

THESES 1922

- Alles, Gordon A A new acridine dye.
- Ames, Paul R The specific heat capacity of heavy petroleum products.
- Beman, Willard JF The Löwig process for caustic soda using trona as a raw material.
- Bridgeford, Frank R. A process for the utilization of pyrite ash.
- Burks, Jesse C Semi-works development of a germanium extraction process.
- Gillies, Robert W An attempt to dehydrogenate cottonseed oil.
- Knight, Alfred W Perchloric acid from ammonium perchlorate and oxides of nitrogen.
- Reynolds, Maynard S The utilization of a deposit of magnesite located near Porterville, California as a source of raw material for the manufacture of C.P. Epsom salts.
- Ritchie, Charles Fisher An investigation on the production of sodium thiosulfate from trona.
- Vesper, Howard G The preparation of carbon monosulphide and hydrocyanic acid by the use of activated carbon.
- Warner, Lester O The reaction between nitrogen and methane in the silent electric discharge.

California Institute of Technology

Pasadena, California

CLASS OF 1922

Department of Chemistry

Undergraduate Theses of

Gordon A. Alles

Paul R. Ames

Willard J. Beman

Frank R. Bridgeford

Jesse C. Burks

Robert W. Gillies

Alfred W. Knight

Maynard S. Reynolds

Charles Fisher Ritchie

Howard G. Vesper

Lester O. Warner

Semi-works Development
of a
Germanium Extraction Process

Thesis

by

Jesse C. Burks

In partial fulfillment of the requirements
for the degree of Bachelor of Science
in Chemical Engineering

California Institute of Technology
Pasadena, California

1922

Semi-works Development of a Germanium Extraction Process .

General Considerations.

The existence of Germanium in the Zinc Sulphide ores of the Joplin, Mo. district is generally known. The element, combined as the oxide GeO_2 is present to the extent of approximately 0.01% . This fact is of no particular interest as far as the economical extraction of the element is concerned, but in addition it is found that during the process of refining of the zinc ore, in the production of zinc oxide, the residue of zinc oxide remaining in the retorts contains Germanium Oxide to the extent of approximately 0.24% . This fact is significant in that it furnishes a source of the otherwise extremely rare element in a comparatively concentrated form. Through Dr. A. A. Noyes it was possible to obtain two hundred pounds of the crude zinc oxide from the New Jersey Zinc Co. , this sample being used in the work described in this paper.

Purpose of Investigation.

In view of the fact that there had been little, if any development of a method of obtaining Germanium or its compounds in any appreciable quantities, and also due to the fact that a demand had been created for enough of the element to carry on an extensive investigation of its properties, the matter of large scale extraction was looked into. The purpose of this work was therefore to attempt

a development of a semi-works scale process ,whereby Germanium or one of its related compounds could be obtained in a practical and economical manner from crude zinc oxide.

Previous Work .

Preliminary work on this problem was started by Mr. Phillip Clarke in January, 1921, and continued until June of that year. A thorough survey of the properties of Germanium and its compounds was made and previous methods of extraction investigated, followed by the development of a more practical method of extraction applicable to large scale operation. The results of his investigations appear in his thesis report : "The Extraction of Germanium from Crude Zinc Oxide." Clarke found that the crude zinc oxide contained Germanium Oxide (GeO_2) to the extent of 0.24% and arsenic oxide to approximately twice that amount. He points out that practically all methods of extraction prior to his investigations, involved a distillation of the dissolved germanium bearing substance, in which a separation was made through the volatility of Germanium Chloride. There were several modifications of this general procedure, some separating the Germanium from the arsenic and zinc chlorides in the first step, by distillation in the presence of an oxidizing agent, under which conditions the arsenic chloride was non volatile. Others, distilling over both the Germanium and arsenic in the first step, rely on redistillation for separation. None of these methods however, did away with the necessity of distilling large

quantities of an extremely corrosive liquid. The disadvantages of such a distillation are manifest.

A consideration of the fact that Germanium was recovered from the distillate in the above mentioned distillations by precipitation with hydrogen sulphide led Clarke to investigate the possibility of making the first step in the process a precipitation of the dissolved Germanium Oxide. This proved to be practically quantitative the procedure being as follows :-

10 gr. of the zinc oxide were dissolved in 30 c.c. of concentrated Hydrochloric acid, heated to dissolve all zinc oxide and allowed to cool to room temperature, lead chloride separating out as needle-like crystals. The solution was filtered and hydrogen sulphide passed through the clear filtrate. A yellow flocculent precipitate of combined arsenic and Germanium sulphides came down and was recovered by filtration on a Buechner funnel. This precipitate was then dissolved by heating in a relatively small amount of hydrochloric acid, nitric acid added to convert the arsenous sulphide to the non volatile arsenic state. The mixture was distilled in a current of carbon dioxide. Germanium chloride came over at about 120°C. and was reprecipitated from the acid solution as white Germanium Sulphide (GeS_2) .

Although the procedure developed by Clarke seemed much more applicable to large scale work than the distillation methods previously outlined, it had a serious drawback in the fact that it necessitated the handling

of strong hydrochloric acid. He substituted sulphuric acid of the same concentration, which gave equally good results. The use of sulphuric acid instead of hydrochloric was advantageous from a standpoint of cost as well as relative corrosive qualities of the two acids.

The remainder of this paper will be taken up in a presentation of the work done in the development of Clarks procedure to a semi-works scale, comprising both laboratory and semi-works experiments.

Laboratory Developments.

(a) Determination of acid concentration

It was first necessary to determine the minimum quantities of 60°Be . sulphuric acid and water required for a given amount of oxide, considering both solution of the oxide and precipitation of the dissolved Germanium. As the oxide was readily soluble in acid, the amount of acid was determined by the requirements for the precipitation of Germanium. Accordingly, 10 gr. charges of the oxide were dissolved in varying quantities of 60°Be . acid, mixed with 100 c.c. of water, agitated to insure complete solution, the precipitated lead sulphate allowed to settle and the solution filtered. After cooling, hydrogen sulphide was passed through the filtrate until precipitation was complete, a condition that was indicated by the absence of further precipitation when gas was passed through the filtrate from the original precipitation, or until there was indication that precipitation would not be complete. The results showed that the most economical mixture for

complete precipitation per 10 gr. of oxide was 25 c.c. of 60°Be. sulphuric acid and 100 c.c. water. Smaller concentrations of acid yielded a precipitate of the combined sulphides that was more or less colloidal in structure, making filtration and recovery difficult if not impossible.

(b) Heat effects and their relation to

Precipitation - Methods of Precipitation .

As the addition of acid to the oxide and water caused a very appreciable temperature rise , approximately 35° C, and , as noted by Clarke , the solubility of Germanium Sulphide increases very rapidly with increased temperature, it was necessary to determine the maximum temperature at which precipitation would take place. The relation of this data to large scale operation is obvious, as precipitation at higher temperatures would eliminate the necessity of cooling after the charge had been agitated with acid. To obtain this data , as well as information as to methods of precipitation, 100 gr. of the oxide were placed in a 2 liter battery jar, 1000 c.c. water and 250 c.c. of 60°Be. sulphuric acid slowly added, the mixture being agitated by means of a motor driven stirrer. After 1 hour , agitation was stopped and the solution allowed to stand. The lead sulphate settled out rapidly, decantation yielding a clear liquid after four hours. The clear liquid was transferred to a 2 liter wide mouth bottle , fitted with a mechanical stirring device that is best described by reference to figure (I). :

A vertical shaft, fitted with a pulley (g) passes

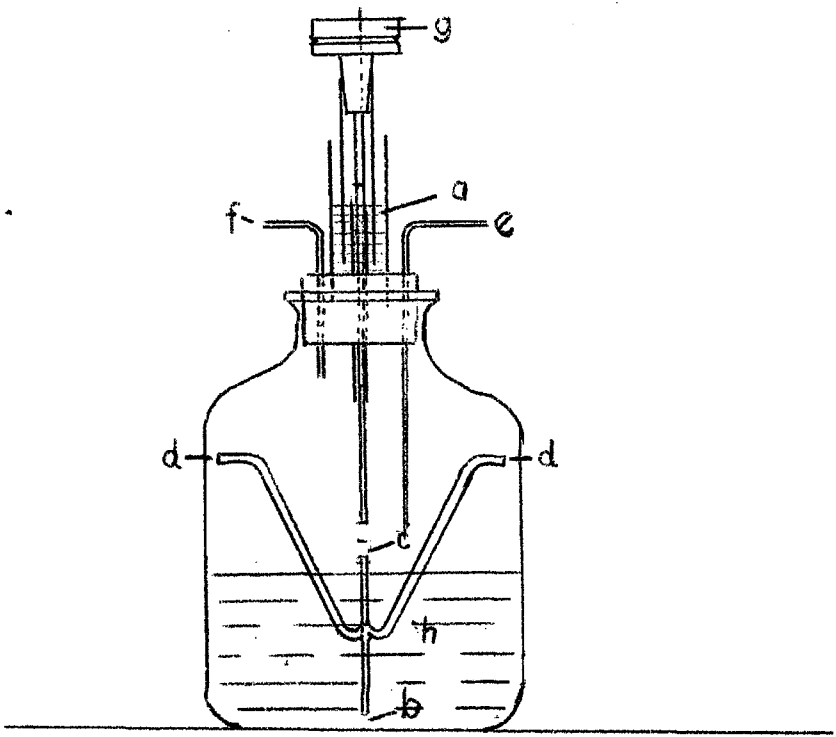


Figure 1

through a mercury filled, gas tight bearing (a). At the end of this rotating shaft is connected a two armed stirrer made of glass tubing with openings at (b) and (d), but sealed at (c). The liquid level is slightly above the cross arms (h). On being rotated, liquid that is in the lower part of the stirring arms is thrown outward by centrifugal force, causing a flow of liquid upward and out against the walls of the container at (d), at the same time pulling liquid in at (b). This causes a circulation of liquid as well as exposure of a large wetted surface. Hydrogen sulphide gas from a Kipp generator, passes in at (e), air first being expelled through (f). This apparatus proved to be very well adapted to precipitations of this nature. It eliminated the necessity of a hood to carry away hydrogen sulphide, since the total amount of gas utilized consisted only of that required for precipitation and to saturate the liquid.

A 15 c.c. sample (called #1) of the clear filtrate was taken before precipitation in the 2 liter jar was started, hydrogen sulphide passed through it until precipitation was complete and the liquid saturated with gas. This was filtered and 10c.c. of the filtrate titrated with KMnO_4 solution. At different stages in the precipitation in the 2 liter jar, 15 c.c. samples were taken, filtered, and 10c.c. portions titrated with KMnO_4 . This afforded a means of observing the rate at which saturation was taking place, the extent of precipitation at different time intervals and the extent

of saturation when precipitation was complete. The ratio of the amount of KMnO_4 reduced by 10 c.c. of saturated liquid to that reduced by any given sample indicated the percentage saturation existing at that time. The extent of precipitation was visually estimated and was accordingly only approximate. ---- In this manner a number of observations were made with regard to the time required, saturation effects and the rate and efficiency of stirring and agitation, as related to temperature. The results of these runs are tabulated below, and graphically represented on page 7a.

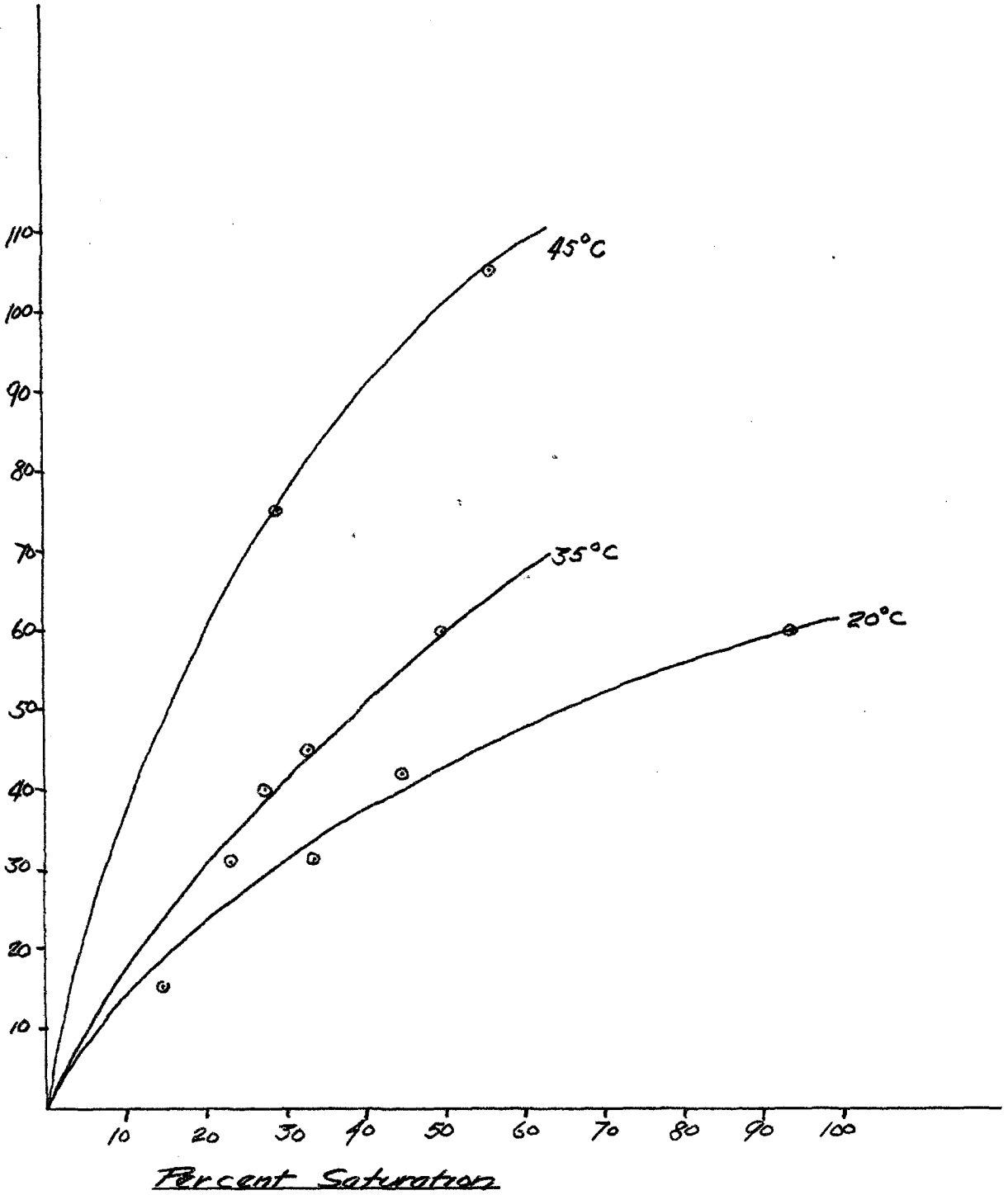
(A) Precipitation at 20°C .

Sample	Time of contact with H_2S	c.c. KMnO_4 used	% pptn.	% saturation
1.	45 min.	40.70	100	100
2.	15	6.95	60	17
3.	30	13.80	95	34
4.	45	17.90	100	44
5.	60	38.60	100	94

Remarks: Precipitation complete after 45 min. agitation.
Solution 44% saturated.

(B) Precipitation at 35°C .

Sample	Time of contact with H_2S	c.c. KMnO_4 used	% pptn.	% saturation.
1.	45 min.	36.00	100	100
2.	30	8.60		24
3.	45	12.00		33
4.	60	19.00		50
5.	75	18.90		50

Rate of Saturation

Remarks: Precipitation complete after 1 hr. agitation.

Solution 50% saturated .

(C) Precipitation at 45°C.

Sample	Time of contact with H ₂ S	c.c. KMnO ₄ used	% pptn.	% saturation
1.	45 min.	36.50	100	100
2.	30	9.40		26
3.	45	9.90		27
4.	60	10.00		27.4
5.	75	10.70		29
6.	105	20.10		55

Remarks: Precipitation was not complete at the end of
1hr. 15 min. agitation . Saturation was 55% .

The results of these runs were interpreted as indicating the fact that for satisfactory precipitation the temperature should be as much under 35°C. as possible. Above this temperature proper coagulation was not obtained. At lower temperatures the precipitate settled out rapidly, leaving a clear liquid that could be decanted off , and that gave no further evidence of precipitation when subjected to contact with hydrogen sulphide. Another interesting fact was that the liquid did not have to be saturated. In fact , less than 50% saturation was sufficient for complete precipitation.

(c) Determination of Yield .

To determine the yield of the process as outlined , 100 gr. of the oxide were agitated with 1000 c.c. of water and 250c.c. 60°C. sulphuric acid,

as previously described. The clear filtrate was transferred to the precipitating jar and agitated with the centrifugal device until precipitation was complete. When the precipitate of the combined sulphides had settled, the clear liquid was decanted off and the precipitate collected on a Buechner funnel. The precipitate was washed free from hydrogen sulphide with dilute acid and dried in an oven at 115°C. The filter cake was removed from the paper and weighed. As this weight represented the combined germanium and arsenic sulphide obtained from a 100 gr. sample, approximately one tenth of this precipitate was weighed out and a quantitative analysis made to determine the percentage of Germanium sulphide in the combined precipitate, the quantitative procedure conforming to that previously used in the analysis of a 10 gr. charge of the original zinc oxide. The procedure, as used by Clarke, is as follows :-

50 c.c. of 68% HBr is added to the weighed sample in a 100 c.c. distilling flask. Distillation is made through a condenser and adapter into a 500 c.c. conical flask containing 10 c.c. of water into which the adapter is dipping. Distillation is continued until the residue is nearly solid and has a volume of 10-15 c.c. The condenser is washed through with a minimum quantity of fuming nitric acid, and fuming nitric acid added to the distillate slowly until all HBr is converted to Br₂. This is heated on a water bath until all Br₂ is expelled and then boiled to a small volume, avoiding the separation

of germanium and arsenic as oxides in the strong nitric acid solution. The liquid is transferred to a platinum crucible and the evaporation finished on a water bath. 1-2 c.c. of hydrofluoric acid are added, the oxides forming a clear slightly colored solution which is evaporated to a syrupy consistency. 10-15 drops of hydrofluoric acid are added and about 25 drops of saturated potassium fluoride solution and 2-3 c.c. 95% alcohol to make precipitation complete. Filtration is made on a filter paper pulp in a platinum Gooch, washed with 95% alcohol until free from potassium salts, and the crucible dried to constant weight at 125°C. Increase in weight represents K_2GeF_6 .

Three such runs were made, the results obtained being as follows :-

Wt. of combined As_2S_5 & GeS_2	Amt. taken for analysis	Wt. K_2GeF_6	Equivalent amt. GeO_2	% Ge Extr'n.
.7293 gr.	.0893	.0563	.0222	74.0
.5956	.1061	.0886	.0349	80.0
.7302	.0712	.0430	.0170	71.0

The fact that a more nearly quantitative recovery was not realized may be attributed to several possibilities, the most probable being failure to make a clean recovery of the combined precipitate. As this loss would necessarily be magnified in small scale work it was not considered improbable that the same procedure would give an extraction of over ninety percent when applied on a semi-works scale. Other losses, such as partial colloidal suspension of the precipitate and incomplete precipitation

would no doubt make up the remaining loss.

(d) Re-utilization of Acid .

From an economic standpoint it was very important to determine the extent to which the sulphuric acid in the process could be used before it had to be removed from the process altogether, and replaced by a fresh charge. The filtrate resulting when the arsenic and germanium sulphides had been removed differed from the original solution of acid in these two respects: decreased acid concentration and the presence of a large amount of dissolved zinc sulphate . To put this liquid back into the process to dissolve more zinc oxide, germanium and arsenic , the acid concentration could be brought back to its original value by addition of concentrated acid. Assuming that the presence of dissolved zinc sulphate would not interfere with precipitation with hydrogen sulphide , the number of times the acid could be utilized would therefore depend on the solubility of zinc sulphate in the sulphuric acid.

A run was made in which the filtrate, after the removal of the combined sulphides, was used to treat a second charge of oxide, enough acid being added to bring the acid concentration up to its original value. Precipitation was satisfactory in every respect , but at the end of this run the filtrate was practically saturated with zinc sulphate , the crystals becoming evident when the temperature was lowered to about 25°C. This result was compatible with data obtained on the solubility of

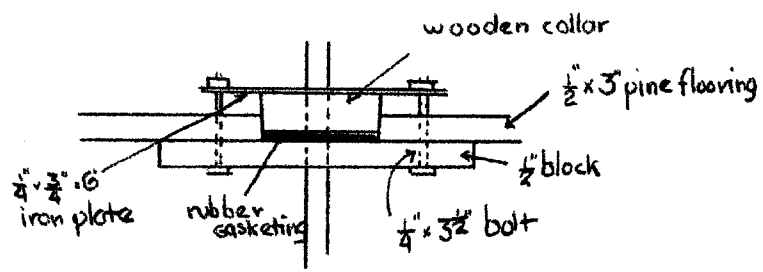
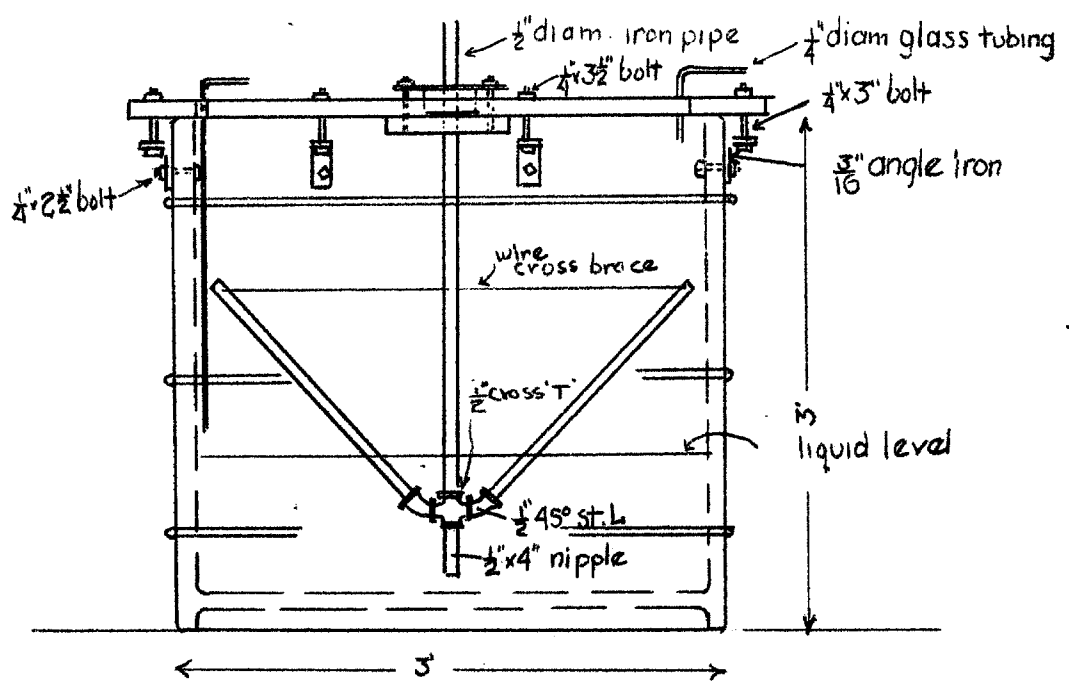
zinc sulphate in sulphuric acid and definitely established the fact that at the end of the second run the acid would have to be removed from the process, neutralized, and the zinc sulphate recovered.

Semi-works Development .

It was decided to use, in the large scale runs, a charge of 50 lbs. of zinc oxide. Accordingly, a 100 gal. redwood tank, the dimensions of which are shown in figure (2) was used, having been given two coats of Biturin Asphalt paint. Mechanical agitation was furnished by means of a wooden stirrer shown in the drawing, rotated at approximately 40 r.p.m.

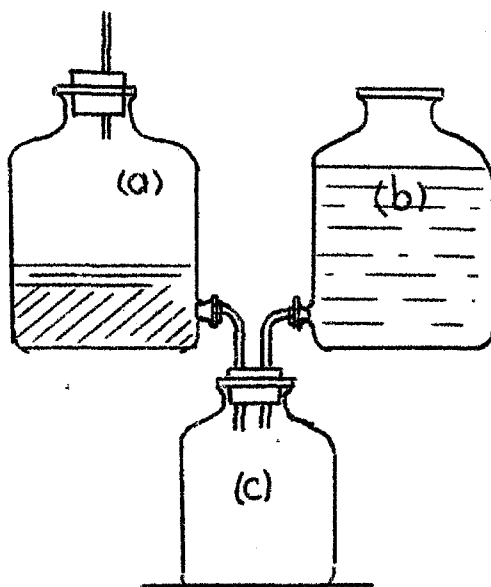
50 lbs. of the oxide were weighed into the tank, followed by 450 lbs. of water. With the mixture being agitated 220 lbs. of concentrated sulphuric acid (sp.gr. 1.834) were slowly added and agitation continued for two hours. During this step the temperature went to 60°C. The solution was allowed to stand twelve hours at the end of which time the lead sulphate had completely settled out, leaving a clear liquid. During this time the temperature had dropped to 32°C. The liquid was transferred to a second 100 gal. tank by means of a vertical, steam driven, Duriron pump. It was possible to transfer approximately ninety five percent of the liquid before it began to come over cloudy, due to agitation of the lead sulphate. Pumping was stopped at this point and the remaining liquid transferred, after being allowed to settle a second time. The lead sulphate was transferred to a small crock for future recovery.

Precipitating Tank semi-works scale



Stuffing Box

Figure 2.

H₂S GeneratorFigure 3

The tank into which the filtrate was pumped was fitted with a gas tight top the construction of which is shown in figure (2) . This top contained a stuffing box, through which ran the vertical section of the stirring device, which is also best described by reference to the drawing, said device being made of $\frac{1}{2}$ " black iron pipe , coated inside and out with Asphalt paint. The stuffing box , or bearing, consisted of a snugly fitting wooden collar, fitting into a counter-sunk aperture in the tank top, and held firmly against a packing consisting of gasket rubber, by means of two plates and bolts , as indicated. The vertical section of the stirrer was attached to the rotating shaft and rotated at approximately 125 r.p.m. This speed was sufficient to throw liquid against the rim of the tank, allowing the liquid to run down the inner walls.

Hydrogen sulphide gas was furnished by a generator consisting of three two liter jars, connected as shown in figure (3) . (a) contained a layer of broken porcelain on top of which was placed iron sulphide. Both (b) and (c) contained dilute sulphuric acid, the purpose of (c) being to collect sediment and prevent clogging of the generator jar (a) . Gas was passed into the closed tank at (A), air being first displaced through (B). (B) was then closed and agitation started, a positive pressure being maintained throughout the run. At intervals a sample was removed from the tank through

the opening (B) by means of a suction line, and the condition of the liquid noted, with regard to completeness of precipitation. At the end of $1\frac{1}{2}$ hrs. precipitation was complete, as indicated by rapid settling of the precipitate and no further precipitation when the filtrate was subjected to passage of a free current of hydrogen sulphide.

The liquid was allowed to stand twelve hours. Filtration was then made by means of a Duriron pump and a canvas filter leaf, built up on a frame of $\frac{1}{4}$ " lead pipe. It was not intended to build up a cake on the leaf, but to remove the large part of the liquid. When this had been accomplished, the precipitate, held in suspension in a small amount of acid was transferred to a crock, and after being allowed to settle, more of the clear liquid siphoned off. The combined precipitate of arsenic and germanium sulphides was finally recovered on a large Buechner funnel.

A second run was made, 50 lbs. of zinc oxide being added to the filtrate from the first run. 68 lbs. of acid were added to bring the acid concentration up to its original value. The only difference in the two runs lay in the fact that after the solution had been subjected to precipitation and allowed to stand, zinc sulphate began to crystallize out. This in no way interfered with results, but made recovery of the combined sulphides more difficult.

Separation of Germanium from Arsenic .

It was originally planned to separate the Germanium from the arsenic , in the combined precipitate, by distillation , regardless of the fact that it would necessarily be a slow process. Clarke had found, however, that the relative solubilities of arsenic and germanium sulphides , in acid , varied considerably with the temperature. To such an extent in fact, that when the combined precipitate from 10 gr. of oxide in 25 c.c. of 12 N acid was heated to between 80-95°C. and filtered, a quantitative separation was made, germanium sulphide being completely dissolved and no arsenic whatever being carried through. This method of separation was attempted on a large scale in the following manner :-

A large evaporating dish (45 cm diam.) was filled with 12 N acid and the combined precipitate added, being stirred mechanically. The temperature was maintained at 95°C. and stirring continued for 1 hr. The hot solution was filtered through a suction filter, with asbestos as the filtering medium. The precipitate was added to a fresh charge of acid and the process repeated, the filtrates from all the extractions being combined. After four extractions the combined filtrates were saturated with hydrogen sulphide at 25°C. A white precipitate characteristic of germanium sulphide came down , but on standing became slightly discolored, indicating that separation had not been complete. It was further evident , from the size of the precipitate, that

this method was not adapted to separation, due to the extremely small amount of Germanium that was recovered from each extraction.

Limited time prevented the separation by distillation, work on the problem being stopped at this point.

The writer acknowledges his indebtedness to Dr. Wm. N. Lacey, under whose supervision this work was carried out, for many helpful suggestions and personal assistance.

Summary.

1. Large laboratory scale and semi-works scale investigations have been carried on toward the development of a commercial process for the extraction of Germanium from crude zinc oxide.
2. The precipitation of arsenic and germanium by hydrogen sulphide from sulphuric acid solution offers a satisfactory method of concentrating a small amount of Germanium present, so that its recovery may be carried out in small scale equipment.
3. A very satisfactory semi-works scale method was developed, for saturating a liquid with a gas with only small loss of the latter. This might prove generally applicable where noxious gases are being handled in large scale experimental work.