THE DISSOCIATION PRESSURE OF
STANNOUS SULFATE

Thesis

by

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Introduction

At temperatures above 200°, stannous sulfate decomposes, forming sulfur dioxide and stannic oxide, according to R. G. Durrant.

(R. G. Durrant, J. Chem. Soc., 107, 622-38 (1915).)
Stannous sulfate is unique among the sulfates which have been studied in that it is the only one which does not decompose to give a mixture of sulfur dioxide, sulfur trioxide and oxygen and basic sulfates. For this reason the dissociation pressure of stannous sulfate is of unusual interest. In this research an attempt has been made to determine the equilibrium pressure of sulfur dioxide from the dissociation of stannous sulfate.

A search of the literature failed to disclose any previous work on this problem, and yielded only a small amount of information, of any kind, concerning stannous sulfate.

Preparation and Purification of Materials

Stannous Sulfate: W. P. Baxter, who conducted preliminary experiments on the dissociation pressure of stannous sulfate, found that pure stannous sulfate could not be made satisfactorily by dissolving tin in sulfuric acid, or by precipitating the sulfate by means of sulfuric acid from a stannous chloride solution. He found that the most satisfactory method was to dissolve stannous hydroxide in dilute sulfuric acid and then crystalize out the stannous sulfate by means of alcohol. The author found that unless very special precautions were taken to prevent oxidation by the air and hydrolysis the material prepared by this method contained from 4% to 5% stannic tin. Consequently, the entire process was carried on in an atmosphere of hydrogen in the apparatus shown in Figure 1, and care was taken never to let the acid concentration of solutions containing stannous sulfate fall below 1.6 N the concentration below which stannous sulfate solutions precipitate a basic salt, according to P. Miller.

(P. Miller, Thesis, California Institute of Technology (1924).)

The procedure was as follows: C. P. stannous chloride crystals were placed in the Flask A, Figure 1. All of the air was then swept out of the reaction flask by a stream of hydrogen which entered at B and escaped at C. The stannous chloride was then dissolved in 6 N sulfuric acid; warmed slightly; and shaken, for several hours, with finely-divided tin. The mixture was then forced over into the filtering apparatus where the tin was filtered out. The filtering flask, containing the solution of stannous sulfate in

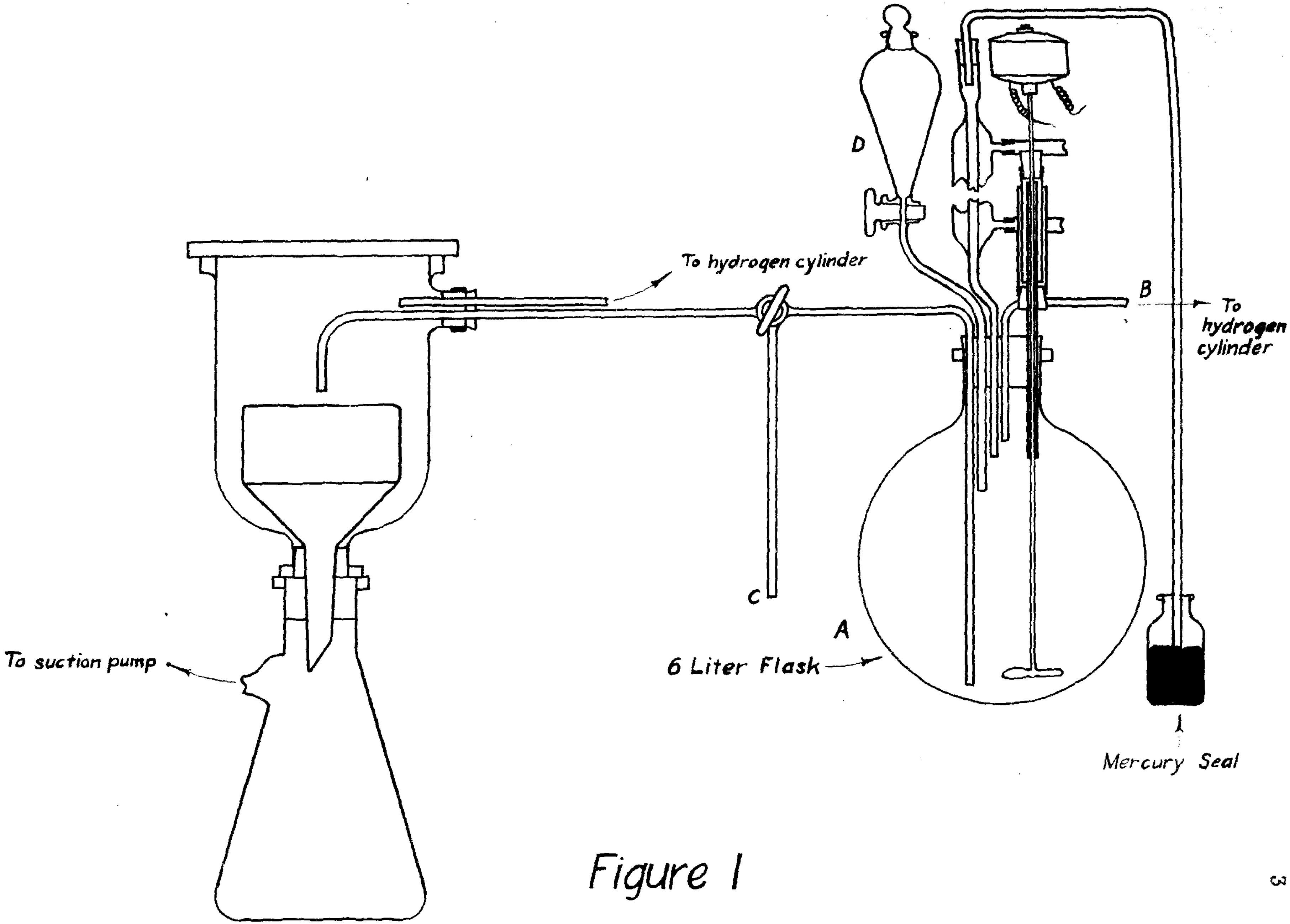
D
To hydrogen cylinder
B
To hydrogen cylinder
C
A
6 Liter Flask
To suction pump
Mercury Seal

Figure 1

dilute sulfuric acid, was then detached from the filtering apparatus and quickly connected at C. Hydrogen was run in at E thus forcing the solution back into the reaction flask through C. The stannous sulfate was then crystalized out by adding alcohol through D. The mixture was filtered, and the stannous sulfate was washed, first with alcohol, and then with ether both of which were forced over onto the filter from the reaction flask.

An analysis of the stannous sulfate thus prepared showed that it contained .5318 gm. of stannous tin per gram of sample. Calculated on the assumption that all of the stannous tin was present as the sulfate, this analysis shows that the sample contained 96.5% stannous sulfate. It also contained some chloride, so it was dissolved in 6 N sulfuric acid, shaken with finely-divided tin, and then recrystalized by means of alcohol. All operations were carried on out of contact with air in the apparatus used during the original preparation. Tests showed that this material was entirely free from chloride and from free acid. An analysis showed that it contained .5338 gm. of stannous tin per gram of sample and .0148 gm. of stannic tin per gram of sample.

To free the stannous sulfate completely from all volatile impurities is an operation of extreme importance for work of this kind and one which was found rather difficult to accomplish. Drying for a period of days in a vacuum desiccator over sulfuric acid and then heating for several hours at a temperature of 110°, during which time all volatile matter was being continuously pumped off by means of a high vacuum pump, failed to remove all of the water. It was found necessary to heat the material at 157°, under a vacuum, for a period of from 24 to 36 hours before it was completely dehydrated. An analysis of the stannous sulfate after it had been subjected to this drying process showed that it contained .5370 gm. of stannous tin per gram of sample, showing that no dissociation had occured.

Preliminary Experiments

The apparatus originally used for measuring the dissociation pressure is shown in Figure 2. Stannous sulfate was placed in the small bulb before it was sealed on to the apparatus. The apparatus was then evacuated, and the stannous sulfate was heated by means of a vapor bath. The mercury in the closed arm of the manometer was kept at a constant level throughout an experiment.

The stannous sulfate was first heated in the vapor of boiling mercury. At this temperature (357°) a pressure was quickly developed which was above 3.5 atm., the capacity of the manometer.

Diphenylamine, which boils at 310°, was then employed in

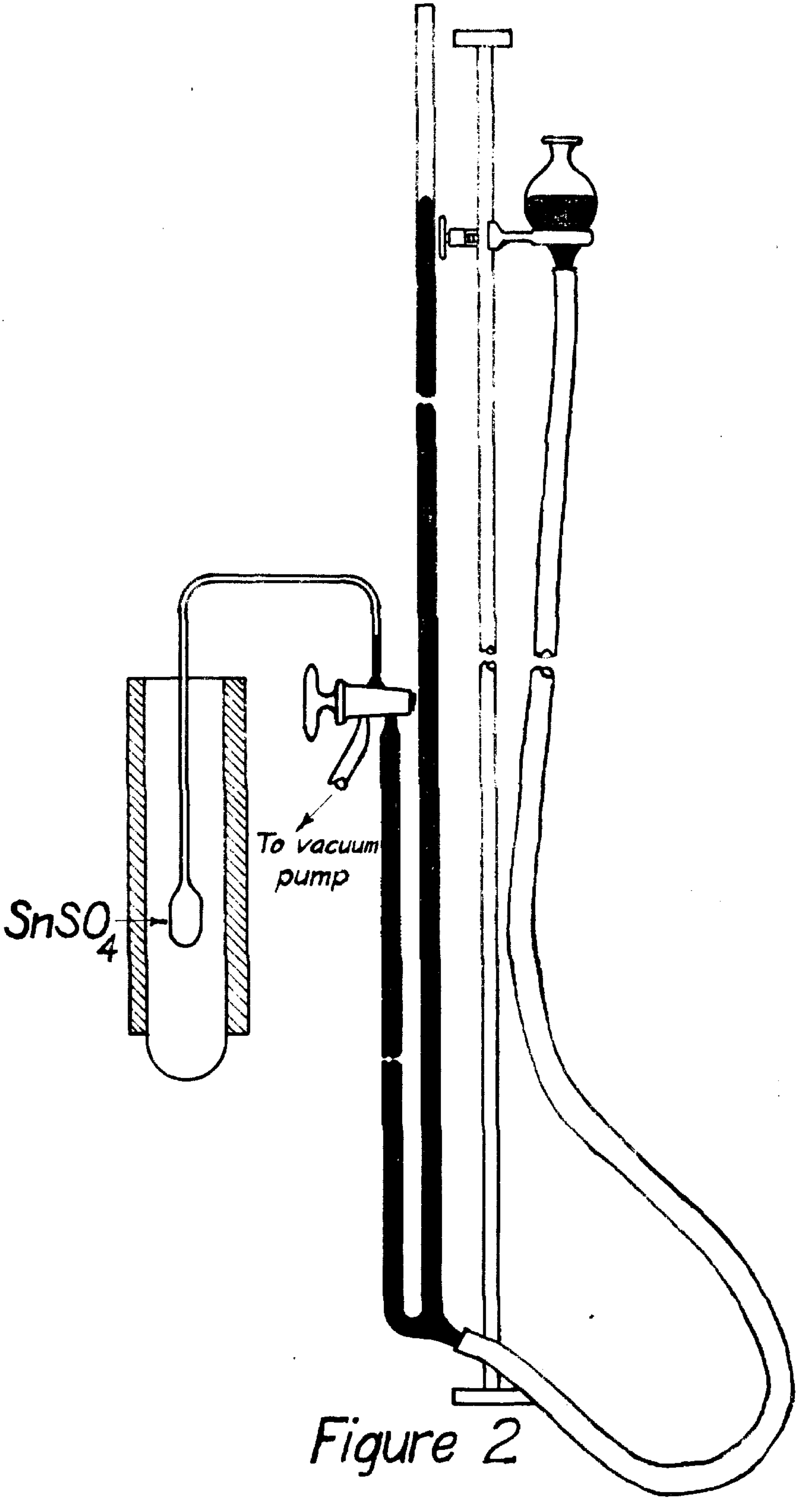

Figure 2

the vapor bath. At this temperature a pressure of 2650 mm. was obtained in about 2.5 hours. At this pressure sulfur dioxide condensed in the cooler portions of the apparatus. The same trouble was encountered at 249°, the boiling point of benzoic acid.

Naphthalene, which boils at 218°, was then employed. After heating the stannous sulfate constantly for 25 days at this temperature, a pressure of only 961 mm. was obtained. At no time did the rate of increase of the pressure diminish in such a way as to indicate that the equilibrium pressure was being approached.

These experiments showed that it would be impracticable to obtain equilibrium at low temperatures, and that, consequently, high pressures would have to be measured. A multistage manometer, having a capacity of about 10 atmospheres, was then constructed. The capillary tube leading from the bulb inwhich the stannous sulfate was placed to the manometer was wound with resistance wire and electrically heated to prevent the condensation of sulfur dioxide. Attempts to measure the dissociation pressure both at 357° and 310° with this apparatus failed, because the capacity of the manometer was not great enough.

An apparatus very similar to the one finally constructed to make accurate measurements of the dissociation pressure, which is described later and is shown in Figure 3, was then constructed to obtain definite knowledge as to the order of magnitude of the dissociation pressure. At 310° the pressure increased at a constantly diminishing rate until a pressure of 30 atm. was reached at which point it remained constant for four hours. At the end of this period it was found that the constant readings were not due to equilibrium having been reached but were caused by the condensation of sulfur dioxide. A higher boiling liquid was then placed in the jacket around the capillary tube. The pressure rose immediately to 34.4 atm. where it remained constant for 2 hours. The apparatus was then shut down over night. When an attempt was made to start up again the next morning, the mercury thread in the capillary tube broke, making it impossible to continue the experiment. Definite proof that equilibrium had been attained was not derived from this experiment; but the very slow rate of increase during the latter part of the experiment, which was evidenced by the fact that during the four hours that liquid sulfur dioxide was in the apparatus only enough gas was given off by the stannous sulfate to cause a small increase in pressure when all of the sulfur dioxide was again vaporized and by the fact that after this increase had occured no further increase was observed during the next 2 hours, was thought to indicate that the pressure obtained was not far from the equilibrium pressure.

At 357° the pressure went up to 47.6 atm. in 3 hours and remained constant for 3 hours. It was thought that equilibrium had been reached. It was then decided to bring the temperature down to 310° and see if the pressure would decrease to the value obtained at 310° when approaching equilibrium from the other side. While changing the vapor bath, the apparatus cooled off allowing sulfur dioxide to condense. When heat was again applied, the apparatus exploded. In this case, as before, definite proof that equilibrium had been reached was not obtained but it was thought that a fairly good idea of the magnitude of the pressure which would have to be measured had been obtained, so an apparatus was designed and built which was capable of measuring pressures ranging from 30 atm. to 60 atm. accurately and which was thought to have a maximum capacity of about 200 atm.

The Apparatus

The apparatus used for making the final measurements is shown in Figure 3. It consisted essentially of a long capillary tube one end of which was sealed off and the other end of which was sealed to a bulb which contained stannous sulfate. In the capillary, tube near the end which was sealed to the bulb, was a short thread of mercury. When

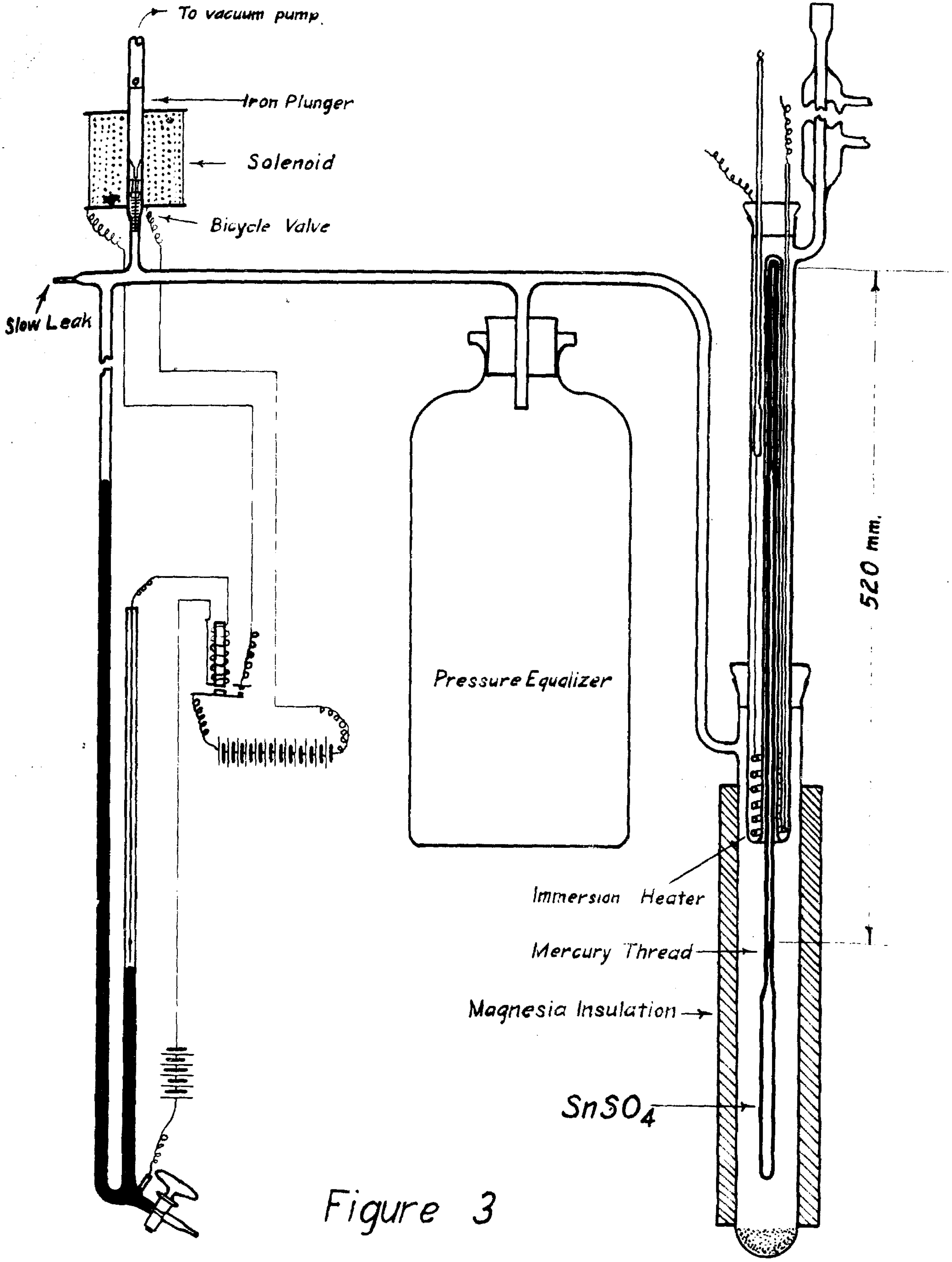
To vacuum pump
Iron Plunger
Solenoid
Bicycle Valve
Slow Leak
Pressure Equalizer
520 mm.
Immersion Heater
Mercury Thread
Magnesia Insulation
$SnSO_4$

Figure 3

the stannous sulfate was heated, the pressure created forced this mercury thread against the gas trapped in the upper part of the tube. The volume and pressure of the gas in the upper end of the capillary tube was determined at the start of the experiment, and the change in volume was noted as the experiment proceeded. The pressure was calculated by means of the gas laws.

The preliminary experiments seemed to indicate that a small change in temperature causes a marked change in the dissociation pressure. They also showed that it was extremely difficult to continue with an experiment after the apparatus had been allowed to cool down due to complications caused by the condensation of sulfur dioxide. It was, therefore, essential that a means of maintaining a constant and accurately known temperature be devised which would permit going from one temperature to another without allowing the apparatus to cool. The vapor pressure of mercury over a range of temperatures which corresponds to the range over which it was desired to measure the dissociation pressure has been accurately determined.
(Smith and Menzies, J. Am. Chem. Soc., 32, 1434 (1910).)
Consequently, an apparatus similar to that designed by Dr. D. F. Smith for maintaining constantly any desired pressure less than atmospheric was constructed. It is shown in

Figure 3. The essential feature of this apparatus is a magnetically-operated tire valve which serves to shut off the apparatus inwhich the mercury is being boiled under reduced pressure, from an evacuated space. A slow leak is maintained in the boiling apparatus which allows the pressure to slowly increase until it reaches the pressure which the operator desires to maintain. At this point the mercury in the open arm of the manometer shown in the diagram, closes the circuit with the result that the valve opens momentarily allowing a little of the air in the apparatus to escape into the evacuated space. This external vacuum is maintained by a pump which runs constantly.

Turpentine, which boils a little above the critical temperature of sulfur dioxide, was boiled in the Jacket B to prevent sulfur dioxide from condensing. The heat required to boil the turpentine was supplied partly by the vapors of boiling mercury and partly by the electric immersion heater shown in the diagram.

The errors introduced into the various measurements by this apparatus are probably smaller than the error caused by the difficulty of actually obtaining equilibrium would have been. At 310°. a change of 6.54 mm. in pressure causes a change of 1° in the boiling point of mercury and at 350° a change of 12.5 mm. causes a change of 1°. No difficulty was experienced in maintaining a pressure which was constant to within less than a millimeter with the pressure-regulating device. Powdered glass was stuck to the bottom of the boiling tube by pouring it into the tube when the bottom was red hot. By this means all trouble from bumping was eliminated. The boiling tube was carefully insulated by means of magnesia. It was therefore thought that since the mercury which was boiled in the apparatus had been carefully purified and since the vapor pressure of mercury has been accurately determined that the temperature at which the stannous sulfate was heated was known to within .2° or .3°. Results were not obtained which would indicate the magnitude of the error in the dissociation pressure caused by such a variation in the temperature.

When loading the capillary tube aparatus, hydrogen was first passed through it before either end was sealed up. The mercury thread was then slipped into its proper place at the lower end of the capillary tube, and the upper end of the tube was sealed off. The barometer was then read, and the distance from the surface of the mercury thread to the top of the tube was measured by means of a meter stick. Precautions were taken to have the capillary tube perfectly clean to avoid sticking of the mercury thread or leaking of gas past it. The distance measured was about 520 mm., and the maximum variation in the averages of the various pairs of readings taken after the mercury thread had been displaced in opposite directions from its point of rest was never more than 2.5 mm. the maximum relative error being .48%. It was found necessary to use hydrogen rather than air above the mercury thread; because when air was used mercuric oxide formed slowly at the temperature and pressure to which the air and mercury were subjected, during the course of an experiment.

The distance from the surface of the mercury thread to the top of the capillary tube was measured, at equal intervals of time as the experiment proceeded, by means of a cathetometer. At 50 atmospheres, which was the pressure for which the apparatus was especially designed, the shortest distance which would have to have been measured by means of the cathetometer was 52 mm. Readings could be checked by means of the cathetometer to within .2 mm., so the relative error in this reading would be .38%. At 100 atm., which was the highest pressure measured, the relative error in this reading was .76%.

When the turpentine in the jacket which surrounded the capillary tube was boiled vigorously no trouble was encountered in maintaining a constant temperature in this part of the apparatus. Since the boiling point of turpentine raises gradually when it is boiled in air, the temperature was observed on a thermometer and recorded when pressure readings were taken so that corrections for any variation in temperature could be made.

The Final Experiments

The first experiment performed with the apparatus described above was conducted at 310°. At the end of 44 hours of continuous heating the pressure had increased to 26.4 atmospheres. Since the rate of increase of pressure did not seem to be diminishing at the end of this time, it was considered advisable to raise the temperature to 330°. After heating for several hours at this temperature, the mercury thread broke, so it was necessary to discontinue the experiment.

The second experiment was also carried on at 310° but with about 5 times the quantity of stannous sulfate. After running continuously for 65 hours, a pressure of 100 atm. was reached. The pressure remained constant at this point for 12 hours. With the idea in mind of raising the pressure and attempting to approach equilibrium from the other side, the temperature was raised to 350°. As a result the pressure immediately increased to 104 atm. This increase corresponded, within the limits of experimental error, with the increase in pressure which would be caused by the expansion of the gases in the apparatus. Continued heating for two hours failed to raise the pressure further, a result for which a definite explanation was never obtained. An analysis of the material taken from the apparatus after the experiment had been completed showed that only 40% of the stannous sulfate had been decomposed.

In the third experiment the stannous sulfate was heated at a temperature of 357°. At the end of 5 hours the pressure had risen to 76.5 atm. and was still going up at a fairly rapid rate. When it had reached 85 or 90 atm. the bulb containing the stannous sulfate exploded, breaking the entire apparatus with the exception of the pressure regulating device. Lack of time prevented the designing and building of another apparatus, so the research was discontinued.

The Products Formed when Stannous Sulfate is Heated

R. G. Durrant

(R. G. Durrant, J. Chem. Soc., 107, 622-38 (1915).) heated .1387 gm. of stannous sulfate in an open test tube to a dull red heat until a constant weight was obtained. The residue weighed .0960 gm. which weight corresponds within 1.35% with .0973 gm. the weight required if the residue was stannic oxide. This result shows that no basic sulfates are formed when stannous sulfate is heated but does not show conclusively that stannous oxide is not formed during the reaction for if any were formed it would be oxidized by atmospheric oxygen to stannic oxide. However, Durrant states that results corresponding to those given above are obtained when stannous sulfate is heated out of contact with air. During the course of this research, some evidence has been obtained which tends to confirm Durrant's conclusion that stannic oxide and sulfur dioxide are the only products formed when stannous sulfate is heated. This evidence may be summarized as follows:

1. Stannous sulfate and stannic oxide are both white when pure, and stannous oxide is black. The stannous sulfate used during this research was originally pure white but darkened slightly when subjected to the drying process described under, "Preparation and Purification of Materials." This material darkened a little more after having been heated to 310^{C} for 77 hours. Since the final color was a light yellow, it can be concluded that a very small amount, if any, stannous oxide was formed.

2. Stannous sulfate, stannous oxide and the basic sulfates of tin are soluble in 6 N hydrochloric acid but stannic oxide is not. The residue left after heating stannous sulfate out of contact with air was found to be

insoluble in this acid, indicating that it was stannic oxide.

3. A sample of stannous sulfate was analyzed and found to contain .5338 gm. of stannous tin per gram of sample and .0148 gm. of stannic tin per gram of sample. After heating a portion of this same material under pressure at 310° for 77 hours, it was found to contain .00261 moles of stannous tin per gram of sample and .00294 moles of SO_4 per gram of sample. It is probable that the stannic sulfate originally present in the sample remained unchanged during the heating. If the sulfate which was originally present in combination with stannic tin is deducted from the sulfate found in the material after it had been heated the amount remaining corresponds closely with the stannous tin present in the final material, indicating that stannous oxide or basic sulfates were not present.

Summary

1. A method of preparing pure stannous sulfate has been described.
2. An apparatus suitable for measuring, over a range of temperatures, dissociation pressures of from 10 to 100 atmospheres has been described.
3. Evidence has been adduced which goes to show that the decomposition of stannous sulfate produces stannic oxide and sulfur dioxide without production of

basic sulfates or of sulfur trioxide.

4. The rate of decomposition of stannous sulfate at temperatures under 200° is very slow. At temperatures above 300° the first part of the decomposition is rapid, but approach to equilibrium is rather slow.
5. The pressure of sulfur dioxide from the dissociation of stannous sulfate has been shown to be above 100 atm. at 310°.
6. At higher temperatures, where the rate would be more rapid, and with apparatus capable of measuring higher pressures; it may well be that the equilibrium pressure of sulfur dioxide from the decompostion of stannous sulfate could be obtained.

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