AN X-RAY STUDY OF SILVER IODIDE

by

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STATEMENT BY AUTHOR

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APPROVAL BY THESIS DIRECTOR

This thesis has been approved on the date shown below:

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Professor of Chemistry

June 14, 1962
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Owing to the economic factors involved, field studies on the use of silver iodide as a nucleating agent in the "seeding" of supercooled water vapor (clouds) have proceeded so rapidly that much desirable laboratory work has remained undone. The original reasoning behind the choice of silver iodide as a possible nucleating agent for the "condensation" of water vapor involved the close similarity between the hexagonal ice structure and the hexagonal silver iodide structure. More recently, however, it has been suggested that this close similarity in structure is not a necessary condition for the effectiveness of a substance as a nucleating agent. (16) The most recent work in this field seems to indicate that the nucleation of ice can be initiated preferentially at grain boundaries or defect sites (8).

One of the problems which was investigated during the course of the present study involved the preparation of silver iodide of relatively small crystallite size; these samples might ultimately be used to observe the effect of grain boundaries on the increase in the number of high energy surface sites as determined by gas adsorption. The preparation of samples of relatively high surface area was also desirable since such material was to be used later in gas adsorption experiments. If small crystallites of silver iodide could be prepared, it was
important that factors affecting their further growth be examined.

A method for the determination of the polymorphic forms of silver iodide was needed to help characterize the different samples produced. Methods to measure the degree of disorder and the crystallite size of different samples needed to be applied to the case of silver iodide in order to further characterize the various samples.
INTRODUCTION

Silver iodide is said by some authors to exist in two crystalline modifications at room temperature. One form is cubic (the \( \gamma \) form) and has the zinc blende structure. (21) The other form is hexagonal (the \( \beta \) form) and has the wurtzite structure. (9) It is generally stated that the cubic form predominates when the salt is produced by any method which leads to a silver excess during the preparation. (21) Conversely, the presence of an iodide or iodine excess during the preparation is said to yield a compound which is predominately hexagonal silver iodide. (3)(14)

The temperature stability regions of these two polymorphs have been extensively discussed. (12)(15)(21) The hexagonal polymorph is considered the stable form at room temperature and atmospheric pressure since all crystals of silver iodide which have been grown slowly under these conditions have the hexagonal structure. (9)(21) The fact that cubic silver iodide can be converted to the hexagonal form at temperatures above \( 134^\circ \text{C} \) is taken as rather shaky evidence that the hexagonal polymorph is the more stable form. (15)(21) No occurrences of a transformation from hexagonal to cubic silver iodide have been recorded. In addition, no pure cubic silver iodide has yet been prepared although Pruppacher (18) has made silver iodide which is said to be 98% cubic.

Above \( 146^\circ \text{C} \), silver iodide exists in a body centered
modification (the $\alpha$ form) in which the silver ion is reported to have considerable mobility. (21) If the body centered silver iodide is allowed to cool slowly it will transform to the hexagonal modification below 146 °C. (21) If, on the other hand, the $\alpha$ form is rapidly quenched to room temperature the silver iodide resulting will be primarily the $\gamma$ form. The formation of the $\gamma$ form by quenching has been attributed to strain energy by some investigators (21) who note that any process which introduces strain appears to produce the cubic modification.

The room temperature structures of silver iodide are representative of a cubic close-packed and a hexagonal close-packed array commonly found in metals. In the case of silver iodide the close-packed layers are made up of the iodide ions, the silver ions occupying the voids between the iodide ions. The smallest repeat distance in the cubic silver iodide would be three of these close-packed layers. This type of repeat is commonly denoted $... $ABCA... $. The hexagonal repeat occurs every two layers and is represented by the series $... $ABAB...$.

It has been shown for a number of substances exhibiting polymorphism of this nature that it is possible to have a repeat distance which is some integral multiple of the repeat in the hexagonal close-packed structure. (20)(23)(27) These stacking polymorphs, or polytypes as they are called, have been demonstrated to occur in zinc sulphide (17) and silicon carbide (19). It has been mentioned that polytypes of silver iodide actually exist (12)
Although no conclusive proof for such existence has yet been given.

Just as it is possible to have stacking polymorphism in a close-packed structure it is also possible that the stacking of the layers will have no definite repeat distance. This type of stacking has been observed for the metal cobalt and has been extensively investigated by Edwards and Wilson (7)(28). Random stacking or disorder of this nature appears to have been observed in silver iodide prepared under certain experimental conditions during the present investigation.

X-ray diffraction procedures provide a method for the qualitative and quantitative analysis of polymorphs. The characteristic diffraction lines for two polymorphs usually provide a means of identification while the relative intensities of these characteristic lines provide a quantitative measure of the amount of each polymorph in the mixture. Theoretical powder patterns over a limited 2θ region which might be expected for pure γ and pure β silver iodide are shown in Figures 6 & 7. If one assumes that any mixture analyzed contains only these two polymorphs it is possible to obtain a quantitative measure of the amounts of each one. A more detailed explanation of the method used in this investigation is given in the discussion.

The width at half maximum intensity of an X-ray diffraction peak can be used as a measure of the crystallite size of a powder (11). This method is most useful for crystallites smaller than 1200 Å.
EXPERIMENTAL

X-ray Data

All experimental X-ray diffraction work undertaken in this investigation was performed on a Norelco X-ray diffractometer and basic unit with current stabilization. A copper X-ray tube and nickel filter were used in all cases. The tube was run at 30 KV and at 15 to 25 ma. as circumstances warranted. The diverging slit was 1°, the receiving slit 0.006". A scintillation counter was used as detector. The sample holders used were of aluminum with a rectangular cavity. The powders were mounted in the sample holder by a method very similar to that of McCreery as described in Klug and Alexander. (11)

In order to produce easily measured traces the diffractometer was allowed to scan the sample at a rate of 1/8° of 2θ per minute. The results of a scan were displayed on a recorder whose integration time constant was set at 8. The areas under the peaks traced out by the chart recorder were measured with a K&E model 14236 planimeter. All measurements of the peak width at half maximum intensity were made on patterns which had been produced in an identical manner.

Preferred Orientation

The X-ray diffraction techniques used in this investigation had the disadvantage of introducing certain preferred orientation effects. These effects were produced when the silver iodide powder
(generally composed of flat platelets) was compressed in the sample holder. The platelets tended to line up in the holder so that the plane of the plate was normal to the line of applied force. Thus the platelets tended to be oriented in such a manner that certain planes were favored in the diffraction process. This preferred orientation caused the diffracted intensity from the oriented planes to be relatively higher than the intensity which would have been expected if the powder had been randomly oriented. It would have been possible to overcome certain preferred orientation effects caused by powders having certain shapes by using various packing techniques or by causing the sample to move. (11) It has been found, however, that these methods are of limited value for a powder made up of flat platelets as is the case for silver iodide. (13)

Manson (13) devised a method of eliminating preferred orientation effects for plate-like substances such as silver iodide which have high absorption and scattering factors. Manson first made successive dilutions of the silver iodide powder with a non-scattering gum. He then plotted the ratio of the intensities of a diffraction peak affected by preferred orientation to the intensity of a peak not visibly affected as a function of the effective density of the silver iodide in the sample. An extrapolation of the resulting curve to zero density of silver iodide in the sample gave the intensity ratio which would result in the absence of any preferred orientation effects.

Manson was able to show that there was a preferred orientation effect in both of the samples he studied and that this orientation
could be eliminated by diluting the samples with gum tragacanth. It was found that the experimental curve (similar to Figure 1) approached the extrapolated value for silver iodide at concentrations as high as $2/3$ gum tragacanth to $1/3$ silver iodide by weight.

The two samples Manson worked with were probably rather coarse by X-ray standards (they probably possessed a good percentage of grains larger than 25 microns). Although it seems reasonable to expect that the effects of any preferred orientation would decrease as the grain size decreased it would seem prudent to attempt to eliminate the preferred orientation effect in all the measurements. For this reason Manson's work was repeated for the region of low silver iodide concentration using silver iodide prepared in this laboratory.

A sample of silver iodide which had been prepared with a silver excess was dried in an oven at ca. 100 °C for two hours. The sample was then ground in a porcelain mortar to pass through a 140 mesh screen. It was then returned to the oven and heated two more hours at the same temperature. The sample was allowed to cool slowly in a desiccator after which it was passed through a 300 mesh screen without further grinding. These steps were followed in an attempt to obtain a finely divided sample with no clumps or cakes. The sample was stored in a bottle covered with light tight paper and dried further in a vacuum desiccator.

Four concentrations of silver iodide in gum tragacanth were prepared from the sample discussed above. The mixtures were prepared by weighing out quantities of silver iodide and gum into pyrex
Manson related the ratios of integrated intensity with what he termed the partial density. The partial density is defined as

\[ p^* = \frac{dm}{v} \]

where

- \( p^* \) is the partial density
- \( d \) is the weight fraction of silver iodide
- \( m \) is the mass of the packed powder
- \( v \) is the volume of the cavity which the powder fills

<table>
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<tr>
<td>Weight Fraction</td>
<td>0.143</td>
<td>0.322</td>
<td>0.450</td>
<td>0.597</td>
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</table>
vials. The vials were then gently rotated along their long axis to mix the two powders. More vigorous mixing later on a Wig-L-Bug blender failed to show any significant difference in the final results. Portions of the samples were placed in a sample holder and run on the diffractometer.

The ratios of the integrated intensities of two diffraction peaks were then plotted as a function of the effective or partial density of the powder as shown in Figure 1. One peak (10\bar{1}0) was not appreciably affected by preferred orientation while the other (0002) was the peak most affected. It can be seen from the graph that the intensity ratios tend to reach a constant value in the region of low silver iodide concentration thus indicating that preferred orientation effects have been eliminated. These measurements tend to confirm Manson's results which showed the preferred orientation to be so small for a mixture of \( \frac{2}{3} \) gum tragacanth and \( \frac{1}{3} \) silver iodide by weight that there is no need for an extrapolation to zero AgI concentration.

**Preparation of Silver Iodide Under Pressure**

The possibility of the preparation of pure \( \gamma \) silver iodide at elevated pressures has been postulated by some investigators. (4) The pressure increase was produced in past experiments either by grinding or by the use of a pellet press with the result that hexagonal silver iodide treated in this manner showed an apparent increase in cubic character. (4) Other investigators working on zinc sulphide have shown that grinding the cubic form appears to give it a certain amount of hexagonal character while grinding the hexagonal form appears to make it more cubic. (25) It has been
shown by Smith (25) that grinding serves to induce disorder in both polymorphs and that if the solids are ground for a sufficiently long time both end members tend to achieve the same disordered state. This provides an answer to the phenomena produced when silver iodide is ground but does not account for the results obtained with the pellet press.

After investigating the effects of preferred orientation in silver iodide this investigator became convinced that the so called pressure effects brought about by the pellet press might possibly be attributed to preferred orientation. In order to test this theory an experiment was designed to produce pressure while the silver iodide was being formed from solution. In this manner a finely divided precipitate would result which could be dried and then diluted with gum to eliminate all preferred orientation effects.

Solutions were prepared which were 0.10 molar in reagent grade silver nitrate and potassium iodide. An 8 inch test tube was placed in a dry ice-acetone bath and 25 ml. of the potassium iodide solution were added. When this had completely frozen 4 ml. of distilled water were added, one ml. at a time, to act as a reaction barrier. When the fourth ml. of water was completely frozen 20 ml. of the silver iodide solution were slowly added to the tube, care being taken to see that the silver nitrate solution was added slowly enough to avoid destroying the ice barrier. When the silver nitrate solution became completely frozen the test tube was removed from the cold bath and placed in an Aminco pressure bomb. The
bomb was sealed and pressure was built up by means of nitrogen pressure from a tank of dry nitrogen. Runs were made at 325 ± 15 psig. and 1000 ± 35 psig., the pressure being maintained until all the solutions had melted and reacted. A control tube was allowed to react in a darkroom to provide a sample which had formed at atmospheric pressure. The resulting precipitates were collected on sintered glass funnels, washed thrice with 20 ml. portions of distilled water and then twice with 20 ml. portions of 95% ethanol. Drying was accomplished by drawing room air through the samples with a water aspirator. It was found that extensive caking of the precipitates could be avoided if they were mixed with the diluent of gum tragacanth before they become completely dry.

The dried samples and gum were run on the diffractometer. Comparison of the intensities of the resulting patterns showed that there was no significant difference in cubic character between either the control and the reaction run at 325 psig. or between the control and the reaction run at 1000 psig. The control tube produced silver iodide that was mostly hexagonal in character.

One must conclude therefore that the effect of a non-directional pressure on the formation of silver iodide is negligible over the range studied. This would seem to indicate that the effect of the directional pressure on the silver iodide from a pellet-type press may have induced a good deal of preferred orientation which led to the mistaken conclusion that the sample had increased in cubic character.

**Silver Iodide Formation In Non Aqueous Systems**

The investigation of silver iodide with which this paper
is concerned will eventually consider the effect of water vapor on the rate of growth of silver iodide crystallites. Needless to say, there would be a distinct advantage to any investigation which could start with silver iodide which had never "seen" water. The further advantages of such material for use in the measurement of the adsorption of water vapor by silver iodide are also obvious. It was for these reasons that it was thought desirable to attempt to prepare silver iodide in a finely divided state without at any time exposing the silver iodide to aqueous solutions.

Precipitation of Silver Iodide From Ethanol

A search for solvents in which the solubilities of silver nitrate and ammonium iodide would be sufficient to yield appreciable amounts of silver iodide on mixing disclosed that ethyl alcohol was a possible solvent. The solubility of silver nitrate in ethanol, 0.83 mole percent at 19°C. (31), was the factor that limited the concentration of the solutions that could be used. One product from a reaction of silver nitrate and ammonium iodide, the silver iodide, has a solubility of $6.3 \times 10^{-19}$ mole percent (31) in ethanol while the other product, ammonium nitrate, has a solubility of 2.16 mole percent at 20°C. (31)

A solution of 1.77 g. silver nitrate in 114.2 g. ethyl alcohol was prepared. Another solution with 1.61 g. ammonium iodide in 100.5 g. ethyl alcohol was also prepared. Only reagent grade chemicals were used; the absolute ethanol came from a previously unopened bottle. The solutions were prepared in screw cap pyrex jars whose lids were kept in place except when additions were
made. After the reactants had dissolved, the ammonium iodide solution was placed in a 400 ml. beaker and stirred rapidly with a Brockenfield counterrotating stirrer while the silver nitrate solution was added. The temperature of both solutions was 28°C. The precipitate was collected on a sintered glass filter and thoroughly dried in a vacuum desiccator.

The resulting powder was mixed with gum tragacanth and examined on the X-ray diffractometer. The results of the diffractometer trace showed that there was no appreciable broadening of the peaks other than that due to the diffractometer. This indicated that the crystallite size of the powder was in excess of 1500 Å.

**Precipitation of Silver Iodide From Iodide Complexes in Ethanol**

It had been previously observed that ammonium iodide was very soluble in absolute ethanol. It was also known that silver iodide could form complex species in the presence of excess iodide ion. (21) If a solution of complexed silver iodide could be rapidly diluted it appeared possible that a finely divided precipitate of silver iodide would result. It seemed possible that silver iodide prepared in this manner might have the small crystallite size and high surface area desired.

To test the theory above 20.0 g. of reagent grade ammonium iodide were dissolved in 350 ml. of absolute ethanol. Next 5.0 g. of dry silver iodide which had been prepared from aqueous solutions of reagent grade silver nitrate and potassium iodide with an iodide excess were dissolved in the solution of ammonium iodide. The
resulting solution was then added rapidly to 1000 ml of "absolute" ethanol which was being vigorously stirred. Noticeable precipitate appeared after a few minutes. The precipitate was filtered on a sintered glass filter and then further dried in a vacuum desiccator. The dried precipitate did not stick together but gave a fine, freely flowing powder.

A krypton surface area measurement made on this silver iodide by N. Storm (26) indicated a surface area of 0.3 square meters per gram. An X-ray diffraction pattern showed that the crystallite size of this material was in excess of 1500 Å.

Preparation of Silver Iodide by the Decomposition of KAg$_3$I$_4$

The compound KAg$_3$I$_4$ has been recently discussed by Burley (3). If this compound could be decomposed very rapidly it was thought that silver iodide with a small crystallite size might possibly be one of the products of the decomposition.

KAg$_3$I$_4$ was prepared by thoroughly mixing 1.7 g. of reagent grade potassium iodide and 7.0 g. of silver iodide; the silver iodide had been prepared from aqueous solutions of reagent grade silver nitrate and potassium iodide with an excess of the potassium iodide solution. The silver iodide and potassium iodide were mixed intimately in a pyrex test tube and heated slowly over a Meker burner. The mixture first turned a rosy red and then began to melt. There was no detectable liberation of iodine (it could not be detected by sight or smell) at any time during the heating. The compound which resulted (KAg$_3$I$_4$) became silver tan in color after cooling to room temperature. The solid was easily powdered and gave
a diffraction pattern quite different from either potassium iodide or silver iodide. The compound was quite soluble in acetone. (It is possible that the compound decomposed in the acetone to give a solution of the iodide complex of silver iodide.) When 200 ml. of acetone containing 2.0 g. of the compound were added to 500 ml. of absolute ethanol, silver iodide was precipitated. The silver iodide was filtered on a sintered glass funnel and dried in a vacuum desiccator. An X-ray diffraction pattern showed that the silver iodide produced from the KAg$_3$I$_4$ was made up of crystallites larger than 1500 Å.

**Preparation of Silver Iodide From Ammine Complexes**

Investigation of complex salts of ammonium iodide and silver iodide analogous to KAg$_3$I$_4$ was started with the idea that thermal decomposition of the ammonium complex might yield the type of silver iodide desired. It was suggested (5) that it might be simpler to try to prepare an ammine complex of silver iodide and then decompose it to yield finely divided silver iodide. J. T. Yoke (30) had noted previously that some compounds "puffed up" to many times their initial volume on decomposition of their ammine complex. It was hoped that this phenomena might occur in the case of silver iodide.

The system used in the preparation of the ammine complexes is illustrated in Figure 2. It consists of (a) a combination mercury manometer and safety valve, (b) a reaction vessel in which the silver iodide and ammonia could be reacted, (c) a drying vessel in which the ammonia could be dried over sodium before being introduced into the reaction vessel, (d) a gas inlet and blow tube and (e) a
FIGURE 2

SYSTEM FOR THE PREPARATION OF SILVER IODIDE-AMMINE COMPLEXES
liquid nitrogen cold trap to prevent any oil from the fore pump from entering the system. The trap also prevented any ammonia from being pumped through the fore pump.

The silver iodide used in the investigation of the ammine complexes was prepared from reagent grade silver nitrate and potassium iodide. Two tenths of a mole of silver nitrate were dissolved in one liter of water while 0.243 moles of potassium iodide were dissolved in 502 g. of water. The potassium iodide solution was stirred with a Brookfield counterrotating stirrer and heated to boiling on a hot plate. The silver nitrate was added rapidly through a 1500 ml. dropping burette. The silver iodide was filtered on a sintered glass funnel and washed four times with 50 ml. portions of distilled water. The sample was then washed twice with 50 ml. portions of 95% ethanol after which it was dried in a vacuum desiccator. No attempt was made to eliminate the last traces of water by heating the sample. This precaution should be taken in a more detailed investigation.

The silver iodide described above served as the starting material for the preparation of silver iodide by the ammine complex method. A dried sample of silver iodide was introduced into the sample bulb. At the same time a small pellet of sodium which had been washed free of kerosene with ethanol was placed in the drying bulb. The system was then evacuated and pumped continuously for four or five hours. At this time the stopcock leading to the sample bulb was closed, the drying tube was immersed in a dry ice-methanol bath and ammonia was admitted to the system through the inlet stopcock. (The tube through which the ammonia was admitted had been
evacuated prior to this time) The liquid ammonia was distilled into the drying vessel and allowed to remain in contact with the sodium at dry ice-methanol temperature for 3 or 4 hours. The ammonia was then distilled over onto the sample of silver iodide. The silver iodide changed color from yellow to white as the ammine complex was formed. It was found that the complex would dissolve in any excess liquid ammonia when the reaction vessel was warmed slightly. This dissolution insured that the silver iodide was all converted to the ammine complex. The reaction vessel was then opened to the vacuum pump; the ammonia was then pumped off and caught in the liquid nitrogen trap. As the excess ammonia was removed the white ammine complex reappeared. After most of the ammonia had been pumped off the sample took on the yellow color of silver iodide. This total decomposition of the ammine complex was expected from a consideration of the stability diagrams of Biltz and Stollenwerk (1).

The fully evacuated sample appeared as one solid lump in the bottom of the reaction vessel. When the reaction vessel was tapped lightly with a length of rubber tubing the lump of silver iodide broke up into a fine powder. If the sample was tapped before all of the ammonia had been pumped off the ammonia escaping from the interior of the lump was sufficient to sweep surprisingly large quantities of the fine powder out into the manifold of the vacuum system.

Two different types of silver iodide were obtained from the ammine complex method. The varieties produced were dependent on the manner in which the complex was allowed to decompose. If the complex
was prepared with a large excess of ammonia and then simply evacuated as described above, the resulting silver iodide gave a diffraction pattern like that of Figure 3. If, on the other hand, the excess liquid ammonia was kept to a minimum the resulting solution would solidify when cooled back down to dry ice-methanol temperatures. This was probably due to the decreased solubility of the ammine complex in ammonia at these low temperatures. Evacuation was started on the frozen solution before the cold bath was removed. The cold bath was then removed and the evacuation allowed to proceed to completion. In this manner the ammonia was "sublimed" directly with a minimum amount of liquid ammonia being formed. The silver iodide formed in this manner yielded a diffraction pattern such as that in Figure 4. The silver iodide formed by the sublimation process was noticeably more yellow than that formed by the other ammine complex method.

Inspection of the diffraction patterns of the two types of silver iodide produced by the ammine complex method showed that the sample produced by the sublimation method (Fig 4) had certain peaks which were quite sharp and others which appeared to be broadened. This preferential broadening was attributed to a random disorder in the stacking of the layers in the hexagonal structure. Further consideration of this phenomena will be found in the discussion.

The surface area of a sample prepared by the sublimation of the ammine complex of silver iodide was found to be 0.6 square meters per gram by N. Storm (26). The degassing qualities of this sample were reported to be far superior to any precipitates which
DIFFRACTION PATTERN OF SILVER IODIDE PREPARED BY THE AMMINE COMPLEX METHOD

Bragg Angle (Degrees 2θ)

(0002)

(1010)

(1011)
DIFFRACTION PATTERN OF SILVER IODIDE PREPARED BY THE AMMINE COMPLEX METHOD
had previously been prepared in the laboratory (26).

The crystallite size of the sublimed samples was determined by measuring the half width of the 0002 peak. The measured half width indicated that material prepared in the manner described above had a crystallite size ca. 650 Å which would make it suitable for use in the measurement of rates of crystallite growth.

**Spray System**

In an attempt to produce still smaller crystallites of silver iodide a system was designed to spray a liquid ammonia solution of the silver iodide-ammine complex into a decomposition chamber and then collect the silver iodide after the complex had been decomposed. According to the work of Biltz and Stollenwerk (1) the complex would decompose at room temperature if the partial pressure of ammonia in the decomposition chamber was less than 50 mm. of mercury.

The system which was finally used consisted of a spraying device, a decomposition chamber and an electrostatic precipitator to collect the final product. The decomposition chamber was made from a cylindrical tube of sheet aluminum 14 inches in diameter and 4 feet long. Both ends of the tube were covered with polyethylene sheeting; the sheeting had been previously provided with connections to fit the spray gun and the electrostatic precipitator. The tube was painted both inside and out with black Tygon paint.

When a run was to be made the Sharp Model #25 spray gun containing the ammine complex dissolved in liquid ammonia was placed at one end of the decomposition chamber. At the other end of the
chamber the electrostatic precipitator (see Figure 5) was placed in position so that the fine particles of silver iodide escaping from the decomposition chamber would become trapped in the precipitator.

The precipitator was connected to a 15 KV transformer which was connected to a 110 volt line through a Variac. It was found that a voltage of 60 volts on the Variac gave the highest collection efficiency on the precipitator. As the powder was collected on the center wire of the precipitator some of it fell into the collection chamber below; the remainder was collected by tapping the center wire after the gas flow had ceased. The material collected from the collection chamber was placed in a sample jar and kept in a vacuum desiccator.

Two preliminary runs were made with the spray system described above. These runs showed that the decomposition chamber did not have a large enough diameter to allow time for all of the ammonia to evaporate from the liquid droplet before the droplet struck the side of the decomposition chamber. Consequently most of the final product was found adhering to the sides of the decomposition chamber. Furthermore, much of the smoke which did pass into the electrostatic precipitator continued on through it; this indicated the need for a more efficient precipitator. It was also found that the temperature of the decomposition chamber would have to be controlled to some extent in order to cause the decomposition of the solid ammine complex.
FIGURE 5

ELECTROSTATIC PRECIPITATOR

30 mil Tungsten Wire

Rubber Stopper

Exhaust 25 mm.

25 mm OD. Collection Tube

Aluminum Foil 37 mm. long

To Transformer

Entrance 38 mm.

Collection Tube Bottom View

Collection Chamber
DISCUSSION

The calculation of the intensity of lines of a powder diffraction pattern is based on the equation (6)

\[ I = \left| \frac{|F|^2 L p'' \exp(-B\sin^2\theta/\lambda^2)}{\sqrt{\lambda}} \right| \left[ I_o e^{\frac{4\pi m^2 c^2}{\lambda^3}} \cos^2 \theta \right] \]

\[ I_o e^{\frac{4\pi m^2 c^2}{\lambda^3}} \cos^2 \theta \]

where 

- \( I \) is the integrated intensity.
- \( |F| \) is the resultant amplitude of the radiation diffracted by a unit cell of the substance in question with reference to the amplitude of one electron.
- \( L \) is the Lorentz-polarization factor \((1 + \cos^2\theta)/\sin^2\theta \cos\theta\).
- \( p'' \) is the multiplicity.
- \( \exp(-B\sin^2\theta/\lambda^2) \) is the temperature factor.
- \( V \) is the volume of the unit cell of the substance under investigation.
- \( I_o \) is the intensity of the incident beam of X-radiation.
- \( e \) is the charge on the electron.
- \( \lambda \) is the wavelength of the incident radiation.
- \( A \) is the cross sectional area of the incident beam which strikes the sample.
- \( m \) is the mass of the electron.
- \( c \) is the velocity of light.
- \( r \) is the radius of the diffractometer circle.
- \( u \) is the linear absorption coefficient of the compound or mixture under investigation.

For a given experimental setup the second term in Equation (1)
becomes a variable in \( u \) only. For a set of polymorphs \( u \) is constant and Equation (1) becomes

\[
I = K \frac{F^2 L p'' \exp(-B \sin^2 \theta / \lambda^2)}{\nu^2} \tag{2}
\]

If the structure of a compound is known it is possible to use this equation to calculate the intensities of a series of hkl reflections which might be expected to occur on a powder diffraction diagram. Taking the case of hexagonal silver iodide as an example, one would begin by considering the atom positions for the compound. For \( \beta \) silver iodide these parameters are:

For silver iodide these parameters are:

\[
\begin{array}{ccc}
x & y & z \\
0 & 0 & 0 \\
0 & 0 & 0.63 \\
1/3 & 2/3 & 1/2 \\
1/3 & 2/3 & (1/2 + 0.63)
\end{array}
\]

To calculate the intensity of the 10.0 reflection one would first calculate

\[
|F|^2 = \left[ \sum f_{\text{Ag}} \cos{2\pi(hx+ky+lz)} + \sum f_{\text{I}} \cos{2\pi(hx+ky+lz)} \right]^2 \\
+ \left[ \sum f_{\text{Ag}} \sin{2\pi(hx+ky+lz)} + \sum f_{\text{I}} \sin{2\pi(hx+ky+lz)} \right]^2 \tag{3}
\]

(6) where \( f_{\text{Ag}} \) and \( f_{\text{I}} \) are the atomic scattering factors for silver and iodine respectively for a particular value of \( \lambda \) and \( \theta \).

In the solution of Equation (2) a value for \( L \) can be obtained from tables (32); values of \( p'' \) are also available (10). A value for \( V \) can be obtained from a knowledge of the unit cell dimensions of the compound. The temperature factor has been taken as unity in this investigation for reasons explained later. Since the value of \( K \) will remain constant for samples investigated under identical experimental conditions it need not be calculated. The final equation then becomes (for \( \beta \) silver iodide)
This process may be repeated for as many reflections as is desired.

Figures 6 and 7 show some theoretical intensities for powder patterns of cubic and hexagonal silver iodide. These intensities were calculated on the assumption that the cubic silver iodide possesses ideal cubic close-packing and that the hexagonal polymorph possesses perfect hexagonal close-packing.

If both of the silver iodide polymorphs mentioned above were to be present in a given powder the intensity relationships for the reflections would be found to be different from the intensities for the pure polymorphs. Figure 3 shows the intensities observed for the first three reflections of a silver iodide powder made by the ammine complex method. Notice that the 00.2 peak is more intense than would be predicted for pure hexagonal silver iodide. The presence of appreciable 10.0 and 10.1 intensities proves that the powder is not pure cubic silver iodide.

It happens that the 00.2 hexagonal peak and the 111 cubic peak occur at exactly the same value of 2θ. This is due to the fact that the interplanar distance remains the same perpendicular to the stacking direction for both the cubic and hexagonal closest packing. Thus, if pure hexagonal silver iodide is mixed with pure cubic silver iodide the intensities of the 00.2-111 peak will be increased relative to the intensities of the peaks on either side which have no cubic contribution. This is what has happened to

\[ I_{10.0} = K \frac{7.814 \times 50.25 \times 6 \times 1}{(137.1)^2} = 125K \]
Calculated Intensity of Cubic AgI
As a Function of Bragg Angle
Calculated Intensity of Hexagonal 2H AgI
As a Function of Bragg Angle
the pattern described in the preceding paragraph.

Since the reflection 00.2-111 does have an intensity contribution from two different polymorphs its intensity may be written

\[ I_{00.2-111} = K R_{00.2} \beta + K R_{111} \gamma \]  (5)

where

\[ R = \int_0^2 p \exp(-B\sin^2\theta/\lambda^2) / \pi^2 \]  (6)

and where \( \beta \) and \( \gamma \) are the volume fractions of the two polymorphs.

The intensity of the 10.0 hexagonal peak would of course be given by

\[ I_{10.0} = K R_{10.0} \beta \]  (ref. 6)

The ratio of the intensities of the two lines would then lead to the relation

\[ \frac{\gamma}{\beta} = \frac{I_{00.2-111} R_{10.0}}{I_{10.0} R_{111}} = \frac{R_{00.2}}{R_{111}} \]  (8)

Substitution of the calculated values for the values of \( R \) gives

\[ \frac{\gamma}{\beta} = \left( \frac{I_{00.2-111}}{I_{10.0}} \right) 0.425 - 0.234 \]  (9)

which is an equation relating the integrated intensity of the two diffraction lines to the proportions of the polymorphs producing these lines. The relation

\[ \gamma + \beta = 1 \]  (10)

then allows the direct calculation of the composition of the mixture.

It is easily seen that the temperature factor may be neglected if the two peaks selected for the analysis appear at values of \( \theta \) which are nearly equal. If the peaks chosen appear at low values
of \( \theta \) the temperature factor will be very close to one and may
likewise be neglected.

Computation of the composition of the sample prepared by
the ammine complex method yields the following

\[
\frac{I_{00.2-111}}{I_{10.0}} = 1.65 \pm 0.08 \quad \text{(measured from diffractometer trace)}
\]

\[
c_{\gamma}/c_{\beta} = 0.70 - 0.23 = 0.47 \pm 0.03
\]

\[
c_{\beta} = 0.68 \pm 0.04
\]

The analytical treatment described in the last section is
strictly valid if and only if the structures of the cubic and
hexagonal polymorphs are based on an idealized close packing of
spheres. This is not strictly true for silver iodide (8) but the
theoretical intensities calculated on this basis and the resulting
analytical expressions can easily be changed if the structures
of the two forms are ever further refined. The last section
also ignores the possible presence of polytypes and their effect
on the analytical scheme. As mentioned previously polytypes are
quite common in the case of zinc sulphide and silicon carbide.
The presence of polytypes would be expected to make the analysis
of diffraction data for silver iodide more difficult, although
F. G. Smith has stated that this is not strictly the case for
zinc sulphide polytypes (23). He stated that a method similar to
that of the last section can be used for all mixtures of zinc
sulphide, even those containing polytypic zinc sulphide (23).
Smith later made some calculations which showed, to his satisfaction,
that "although the method is not quantitative in the case of those
polytypes which are near the hexagonal end and have small \(c\)-periods
the systematic departures from the calculated curve get less as 
\( c \) increases" (24).

Theoretical X-ray diffraction patterns were calculated for 
two polytypic structures of hexagonal silver iodide, 4H (with a 
repeat distance twice that of \( \beta \) or 2H silver iodide) and 6H (with a 
repeat distance three times that of 2H silver iodide). The 
structures of these compounds were derived assuming close packing 
of spheres.

If the repeating unit for the 4H silver iodide is \(...ABAC...\)
the atom positions can be represented by

\[
\begin{array}{ccc|ccc}
\text{Ag} & & & & I \\
0 & 0 & 0 & x & y & z \\
1/3 & 2/3 & 1/4 & 1/3 & 2/3 & 0.315 \\
0 & 0 & 1/2 & 0 & 0 & 0.815 \\
2/3 & 1/3 & 3/4 & 2/3 & 1/3 & 1.065 \\
\end{array}
\]

Similarly, the coordinates for the 6H structure \(...ABCACB...\)
will be

\[
\begin{array}{ccc|ccc}
\text{Ag} & & & & I \\
0 & 0 & 0 & x & y & z \\
1/3 & 2/3 & 1/6 & 1/3 & 2/3 & 0.210 \\
2/3 & 1/3 & 1/3 & 2/3 & 1/3 & 0.377 \\
0 & 0 & 1/2 & 0 & 0 & 0.710 \\
2/3 & 1/3 & 2/3 & 2/3 & 1/3 & 0.877 \\
1/3 & 2/3 & 5/6 & 1/3 & 2/3 & 1.043 \\
\end{array}
\]

The intensities of a number of powder diffraction lines 
have been calculated using Equation 2 and the parameters above.
The results are shown in Figures 8 and 9.

Hexagonal or cubic character is attributed to this type of 
polymorph on the basis of the stacking within the layers. If a given 
layer is surrounded on both sides by similar layers, as is the case
FIGURE 8

Calculated Intensity of Hexagonal $^{4}$H Silver Iodide As a Function of Bragg Angle

$I_{\text{calc.}}$ vs. Bragg Angle (degrees $2\theta$)
FIGURE 9

Calculated Intensity of Hexagonal 6H AgI
As a Function of Bragg Angle
for β silver iodide (i.e. ...ABABAB... or ...hhhh...(1)), the layer is said to be hexagonal.(23) If the layer in question is surrounded on either side by unlike layers, as is the case for cubic silver iodide (i.e. ...ABCABC... or ...cccc...(1)), the stacking is said to be cubic. On this basis hexagonal 4H silver iodide would have 50% hexagonal packing (...ABAC... or ...chch...), while hexagonal 6H, with the stacking ...ABCAAB... or ...hchhc..., would possess 33 1/3 % hexagonal packing. If, as Smith proposed, the sum of the intensities of the lines from 10.0 up to but not including 00.1 (where l = 4 for 4H and 6 for 6H) are compared to 00.1 by the method of the last section, the resultant composition should be that predicted by the stacking sequence (i.e. 50% hexagonal for 4H silver iodide and 33 1/3 % hexagonal for 6H silver iodide). A calculation shows that the composition predicted by relating the theoretical intensities would be 55% hexagonal for the 6H silver iodide and greater than 100% hexagonal for the 4H silver iodide. There does not appear to be any simple relationship between the polytypes investigated and the hexagonal and cubic polymorphs.

It appears possible that the presence of certain unique diffraction peaks for the 4H and 6H polytypes would allow their identification if they were present in quantities greater than 25% for 4H and 15% for 6H silver iodide. In order to facilitate

(1) The notation "h" or "c" denotes layers which have hexagonal or cubic character (23).
this identification theoretical intensities should be calculated for a
greater number of diffraction lines. It would also be necessary to
calculate theoretical patterns and intensities for other possible
polytypes which might occur. There are a number of possible polytypes
which should be considered, some based on a hexagonal lattice, others
based on a rhombohedral lattice. The existing polytypes for zinc
sulphide and silicon carbide would serve as possible structures which
might be considered with reference to silver iodide.

Random Stacking

Edwards and Lipson (7) have discussed the effects attributed
to random stacking of layers in a polytypic substance. They observed
that the metal cobalt displayed varying amounts of cubic and hexagonal
character which were dependent on the previous history of the sample.
This dependence is also evident for silver iodide. Edwards and Lipson
also found that certain diffraction lines for cobalt were anomalously
broadened in a manner that could not be explained by consideration
of crystallite shape or size. They found that lines whose indices
obeyed the relationships

$$\frac{1}{3} (h-k) \text{ integral or } l = 0$$

were not broadened. A. J. C. Wilson (28) in a more mathematical
treatment, extended and modified the work of Edwards and Lipson, and
was able to relate the integral breadth of the broadened peaks to a
quantity he called $\alpha$ (the probability of a stacking fault). In
this manner Wilson was able to predict the frequency with which the
stacking faults occurred.

As stated previously some of the silver iodide prepared
during the course of this investigation was found to exhibit anomalous broadening of certain diffraction peaks. Figure 4 shows a partial powder pattern for this silver iodide. The only broadened peak shown here was 10.1 but other broadened peaks were found on the pattern. These broadened peaks were found to result for all reflections other than those with \( \frac{1}{3} (h-k) \) integral or \( l=0 \). Since the broadened peaks were identical with those noted by Edwards and Lipson for cobalt it appeared as if the silver iodide in question exhibited a random stacking sequence.

The 10.1 peak of the disordered silver iodide (Figure 4) was examined in the light of Wilson's analysis. It was found that the probability of a stacking fault was ca. 0.23. Thus a stacking fault would be expected to occur once in every four layers.

**Ammine Complex Method**

The preparation of silver iodide by the ammine complex method has several advantages over silver iodide prepared from aqueous solution. Probably the greatest advantage is that the method makes possible the complete elimination of water from the sample. The silver iodide could be prepared initially from the direct combination of silver and iodine and kept in a vacuum system until needed in the ammine complex method. The final sample from the ammine complex system could then be stored on a vacuum line until needed. The preparation of small crystallites of silver iodide which could be made to increase in size when heated would allow the correlation of crystallite size with other properties of the compound (such as surface area and surface activity). Preliminary experiments indicate that the
silver iodide prepared by the ammine complex method does not change its polymorphic composition on heating at temperatures up to 100 °C. The crystallite size, however, does increase at these temperatures. The crystallite size of an evacuated sample was found to have increased from ca. 650 Å to more than 1500 Å during a period of one hour at 100 °C. It is interesting to note that heating the disordered silver iodide (prepared by the sublimation of the solid ammine complex) at 100 °C. failed to alter the degree of disorder. The peaks which were indicative of random stacking in the compound were not changed even though the other peaks became much sharper, thus indicating an increase in crystallite size.

The spray system would appear to have a distinct advantage over the vacuum system of preparation. Although this investigation has not proceeded far enough to demonstrate the fact, the preparation of silver iodide by spraying the ammine complex into a decomposition chamber should lead to crystallite and particle sizes far less than those obtainable on the vacuum system. Not only would smaller crystallites and particles result but the spray system should allow control of the particle size if the concentration of the silver iodide in the liquid ammonia were regulated properly. Such a method of preparation of silver iodide smokes would be of great practical importance. The spray system is not without its disadvantages; the collection of the resulting smoke by means of an electrostatic precipitator exposes the sample to ultraviolet light. The effects of exposure of silver iodide to U.V. light have been studied. There are definite effects which have not yet been explained (4).

There does exist an apparent disadvantage to both the ammine
complex methods for the preparation of silver iodide. Birstein (2) has reported that ammonia is chemisorbed on silver iodide. If the silver iodide formed by the ammine complex method is to be used for surface studies it would seem wise to repeat Birstein's work on the chemisorption of ammonia on silver iodide.
CONCLUSIONS

Probably the best method to be used in the characterization of the polymorphic composition of silver iodide samples is to measure the integrated intensities of the 10.0 and 00.2-111 peaks. The intensities of these two peaks could be related to the composition of the sample if the observed intensities are compared with the theoretical intensities which might be expected for a mixture of hexagonal 2H and cubic 3C silver iodide. Although there is no definite evidence yet for the existence of polytypic structures of silver iodide it would be prudent to measure the integrated intensities of a number of other major lines (10.1, 11.0, 10.3, 11.2) in the event that further work on the polytype problem discloses methods which might require a knowledge of the intensities of these peaks for complete elucidation of the polymorphic and polytypic composition.

It appears that the ammine complex method of silver iodide preparation provides a convenient method for the preparation of powdered silver iodide of small crystallite size and relatively high surface area without the need of grinding or exposing the sample to water vapor at any time. Samples prepared by this method do not change in polymorphic composition on heating in vacuo at 100 °C, although there is a rapid increase in crystallite size at this temperature. There is no apparent change in crystallite size with time at room temperature.
Manson's observation that the tendency of silver iodide to exhibit preferred orientation effects when examined by X-ray diffractometer methods has been confirmed.
SUGGESTIONS FOR FURTHER STUDY

If the silver iodide prepared by the ammine complex method is to be used in studies of the surface properties of silver iodide, it would be desirable to investigate the possible effects of chemisorption of ammonia on the surface of the silver iodide.

The calculation of theoretical powder patterns for a number of possible polytypes of silver iodide would allow a better estimate of the degree of accuracy with which the polymorphic composition might be determined. Particular attention should be paid to characteristic lines which might allow the identification of a certain polytype. Since the intensities of the powder diffraction lines of the polytypes decreases rapidly with increasing repeat distance it would be a good idea to calculate intensities for possible polytypes having small repeat distances. (viz. 8H, 10H, 3R and 9R)

Methods of preparation of silver iodide described in this paper would allow the preparation of small crystallites of silver iodide on which a detailed study of crystallite size growth might be conducted. The effect of water vapor on the rate of growth of the crystallites would also be possible.

Further work needs to be done on the preparation of silver iodide using the spray system described in this paper. The present study shows a need for a larger decomposition chamber and control over the temperature in the chamber. Further dilution of the complex
with liquid ammonia should eventually provide a means of preparation of samples of silver iodide having very large surface areas (viz. 10 square meters per gram) and very small crystallite size. The method should also allow the size of the particles to be controlled by the regulation of the concentration of the silver iodide in the liquid ammonia. An improved precipitation system would be necessary if the finest portion of the smoke were to be collected.
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