE 3

Square root of calculated intensities for (hkn)
of K_2OsBr_6 plotted as functions of the bromine
parameter, u .

Determination of the Bromine Parameter.

The method used was the same as for potassium chlorosmate. In figure 3 are plotted the calculated values of $\sqrt{I_{nnn}}$ against the parameter, u , while the arrows show the regions eliminated.

The visually estimated intensities are:

(111)	(222)	(333)	(444)
5	10	0.5	10

The parameter is thus limited to the region between 0.213 and 0.288. Further limitation is made by the observation that the Laue reflection of $(13.\bar{3}.\bar{3})$ at $\lambda = 0.435$ is more intense than that of $(\bar{3}.\bar{1}1.\bar{3})$ at $\lambda = 0.426$. The calculated intensity curves for these planes are found in figure 4.

The parameter is thus restricted to the region 0.224 to 0.249. The final choice of u is made by means of the quantitative relationships given in table IV.

Table IV. Intensity relations for Laue reflections of K_2OsBr_6 .

Plane	λ	d_{hkl}	Exposure	Comparison	Plane	λ	d_{hkl}	Exposure
$(\bar{3}.\bar{3}.\bar{1}1)$.358	0.875	73	>	$(\bar{7}39)$.343	0.875	7
$(\bar{7}39)$.343	0.875	23	>	$(\bar{3}.\bar{3}.\bar{1}1)$.358	0.875	73
$(\bar{3}.\bar{3}.\bar{1}3)$.385	0.755	45	>	(959)	.380	0.755	23
(959)	.380	0.755	23	>	$(\bar{3}.\bar{3}.\bar{1}3)$.385	0.755	23
(195)	.356	0.996	7	\cong	$(\bar{7}73)$.354	0.996	73
(195)	.356	0.996	7	>	$(\bar{7}73)$.354	0.996	45
(997)	.341	0.710	23	>	$(11.\bar{3}.\bar{9})$.342	0.710	45
$(11.\bar{3}.\bar{9})$.342	0.710	73	>	(997)	.341	0.710	23

These comparisons lead to the following intensity relationships:

$$10.4(\bar{3}.\bar{3}.\bar{1}1) > (\bar{7}39) > 3.2(\bar{3}.\bar{3}.\bar{1}1) \quad 10.4(\bar{7}73) > (195) > 6.4(\bar{7}73)$$

$$2(\bar{3}.\bar{3}.\bar{1}3) > (959) > (\bar{3}.\bar{3}.\bar{1}3) \quad 3.2(11.\bar{3}.\bar{9}) > (997) > 2(11.\bar{3}.\bar{9}).$$

The plotted intensities of Laue reflections in figure 5 show that u must lie between 0.243 and 0.245. Taking u as 0.244 ± 0.001 , the osmium-bromine separation in the complex is $2.51 \pm 0.01 \text{ \AA}$. Subtracting from this the normal electron-pair bond radius for bromine, 1.14 \AA , the octahedral electron-pair bond radius of quadrivalent osmium was found to be $1.37 \pm 0.01 \text{ \AA}$.

The author is indebted to Dr. O. L. Sponsler of the University of California at Los Angeles for the use of apparatus employed in preparing the powder photograph of potassium bromosmate and to Dr. S. Weinbaum of this Institute for much helpful advice throughout the present work.

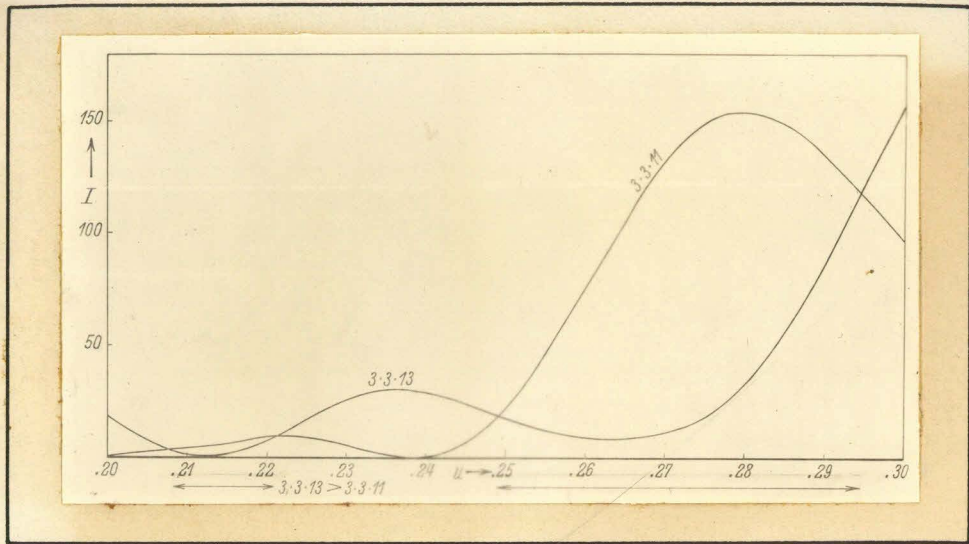
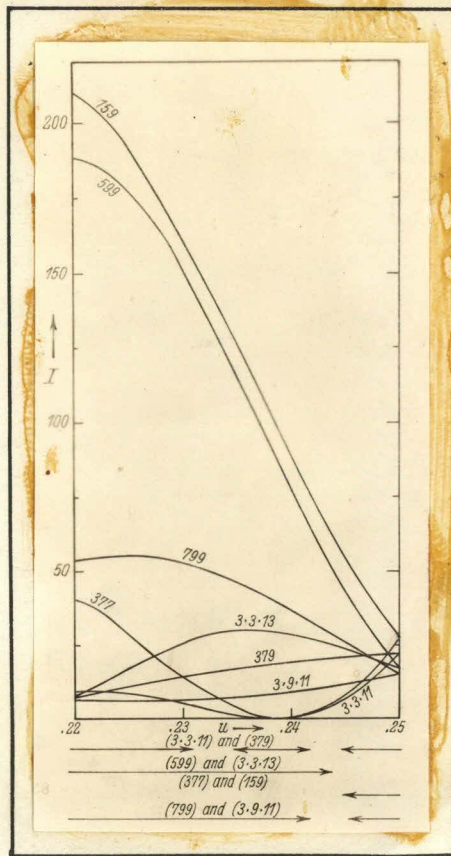


FIGURE 4



Calculated intensities
of some Laue reflec-
tions of K_2OsBr_6 as
functions of the bromine
parameter, u .

FIGURE 5

Summary.

With the aid of Laue and oscillation photographs, potassium chlorosmate and potassium bromosmate have been shown to have the ammonium chloroplatinate structure. The edge of the unit cube was found to be $9.729 \pm 0.02 \text{ \AA}$ for potassium chlorosmate and $10.30 \pm 0.03 \text{ \AA}$ for potassium bromosmate. The halogen parameters were found to be 0.243 ± 0.002 and 0.244 ± 0.001 respectively. These values give an osmium-chlorine separation of $2.36 \pm 0.02 \text{ \AA}$ and an osmium-bromine separation of $2.51 \pm 0.01 \text{ \AA}$ in the complexes. Subtracting the normal electron-pair bond radius for the halogen in each case, the octahedral electron-pair bond radius for quadrivalent osmium is found to be $1.37 \pm 0.02 \text{ \AA}$ in K_2OsCl_6 and $1.37 \pm 0.01 \text{ \AA}$ in K_2OsBr_6 .