

THE EFFECT OF HEAT ON THE SURFACE AREA OF SILVER IODIDE

by

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ABSTRACT

Several methods of making silver iodide were investigated. The thermal decomposition of silver iodate resulted in a yellow material with the lattice spacing of silver iodate. Preparation of silver iodide by precipitation from dilute and concentrated solutions ranged in specific surface area from 0.1 - 1.2 m²/g. The precipitated silver iodide was contaminated by ammonium nitrate. Grinding caused a great loss of surface area. The surface area also decreased on standing. This loss was not due to the pressure of the sample on itself. It may have been due to ageing or to repeated manipulation and exposure to water vapor.

The measurement of the surface area of silver iodide by the application of the BET equation to the adsorption of krypton is described in detail. The various samples were heated at several temperatures and the change in surface area with time of heating measured. There was no significant sintering at 55°C in 60 hrs. At 77°, 100°, and 125°C there is sintering. A rate constant was calculated at 77°. Using the equation

$$\Delta A = kt^m$$

k is 0.0285 and m is 0.458.

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INTRODUCTION

Artificial stimulation of rainfall has been the object of widespread investigation. Nucleation of ice crystals by foreign material and the subsequent growth of the ice crystals was originally thought to be due to an epitaxial effect. Vonnegut (1947) (1) searched the literature and found that the structure of hexagonal silver iodide closely resembled the hexagonal crystal structure of ice. But, when finely ground silver iodide was introduced into supercooled water vapor, very little nucleation occurred. However, when "active" silver iodide, formed by heating the silver iodide above its melting point on a hot wire or by generating silver iodide from a smoke generator, was added to the supercooled vapor a large amount of nucleation occurred (2). The amount of nucleation which took place was measured by visually estimating the density of the resultant ice crystals or by counting the number of ice crystals falling on a unit area of a glycerol coated surface.

When one considers the processing of the above samples, it seems quite logical to assume that the surface produced by grinding silver iodide to a fine powder and the surfaces produced by heating the silver iodide above its melting point on a wire or in a smoke generator would be quite different. Since nucleation must take place at the surface of the silver iodide, the difference in nucleating ability might well be due to a surface property of the silver iodide. In any case, it is quite obvious that the nucleating ability of silver iodide is dependent on the history of the sample.

Mason (1955) (3) found that the rate of growth of ice on crystallographically similar surfaces of ice crystals differed markedly under fixed experimental conditions. He has further proposed that a similarity of crystal structure is not a necessary condition for the nucleation of ice crystals by foreign materials (4). These and other findings seem to indicate that nucleation and growth of ice crystals may be a function of the surface properties as well as of the crystal structure of the nucleating material. A study of the surface properties of silver iodide is of importance to the further understanding of the nucleation of ice crystals by silver iodide and the subsequent growth of the crystals.

An accurate knowledge of the surface area of the silver iodide samples to be studied is necessary to the quantitative study of any surface property. In order to measure accurately the surface area and other surface properties, one must have a sufficiently large specific surface area so that the sensitivity of his instruments will not be exceeded. Therefore, the first aim of this study is to prepare a suitable sample for the study of several surface properties of silver iodide.

We postulate that nucleation and growth is a function of surface properties and that these properties vary with the history of the sample. A knowledge of how these properties vary with environmental stresses will be of great importance to the investigator when he compares his results with those of other investigators in the field. Indeed, even proof that these properties do vary will be of help in evaluating contradictory results. The first and perhaps the most obvious property to evaluate is that of specific surface area and its change with stress. Therefore, the second part of this study is concerned with the change of surface area with

time at various temperatures.

In order to measure a total surface area, one must have a measuring device of suitable dimensions. Since a real surface has many irregularities on the order of molecular size, a small molecule makes a good measure. If one, knowing the working diameter of the gas molecule, can determine the volume of the gas in an adsorbed monolayer he may then calculate the surface area of the solid on which the gas is adsorbed. Brunauer, Emmett, and Teller (5) derived an equation for multilayer adsorption from which the number of molecules in the monolayer may be calculated. Although the assumptions are obviously in error, the theory gives satisfactory results in terms of surface area. The authors assume that all sites on the surface are equivalent energetically and that there is no lateral interaction between the adsorbed molecules. They further assume that there is multilayer adsorption. In all but the first layer, the energy of adsorption is equal to the energy of liquefaction, and the energy of adsorption in the first layer is greater than the heat of liquefaction. The expression that they derived is as follows

$$p/V(p_0 - p) = \frac{1}{V_m c} + \frac{c - 1}{V_m c} (p/p_0)$$

p the pressure of gas in the system

p_0 the extrapolated liquid vapor pressure of the gas
at the temperature of the system

V the volume of gas adsorbed

V_m the volume of the monolayer of gas

When p/p_0 is plotted against $p/v(p_0-p)$, the slope plus the intercept of the resulting straight line is equal to the reciprocal of the volume of

the monolayer in cc. at STP. The surface area may then be calculated from the amount of gas adsorbed in the monolayer, if one assumes an area per molecule in the monolayer.

From the BET equation, we may also calculate a heat of adsorption for the first layer at about monolayer coverage. This is equivalent to the energy of the last sites to be covered (the low energy sites). This energy may be calculated from the BET equation as follows

$$c = Ke^{(E_1 - E_L)/RT}$$

E_1 = energy of adsorption of the first layer

E_L = energy of liquefaction

assuming

$$K = 1$$

$$\ln c = \frac{E_1 - E_L}{RT}$$

$$E_1 = \frac{\ln c}{RT} + E_L$$

In order to obtain a good value for E_1 , the experimental data must be excellent, since the calculation of c includes the volume of the monolayer squared and the difference in the energies is proportional to the natural log of c .

In order to obtain experimentally valid measurements at low surface areas, one must use low pressures to minimize the dead space errors. Therefore, one must choose a gas with a low p_0 at liquid nitrogen temperatures so that the valid range of p/p_0 , 0.05-0.35, occurs at low pressures. The gas molecule must also be small enough to follow the surface irregularities. Krypton has been found suitable in these respects for low surface area measurements (6), when the working diameter of the molecule is calculated from the volume of a monolayer on a sample of known surface area. In

addition, krypton is an inert gas and will not react chemically with the material to be measured. Therefore, krypton has been used for the surface area measurements in this investigation.

EXPERIMENTAL

Sample Preparation

The original plan for this research called for a 700 gram sample with a minimum surface area of one square meter per gram, made and stored in the dark, and uncontaminated by organic materials.

Precipitation by Analytical Procedure

The optimum monovalent ion concentration for the coagulation of a silver iodide sol in water is 0.142 M (7). Therefore, the first trial batch was prepared by dropwise addition of an 0.284 M solution of potassium iodide to an 0.284 M solution of silver nitrate to the stoichiometric end point. The rate of addition was about 20 ml per minute. The solution was kept at the boiling point and stirred rapidly. The precipitate was washed with hot water until there was no further test for nitrate by oxidation of diphenylamine (8). All manipulations were carried out under a red safe light. The surface area as determined by krypton adsorption was approximately 0.5 m²/g.

Decomposition of Silver Iodate

Mellor (9) states that silver iodate decomposes on heating to silver iodide. If there were no appreciable sintering of the silver iodide as it was formed the decomposition of the silver iodate might result in a silver iodide sample of large surface area. A sample of silver iodate was prepared by the addition of 21.4 g of potassium iodate in 100 g of water to 17.0 g of silver nitrate in 100 g of water and the precipitate filtered, washed, and dried. The silver iodate was then heated at 400°C for 48 hrs.

The sample turned yellow resembling silver iodate. However, an X-Ray diffraction pattern of the resulting sample showed no change from the silver iodate crystal structure. Later work also indicated that sintering at this temperature would be too great to give an acceptable surface area.

Precipitation from Concentrated Solution

Birstein (10) reports surface area of $12.5 \text{ m}^2/\text{g}$ on precipitation from concentrated solution. Therefore, a trial sample was made essentially duplicating the procedure that he used. 59.6 g of ammonium iodide in 200 ml of distilled water and 67.8 g of silver nitrate in 200 ml of distilled water were poured rapidly together. The supernate was decanted and the precipitate transferred to a Buchner funnel fitted with Whatman number 50 filter paper. The sample was then washed at room temperature by making a slurry with about 50 ml of water and drawing off the water with an aspirator. The washing was repeated four times until there was no test for nitrate in the wash water. The cake was then partially dried by drawing air through the filter. Next, the cake was gently broken up and placed in a vacuum dessicator with a liquid nitrogen trap on the pump line. After an hour, the partially dried sample was again gently broken up so that no piece exceeded 2 mm in diameter. The surface area was approximately $0.9 \text{ m}^2/\text{g}$.

Precipitation from Concentrated Solution with Alcohol and Acetone Washes

It was suggested (11) that the surface area decreased during drying. Appreciable crystal growth might occur while the surfaces were still in contact with a layer of water molecules. Therefore a second sample was made by the above technic. The precipitate was further washed with two aliquots of ethyl alcohol and one of ether. The cake was then broken up to a maximum

size of 2 mm in diameter and stored under a vacuum. The surface area essentially duplicated that of the first sample. However, the sample was much easier to break up. Therefore, this method which required less manipulation was chosen for making future samples. The residue of alcohol and ether was assumed to be completely removed by vacuum distillation.

Precipitation From a Nucleated Solution

Jaycock and Parfitt (12) described a method for forming a large number of silver iodide nuclei. One might be able to get a large surface area by forming more particles on a large number of existing nuclei. A nucleating solution was prepared by adding ethyl iodide to 200 ml of an alcohol solution of silver nitrate so that the initial concentration of silver and iodide ions available was 1mM. This solution should contain about 10^{10} nuclei per milliliter. Silver nitrate and ammonium iodide solutions of the same concentrations used previously were poured into the nucleating solution after it stood twenty minutes. The precipitate was washed as in the previous trial. The resultant cake was very dense and required more vigorous treatment to break it up into a usable size. Therefore, the low surface area of $0.1 \text{ m}^2/\text{g}$ may be an artifact in the handling of the cake. The effect of grinding of the silver iodide will be dealt with later.

Preparation of the 700 g Sample

For the large sample, 678 g of silver nitrate in 2 L of water and 596 g of ammonium iodide in 2 L of water were poured together and treated as the trial sample. Due to the large quantities involved, the filtering took over an hour and the high humidity in the laboratory caused the sample to take up water rapidly. The resulting cake was very difficult to break

up and quite lumpy. Since X-Ray diffraction studies which were to be done after the heat treatments required a powdered sample, the silver iodide was gently powdered by pressing between two large watch glasses with a slight circular motion. The surface area was less than $0.02 \text{ m}^2/\text{g}$.

After examining the variables in the preparation of the samples, it was conjectured that the surface area loss was due to the length of time that the sample was in contact with water. A small check run was made and the original results were duplicated. Therefore, it was decided that a pooled sample should be made.

Six separate batches of about 120 g each were made by precipitation from concentrated solution. The physical characteristics of the samples varied quite widely. The precipitates varied from a fine precipitate which was very hard to filter to a spongy easily filtered mass. The spongy precipitates gave the greater surface areas. It was impossible to tell whether this effect came from the initial precipitation conditions (which vary widely when two solutions are simply poured together) or from the variable time in contact with water and the more vigorous breaking required by the dense cake left by the fine precipitates. The surface areas varied from about $0.1 - 1.2 \text{ m}^2/\text{g}$. The initial colors were varying shades of pale yellow. The color change in response to light varied widely. The color change ranged from orange to black requiring anywhere from a few minutes to days of exposure to daylight. These effects indicated that the samples must have quite different surfaces.

Effect of Grinding on Surface Area

We decided, on further reflection, that the gentle grinding which was used on the 700 g sample seemed a possible source of the loss of surface

area. Two aliquots were taken from the same batch. One was powdered between two watch glasses and the other used as a control. The control had a surface area of about $1 \text{ m}^2/\text{g}$ while that of the powdered sample measured less than $0.03 \text{ m}^2/\text{g}$.

Duplication of Surface Areas on Same Batch

A control sample was then tested to see if it would be possible to duplicate the surface area of aliquots by the proper sampling of the granular samples. The duplicate samples were taken by quartering and requartering the whole sample discarding alternate quarters. Care was taken to keep any grinding effects to a minimum. The areas were approximately 0.35 and $0.31 \text{ m}^2/\text{g}$. The results were considered suitable for our purposes.

Sample Contamination

When a sample of silver iodide precipitated from concentrated solution was heated under vacuum, a white precipitate deposited in the vacuum system above the heated area. After heating a twenty gram sample at 50°C for two days, slight deposits still formed on the glass which had been cleaned of the old deposits with a heat gun. The sublimate was dissolved out of the vacuum tubing and tested for the ions listed in Table I. The results of the spot tests show that the substance was ammonium nitrate. Mr. Nichols in preparing samples for the measurement of crystallite size had occasion to make a sample with ammonium iodide and silver nitrate using dilute solutions, slow addition, and thorough washing. This sample also proved to be contaminated with ammonium nitrate. It was decided to go ahead using the samples precipitated from concentrated solution since there was also contamination in the sample precipitated by methods designed to minimize contamination and since the duplication of Birstein's adsorption studies (10) was also of

interest to this laboratory.

Table I
Spot Tests on the Sublimate

Ion	Test	Sensitivity	Results	
			Water	Unknown
NO_3^-	Oxidation of diphenyl amine (8)	5%	+	++++
I^-	Oxidation to free iodine on starch paper (13)	0.025%	-	-
NH_4^+	Red litmus test (14)	0.01%	-	++
Ag^+	Catalytic reduction of cerium ammonium nitrate (15)	0.05%	-	-

Preparation with Liquid Ammonia

While it was felt that a sample of average characteristics could be obtained from a pooled sample by the sampling technic described earlier, there was still concern about the amount of manipulation necessary to obtain many samples from the batch. The grinding involved might substantially reduce the sample area since many aliquots must be taken. It had been found that if a previously prepared sample was dissolved in liquid ammonia and reprecipitated (15), a precipitate with a surface area of about $0.6 \text{ m}^2/\text{g}$ was obtained. The dry sample was finely divided. New equipment for the adsorption studies made this lower surface area acceptable. Therefore, it was decided to use this method in order to avoid grinding effects.

A system was made, Fig. 1, which would accommodate 600 ml of liquid

ammonia. From observations of the solution of smaller samples, it was concluded that this would be ample volume to accommodate 700 g of silver iodide. About 150 ml of liquid ammonia was collected in the holding bulb, containing a few grams of metallic sodium, by flowing in gaseous ammonia at about one atmosphere while the bulb was immersed in an alcohol and dry ice bath. The bath was then transferred to the sample bulb containing 200 g of silver iodide and the ammonia distilled over. The bath was then removed and the bulb warmed with warm water; the solid silver iodide dissolved. The ammonia which boiled off was removed by a water aspirator until only the solid white complex remained. The complex was then decomposed by pumping with a vacuum pump through a liquid nitrogen trap for about six hours. The sample was a solid lump.

A second sample was made by altering the procedure. The liquid ammonia from the solution was distilled back into the collecting bulb surrounded by a liquid nitrogen bath. The complex was completely decomposed before exposing the silver iodide to water vapor. The sample fell into a fine powder and a few small lumps with the exception of a large lump of complex remaining in the center. All lumps were discarded and the sample stored in the dark under vacuum. Since research plans had been modified and since the material was deemed suitable for sintering studies, these two hundred grams, processed in the light, were considered acceptable working material.

The Silver Iodide Sample Used in the Sintering Studies

The silver iodide used in the ammonia treatment consisted of the residue of many trial batches. Most were made by precipitation from

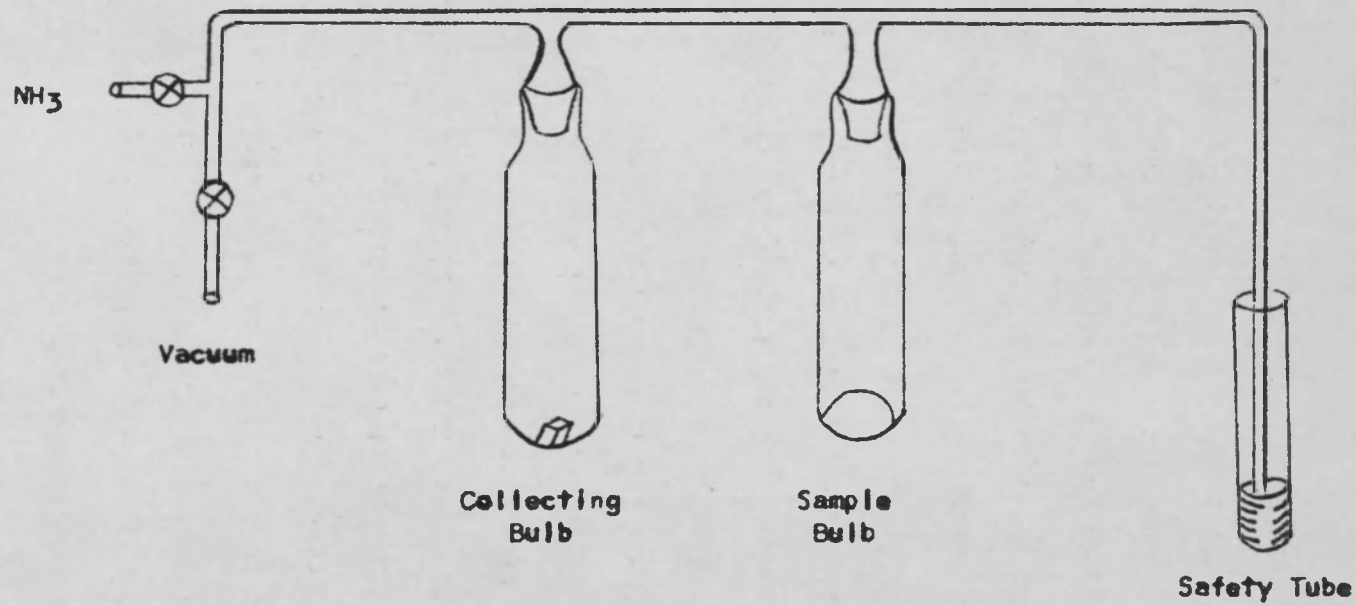


Fig. 1

concentrated solutions of ammonium iodide and silver nitrate. About 5% was made from precipitation from dilute solutions of potassium iodide and silver nitrate. This sample was slurried with water and the water decanted a total of ten times over a period of three days. The final wash had stood in contact with the samples overnight. It gave no test for iodide. However, on heating the product of the ammonia treatment, ammonium nitrate was again sublimed from the silver iodide. The sample, while not all that was desired, was considered suitable for the sintering measurements.

Pressure Sensitivity

A trend toward lower surface areas with time was observed on the zero time sintering samples, Table II. Since the silver iodide had been kept under vacuum and the handling had been kept to a minimum, it was conjectured that the pressure of the sample on itself might be causing the decrease in surface area. Therefore, two identical aliquots were taken from the main sample and placed in sample holders. A rod of slightly less than the inner diameter of the holder, exerting a pressure of 0.0961 atmospheres, was inserted over one aliquot for 26 days. The standard aliquot had a surface area of $0.393 \text{ m}^2/\text{g}$ and the treated aliquot had a surface area of $0.356 \text{ m}^2/\text{g}$.

Table II

Variation of Surface Area With Time	
Date	Surface Area of Zero Time Sample
3/13/62	0.576 m ² /g
3/27/62	0.516
4/2/62	0.528
4/25/62	0.491
5/14/62	0.471
5/28/62	0.443
6/11/62	0.437
6/24/62	0.438
7/16/62	0.393

Measurement of Surface Area

The surface areas were calculated by means of the Brunauer, Emmett, and Teller equation (16) applied to krypton adsorption isotherms. A vacuum system, designed for krypton measurements of low surface areas, was constructed in this laboratory and modified from time to time as the need became evident. The final system is shown in Fig. 2. The parts are as follows:

- 1 Krypton Reservoir
- 2 Krypton Bulb
- 3 Helium Reservoir
- 4 Gas Manifold
- 5 Capillary Tubing (to slow gas feed)
- 6 Liquid Nitrogen Trap (to protect ion gauge from mercury vapor)
- 7 Ion Gauge

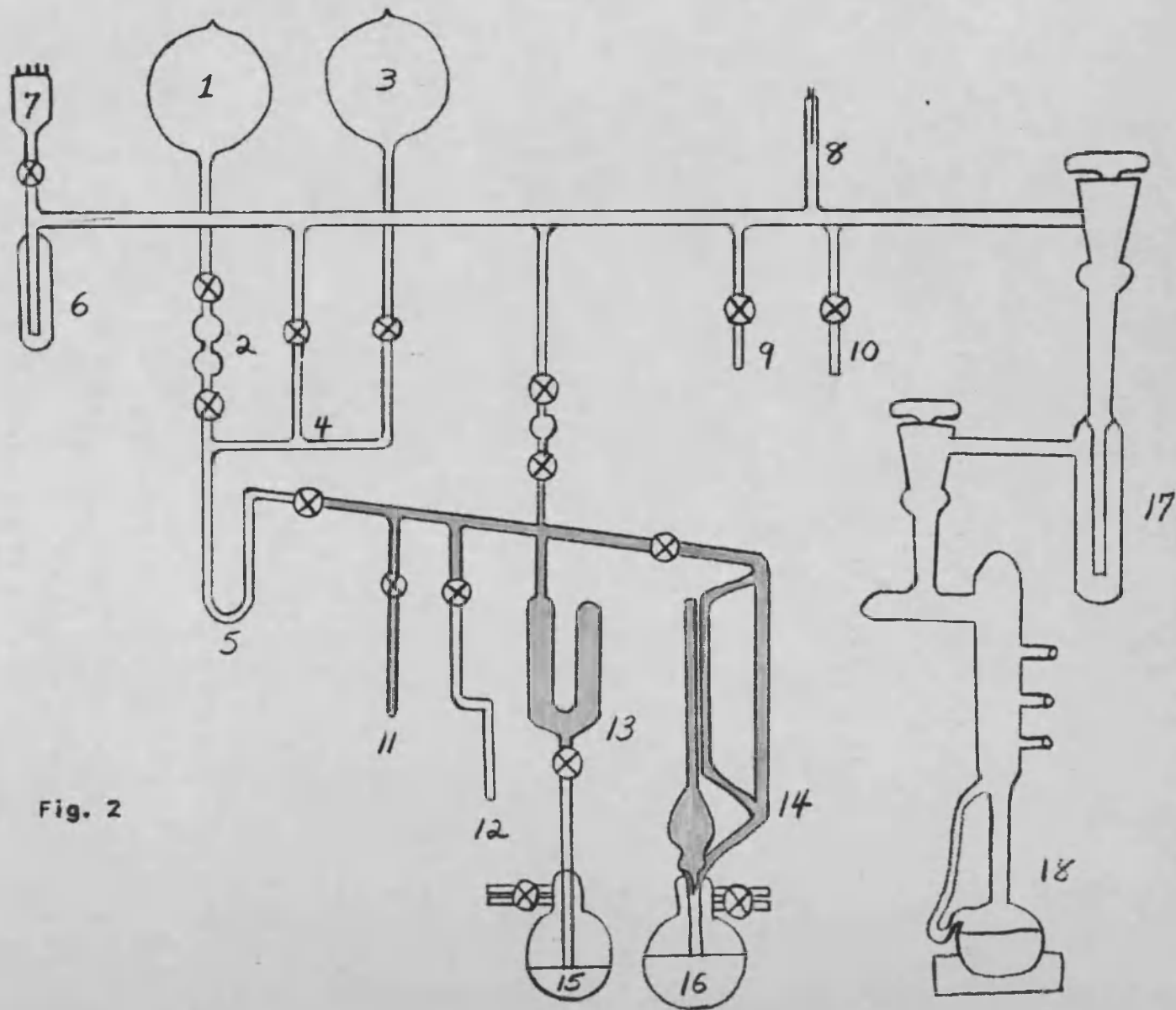


Fig. 2

- 8 Pirani Gauge
 - 9-10 Blow Tube and or Preliminary Drying Point
 - 11 Sample Tube
 - 12 Water Tube
 - 13 Doser
 - 14 McLeod Gauge (volume 53 cc, bore 4 mm diameter)
 - 15-16 Mercury Reservoirs
 - 17 Liquid Nitrogen Trap (to keep pump vapor from main part of system)
 - 18 Mercury Vapor Pump
- Shaded Area Total Dead Space

Gases Used for Measurements

The krypton and helium were obtained from Air Reduction Co. in sealed bulbs. The purity was 99.98 and 99.999 mole % respectively.

System Pressure and Leak Rate

After pumping the system for five days, it held a vacuum of about 2×10^{-6} mm of Hg. It was not possible to determine the exact leak rate since the ion gauge acts as a pump. However, over the period of one hour, the system closed off from the pump showed no increase in pressure measurable by the less sensitive Pirani gauge and registered a stick vacuum on the McLeod Gauge.

Stopcock Maintenance

Apiezon N was used on the stopcocks during most of the runs. Apiezon T was used when the laboratory temperatures exceeded 30°C . The Apiezon T was very difficult to degas and often led to leaks. Therefore, it was used as little as possible. The stopcocks were regreased whenever it became necessary because of leaks or hardening of the grease. In order

to minimize leakage at the stopcocks, they were worked back and forth daily.

Cleaning the Vacuum System

The system was pumped down a minimum of twelve hours after the sample was sealed to it and for two to four days after regreasing stopcocks or major repairs. This time was necessary to dry the sample and to desorb water vapor from the walls of the system as well as gases from the stopcock grease. The system was never baked out. On one occasion, when it was impossible to obtain a straight line BET and no leak could be detected, the system was flamed out with a hydrogen flame. On application of the flame to the outside of the tubing, a bright yellow deposit appeared on the cool walls close to the point of heating. On further heating, the yellow contaminant sublimed and could be driven over into the liquid nitrogen trap. When the samples were heated on the vacuum line, both ammonium nitrate and iodine were given off. Although iodine was never seen in the system, 800 g of a similar silver iodide sample gave off visible iodine vapor when heated in a vacuum at less than 100°C . Therefore, the contaminant which was bright yellow might have been mercurous iodide. It is bright yellow and sublimes at 140°C (17). After the system was flamed out straight line BET plots were again obtained.

Measurement of the Adsorption Isotherm

The silver iodide was placed in a four inch length of 6 mm glass tubing, which had been sealed at one end, to a depth of about 1 1/2 inch. The tubing was then wrapped with black electrical tape for about two inches to keep the light reaching the sample at a minimum. A separate piece of tubing with a constriction, plugged with a small bit of glass

wool, was sealed on the system first. This prevented the sample from blowing into the system on evacuation and provided a thick wall for removing the sample from the system while it was still under vacuum. The sample portion of the tube at no time became warm to the touch. The system was then pumped down for a minimum of twelve hours. The system was closed off from the pumps and simultaneously tested for leak rate and sample dryness with the Pirani gauge. If no increase in pressure was observed in twenty minutes, a large slug of krypton was frozen onto the sample and then pumped off at room temperature for a half hour. When this preliminary slug of krypton was omitted, the first point taken on the BET plot was often in error. It is believed (19) that some surface contaminants may be removed with the krypton. It was also necessary to use a preliminary slug after each heating cycle.

About 1.3 g of sample was used. The total dead space was about 170 ml and the sample case dead space about 15 ml. At these low surface areas, the amount of gas in the sample case dead space was often so close to the amount adsorbed per aliquot of gas that a small error in this dead space made a large error in calculating the amount adsorbed. Therefore, the points were taken one at a time. All the krypton was pumped off at room temperature between measurements rather than using successive slugs of gas as is routine procedure. The pumping time for complete removal of krypton at room temperature was found to be one half hour.

The sample was at the liquid nitrogen boiling point during the measurement. Great care was taken to keep the liquid nitrogen dewar position and the relative depth of the liquid nitrogen constant in order to eliminate any change in apparent dead space. The liquid nitrogen was

assumed to vary no more than $\pm 0.2^\circ\text{C}$ giving a negligible error in p_0 . The error due to thermal transpiration at these pressures and tubing diameters is negligible (20).

Variation in the laboratory temperature of $\pm 5^\circ$ during individual measurements resulted in many questionable points. These points along with the other points obviously in experimental error were discarded.

The dead space was determined with helium using the relationship

$$p_1 V_1 = p_2 V_2$$

The initial volume of gas was trapped in the doser by raising the mercury from the reservoir. The height of the mercury in each arm of the U shaped doser was measured at room temperature with a cathetometer calibrated to 0.001 cm. The readings could be reproduced to ± 0.003 cm. The doser arm was made of precision bore tubing. The tip had been previously calibrated with mercury by weighing three aliquots with the tip of the meniscus at the calibration line. The correction for the volume between the surface of the meniscus and the plane of the calibration line was calculated by Dr. Corrin from the approximate shape of the mercury meniscus and twice the amount added to the tip volume. Using these values, one may find the volume and the pressure of the dose at room temperature as follows:

$$p = \Delta h$$

$$V = V_{\text{tip}} + \pi r^2 \Delta h'$$

where

h' = the difference between the height of the calibration line and the tip of the meniscus

and then converted to the volume at standard temperature and pressure.

The volume of the krypton slugs at STP ran from 0.15 - 0.45 for the 1.3 g

silver iodide samples.

The final pressure was measured by a McLeod gauge, previously calibrated by Norton Glossman, where

$$p = p' (\pi r^2 h / V) \quad (21)$$

p' = the difference in height of mercury in the legs of the McLeod

h = height from the mercury to the tip of the McLeod

r = radius of the tubing

V = volume from the cut off to the tip

The correction for the shape of the meniscus was neglected, since, when calculated on the basis of a hemispherical shape, the correction was less than 1%. The final volume at STP was calculated from the dead space volume and corrected for temperature and pressure.

The isotherms were interpreted according to the BET equation. Although BET straight lines giving internally consistent results may be obtained using almost any value for the extrapolated liquid p_0 given in the literature, the absolute surface area is highly dependent on the p_0 chosen (22).

The p_0 used in the calculation of the BET curves in this paper were calculated from the experimental pressure of the vapor in equilibrium with solid krypton at liquid nitrogen temperature. The observed pressure over the solid was 0.162 cm Hg. The temperature of the liquid nitrogen at this pressure was calculated using Freeman and Halsey's data for solid krypton (23) as follows

$$\log p_s = A - B/T$$

$$\log 1.62 \text{ mm} = 7.7447 - 579.6/T$$

$$T = 76.9^\circ\text{K}$$

Next the saturation pressure of the super cooled liquid at this temperature was calculated from the Freeman and Halsey equation.

$$\log p_l = A' - B'/T$$

$$\log p_l = 6.9861 - 491.9/769$$

$$p_l = 3.89 \text{ mm}$$

This value of p_0 gave straight lines for the p/p_0 range of 0.09 to 0.35 as seen in Figs. 3, 4 and 6. To obtain an absolute surface area, an isotherm, Fig. 3, was run on the Harkins and Jura anatase, TiO_2 , standard of $13.8 \text{ m}^2/\text{g}$ and the BET monolayer capacity calculated using the above p_0 . The working diameter, 18.2 \AA^2 , was calculated for the krypton molecule from the experimental V_m and the standard area.

Heating the Sample

After a zero time isotherm was run, the sample was heated on the system while under vacuum by means of a 1 L silicone oil bath. The bath was controlled by a mercury regulator and heated by a high resistance wire heater. The voltage to the heater was controlled so that the heater remained on about 30 sec per cycle. The bath was stirred rapidly enough so that a small whirl appeared on the surface of the oil. Due to the small size of the bath the temperature varied over a 4°C range per cycle. The mean temperature as measured by a mercury thermometer is reported. The time was recorded from the time of immersion of the sample case in the bath until the bath was removed. The sample was allowed to cool in air.

The sample heated in water vapor was allowed to stand with water

BET Plot of Standard Sample

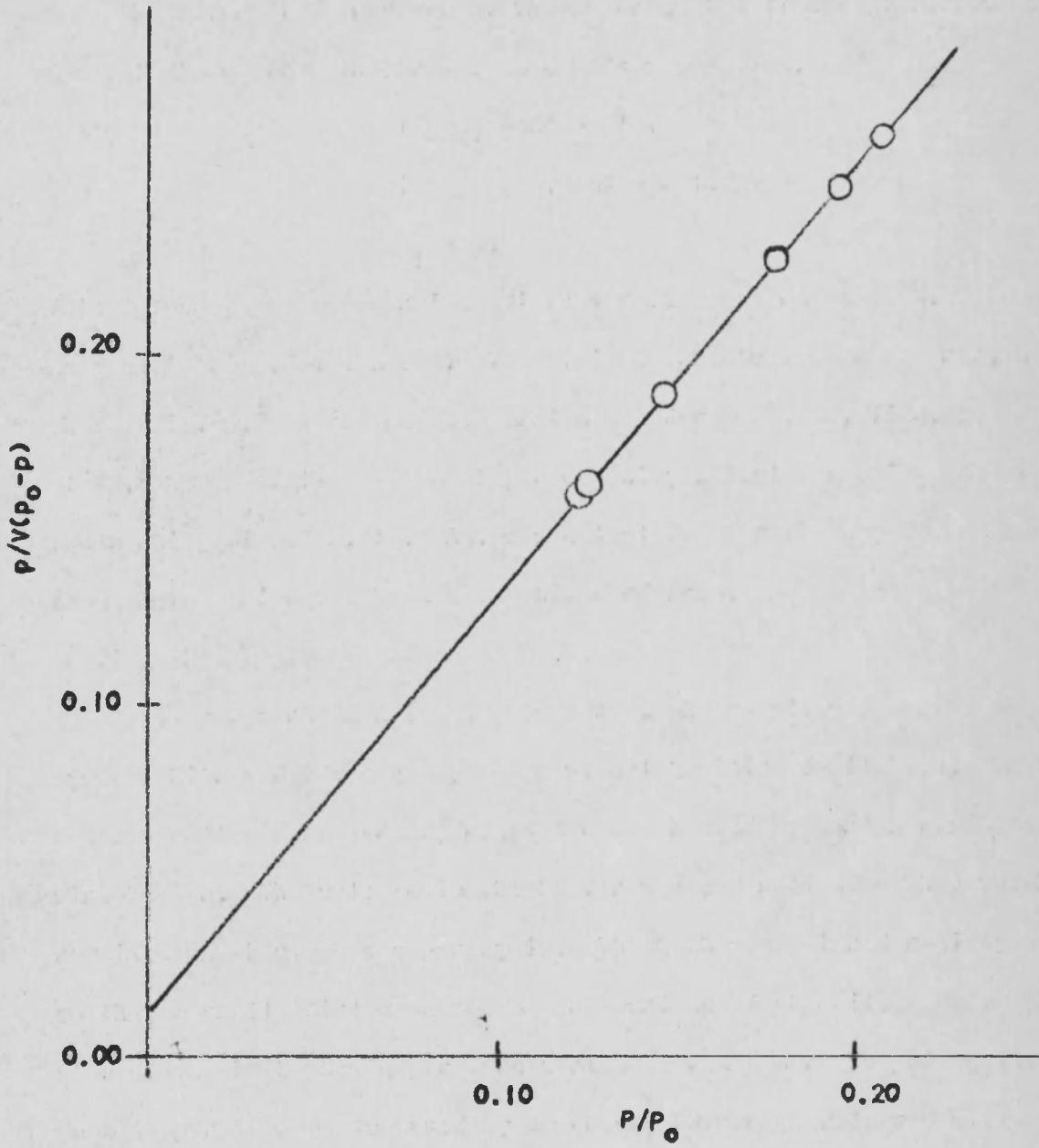
 $13.8 \text{ m}^2/\text{g}$ $P_0 = 3.89 \text{ mm Hg}$ 

Fig. 3

vapor in equilibrium with water at 0°C from 10 minutes before heating until the heating was completed. The water vapor was then pumped off and the sample dried on the system for a minimum of 48 hrs. before the isotherms were run. The water was kept at 0°C by a distilled water ice bath which was stirred from time to time during the heating period.

Sample Weight

After the isotherms for a given run were completed, the sample was removed from the system while still under vacuum. The sample case was weighed before and after the sample was removed, and the sample weight calculated by difference to 0.01 g. No buoyancy correction was made.

Results and Discussion

The Properties of Silver Iodide as a Function of Its Preparation

The decomposition of silver iodate with heat in air resulted in a material which had the color of silver iodide. However, it retained the lattice spacings of silver iodate and we have no proof that silver iodide was formed.

The precipitation of silver iodide from dilute solution resulted in a surface area similar to that of the samples precipitated from concentrated solution, Table III. This precipitation which was expected to produce a clean sample resulted in a sample contaminated with ammonium nitrate.

The precipitation of silver iodide from a solution with added nuclei resulted in a sample of low surface area, Table III.

The precipitation of silver iodide from concentrated solution produced samples of widely varying physical properties which suggest that the samples prepared by pouring together concentrated solutions of ammonium

Iodide and silver nitrate, varied widely in surface properties. The precipitates varied from a hard to filter fine precipitate to a spongy easily filtered mass. The fine precipitates resulted in a hard cake which was difficult to break into usable size. The initial colors were various shades of light yellow and the change in color varied widely in response to light. The surface areas varied from about 0.1 - 1.2 m²/g. In six trials the Birstein surface area of 12.5 m²/g was not duplicated. The variation in surface properties is not surprising since the conditions of precipitation vary widely when two solutions are simply poured together.

The sample prepared by dissolution in liquid ammonia was finely divided and had a surface area of about 0.6 m²/g.

Table III

Method of Preparation	Surface Area
	m ² /g
ppt. dilute sol.	0.5
ppt. nucleated sol.	0.1
ppt. concentrated sol.	0.1 - 1.2
ppt. from liquid NH ₄	0.6

It may be seen from Table III that the surface area of the samples did not vary significantly with the method of preparation. In most cases, the lower surface areas came from cakes which were more difficult to break up than the others. It is impossible to tell whether the differences in surface area resulted from the conditions of precipitation or from the manipulations after precipitation.

Sample Contamination

All the samples made by precipitation which were tested showed contamination by ammonium nitrate. The samples precipitated from both concentrated and dilute solutions appeared to have a large amount of surface contamination since the contamination was found by the sublimation of the ammonium nitrate from the silver iodide far below the melting point of the silver iodide. In view of the rigorous washing that the silver iodide had received, it would seem that the ammonium nitrate is very strongly adsorbed on the surface.

The sample precipitated from liquid ammonia also had surface contamination by ammonium nitrate. But it is impossible to tell whether the contamination resulted from surface contamination remaining on the silver iodide used as a starting material or from ammonium nitrate occluded in the starting material. The most likely conclusion is that it resulted from both.

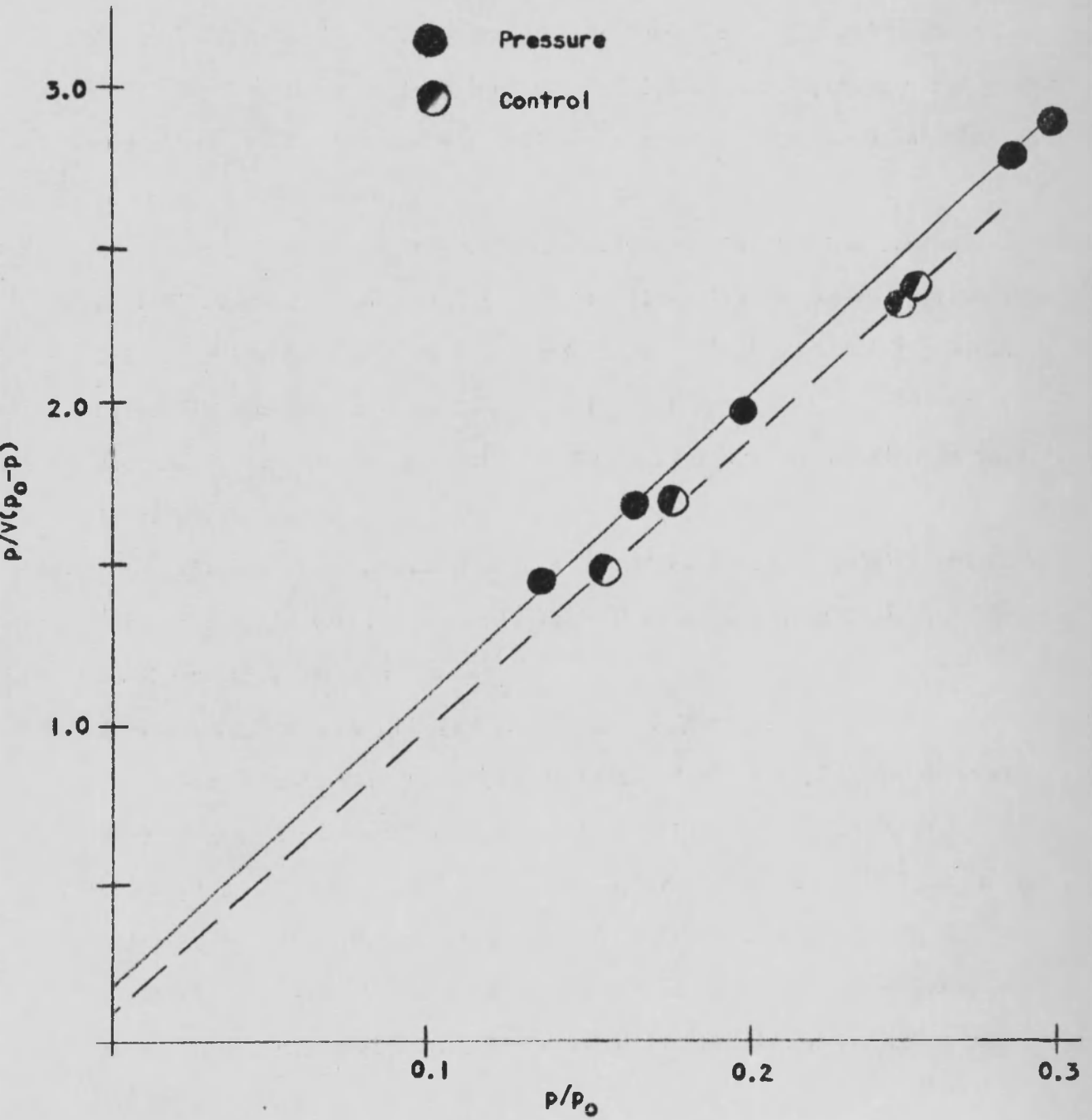
Since contamination often has an effect on the specific surface area of a solid (24), the sample contamination may have an influence on the results of this study.

Surface Area as a Function of Handling and Storage

The more handling a sample required after precipitation the more surface area loss occurred. When a sample was ground gently between two watch glasses it lost surface area by a factor of 30. This loss is not simply a function of pressure. The sample with a weight on it for 26 days lost only 11% of its surface area, Fig. 4. It is more likely a function of pressure and the deformation of the silver iodide by the grinding motion.

Fig. 4

BET plots of Pressure Test



Initial Surface Area as Function of
Time of Standing

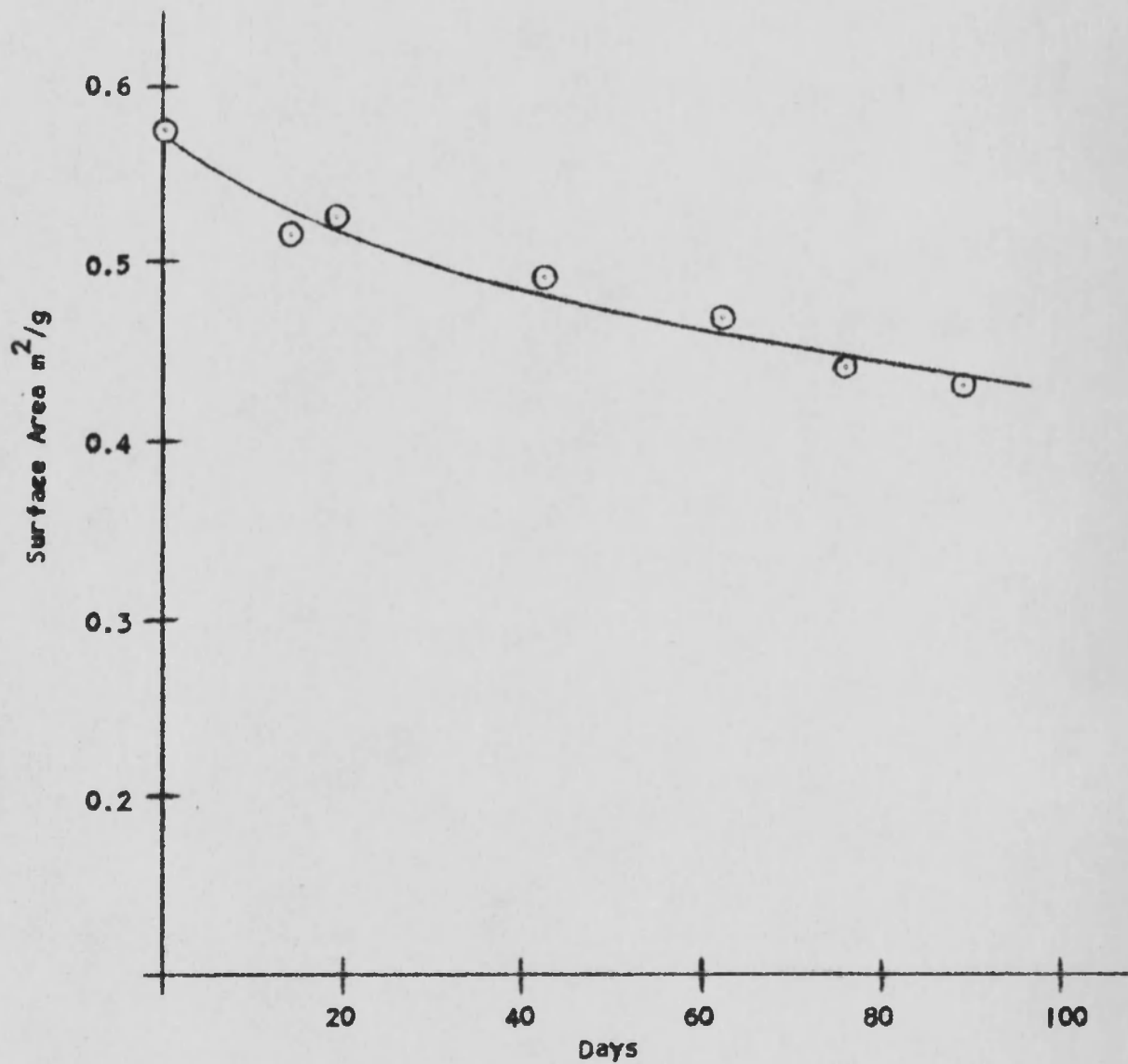


Fig. 5

The sample used for the surface area measurements lost area on standing in a vacuum over the period of the investigation as seen in Fig. 5. If one extrapolates the curve out to the number of days the control sample was stored, one gets approximately the same surface area as was measured on the control sample. The main sample had been opened to the air and handled only when it was necessary to obtain a new aliquot. These dates correspond to the time of the zero measurements given in Fig. 4. There seems to be a definite relationship between the time of storage and the loss of surface area. This loss is larger than one would expect from the pressure of the sample standing on itself since the sample was only about an inch deep. Since the times that the sample was open to the air and handled are at fairly evenly spaced intervals, it is impossible to tell whether this relationship is a function of ageing or of exposure to air and manipulation.

The Effect of Temperature on Surface Area

The results of heating the silver iodide samples are summarized in Table IV, and a set of representative BET plots given in Fig. 6. The surface area data obtained from these plots are sufficiently accurate for the purposes of this investigation which is essentially exploratory. The experimental data are not sufficiently accurate to obtain reliable c 's in order to calculate the energy of adsorption of the first layer of krypton. There appear to be trends in the variation of c with the time of heating but since these may very likely be artifacts, any consideration of these trends would be pure speculation.

Summary of Data

Date	Temp.	t _{hr}	C	A/g	A/g*	% Decrease
3/13	0	0	33	0.576 m ² /g	-	-
3/14	53°C	12	24	0.576	-	0
3/19	100°	12	22	0.319	-	45
3/20	147°	12	41	0.186	-	68
3/27	100°A	0	39	0.516	-	-
3/27		6	18	0.350	0.358 m ² /g	32
3/28		6	15	0.327	0.335	36
3/31		15	18	0.276	0.282	46
4/2	100°B	0	40	0.528	-	-
4/9		6	18	0.349	0.349	34
4/10		6	17	0.311	0.311	41
4/11		12	23	0.266	0.266	49
4/12		12	25	0.244	0.244	54
6/24	100°	0	38	0.438	-	-
6/26	H ₂ O _v	6	45	0.310	0.374	29
6/28		6	32	0.266	0.320	29
6/31		12	31	0.219	0.258	51
7/8		25.5	26	0.188	0.226	57
4/25	125°	0	38	0.491	-	-
5/5		3	48	0.278	0.298	43
5/7		3.5	21	0.246	0.264	50
5/8		6	19	0.214	0.230	56
5/9		12.8	18	0.206	0.222	59
5/14	77°	0	41	0.471	-	-
5/15		6	53	0.406	0.455	14
5/17		6	56	0.381	0.427	14
5/21		12.7	42	0.348	0.390	26
5/24		18	31	0.312	0.350	34
5/26		29	27	0.298	0.334	37
6/11	55°	0	42	0.437	-	-
6/12		12	47	0.425	0.514	3
6/19		6	35	0.431	0.520	1.5
6/21		18	36	0.425	0.514	3
6/22		24	50	0.410	0.495	6

*Areas corrected to an initial area of 0.528 m²/g

BET Plots of 100°C

Run 2

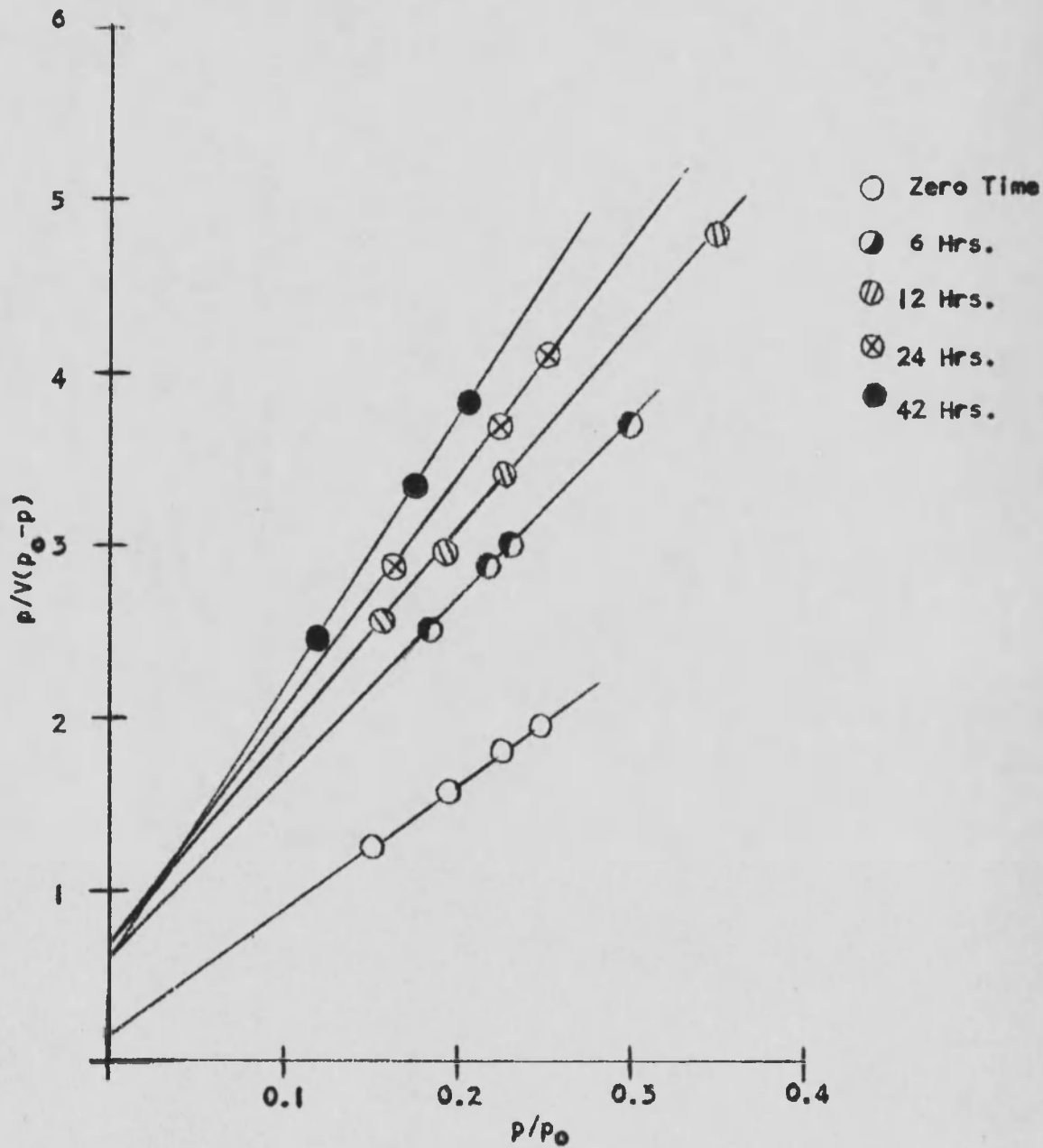
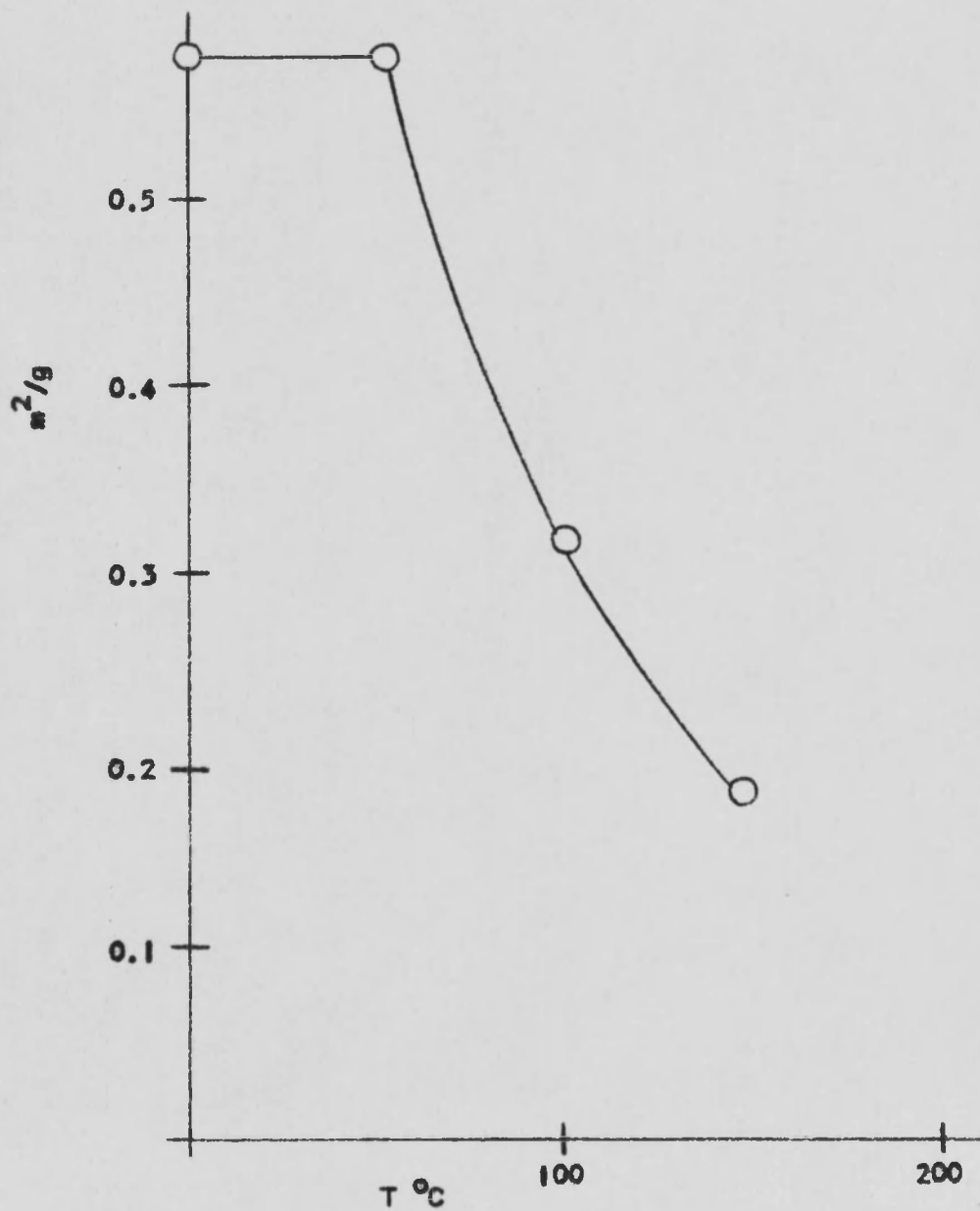


Fig. 6

Fig. 7

Surface Area vs Temperature
of Heating for Cumulative
12 hr. Periods



The first trial run is plotted in Fig. 7. The sample was heated at each temperature successively for 12-hour periods. There was no change at 53°C in twelve hours. At 100°C, there was a loss of 45% of the surface area on twelve hours heating. At 147°C, there was a further loss of 17%.

The results of the runs at various temperatures are plotted in Fig. 8. In agreement with the first trial run, there is no significant sintering with time at 55°C. At 77°C, the sintering is pronounced. At 100°C three samples were run. Two were heated under vacuum in the same manner as the other samples and one was heated while in equilibrium with water vapor at a pressure of 4.58 mm of Hg. The results are graphed in Fig. 9. They show that there is no significant difference between heating the sample in a vacuum and heating the sample with water vapor at that pressure. The effect of heating the samples was progressively greater at 125°C.

From Fig. 8, it may be seen that there is a large initial drop in surface area followed by a leveling off of the loss with longer time of heating. The final surface area seems to be limited by the temperature of heating at first glance but it is likely that the same limiting surface area might be reached if the times of heating were carried out until the limiting values were reached.

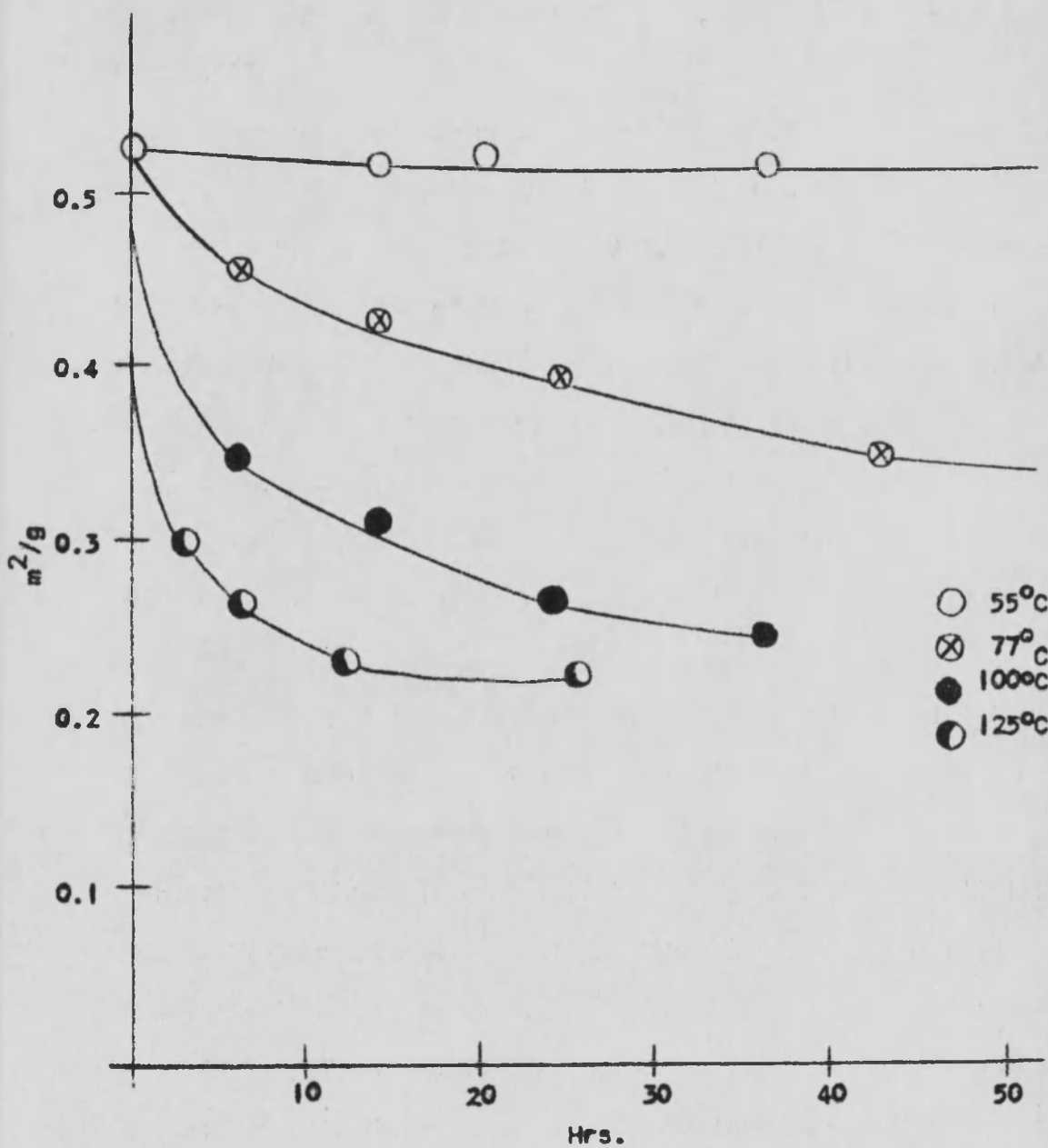
In only one case, 77°C, was there sufficient data to calculate a sintering rate. The rate constant was calculated as follows.

$$\text{If} \quad \Delta A = Kt^m \quad (1)$$

$$\text{Then} \quad \log \Delta A = m \log t + \log k \quad (2)$$

$$\text{and} \quad k = \Delta A/t^m \quad (3)$$

Fig. 8
Surface Area vs Time of Heating
Corrected for initial surface area



Surface Area as Function of Heating
at 100°C

Corrected for initial surface area

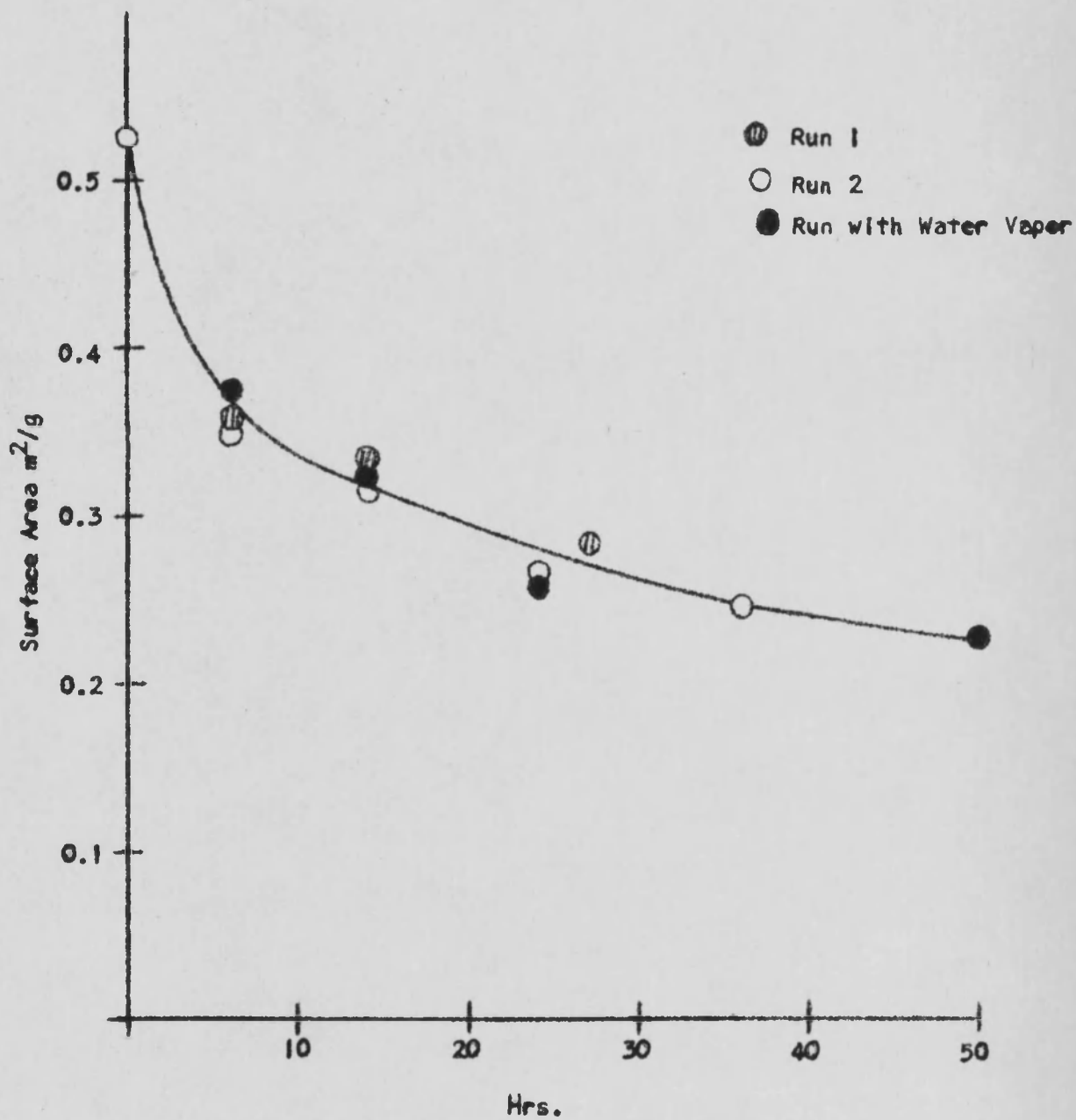


Fig. 9

The graph of the straight line, (2), is shown in Fig. 10. The rate of change with time is constant through 42.7 hours and then shows a decrease at 72.5 hours. The rate constants are listed below each point and are internally consistent. The change in surface area is proportional to the 0.458 power of time and the average rate constant is 0.0285. The deviation of the 72.5 hour point from the rate equation suggests that there might be two processes involved in the loss of surface area on heating but the data are insufficient to draw any conclusions.

Summary of Results

When silver iodate was heated to 400°C for 48 hrs, the resultant yellow material retained the lattice spacings of silver iodate.

Silver iodide samples with surface areas of from 0.1 to 1.2 m²/g may be obtained by precipitation from concentrated solution. We were unable to duplicate the 12.5 m²/g surface area obtained by Birstein by precipitation from concentrated solution.

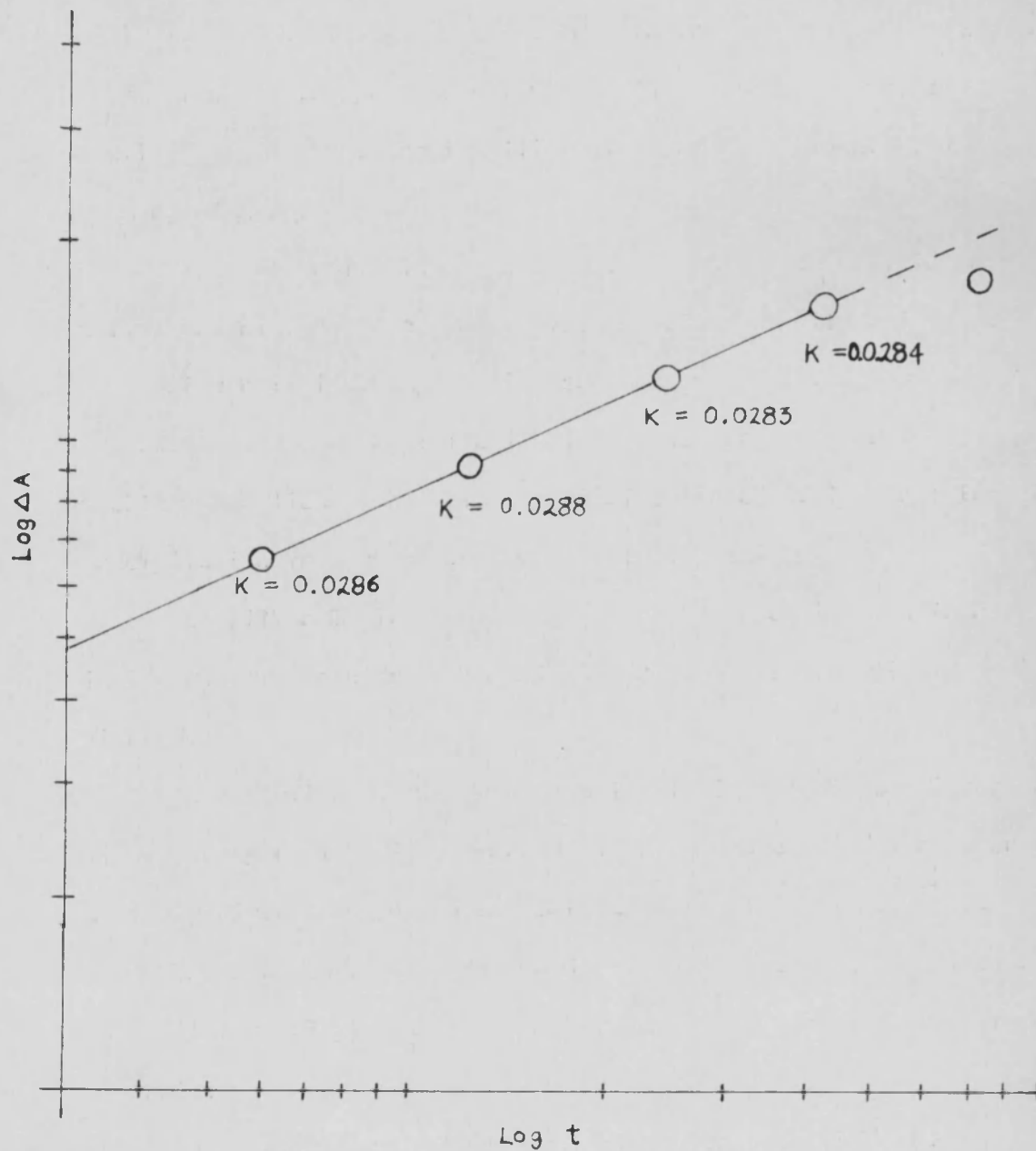
The silver iodide samples prepared by precipitation from ammonium iodide and silver nitrate solutions were contaminated with ammonium nitrate.

The solution of silver iodide in liquid ammonia and its reprecipitation by evaporation of the ammonia in the absence of water vapor produced a finely divided sample with a surface area of about 0.6 m²/g.

The surface area of silver iodide will decrease by a factor of 30 on gentle grinding, although the surface area loss with pressure is only moderate.

The surface area of silver iodide decreases with time of storage under vacuum. It is not possible to tell from our results whether this

Fig. 10
Graph of the Rate Equation
for 77°C



effect is from manipulation, periodic exposure to the atmosphere, or ageing at room temperature.

There is no significant sintering of the silver iodide at 55°C for 60 hrs. At 77°, 100°, and 125°C there is significant sintering. The rate of sintering increases with increasing temperature. A rate constant was calculated from the equation

$$\Delta A = Kt^m$$

K was equal to 0.0285 and m equal to 0.458 at 77°C.

Since specific surface area may be affected by contamination, these results may be influenced by the nature of the sample.

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