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SOME EQUILIBRIUM RELATIONS IN THE SYSTEM MAGNESIUM OXIDE-  
SULFUR DIOXIDE-WATER (ACID REGION) AT  
PRESSURES BELOW ATMOSPHERIC

BY

DONAT BENNES BRICE

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A

THESIS

submitted to the faculty of the  
SCHOOL OF MINES AND METALLURGY OF THE UNIVERSITY OF MISSOURI  
in partial fulfillment of the work required for the  
Degree of  
MASTER OF SCIENCE IN CHEMICAL ENGINEERING  
Rolla, Missouri  
1947

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Approved by

Frank H. Conrad  
Professor of Chemical Engineering

### ACKNOWLEDGEMENT

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## TABLE OF CONTENTS

	<u>Page</u>
Illustrations.....	1
Tables.....	11
Introduction.....	1
The Experimental Part.....	3
Materials Used.....	3
Apparatus.....	3
Preparation of Equilibrium Mixtures.....	5
Methods of Analysis.....	6
Proof of Method.....	8
Experimental Results.....	12
Summary.....	21
Literature Cited.....	22
Bibliography.....	23
Index.....	24

## ILLUSTRATIONS

<u>Figure</u>		<u>Page</u>
1	Equilibrium Flask and Weighing Pipette	4
2	The Solubility of Sulfur Dioxide in Water at 25° C.	11
3	Pressure-Concentration Curves for the Liquid Phase of the System MgO-SO <sub>2</sub> -H <sub>2</sub> O. Temperature 25° C.	15
4	Pressure-Concentration Curves for the Liquid Phase of the System MgO-SO <sub>2</sub> -H <sub>2</sub> O. Temperature 15° C.	17
5	Temperature-Concentration Curves for the Liquid Phase of the System MgO-SO <sub>2</sub> -H <sub>2</sub> O	19

## TABLES

<u>Table</u>		<u>Page</u>
1	Solubility of Sulfur Dioxide in Water (25° C.)	9
2	Analysis of the Liquid Phase of the System MgO-SO <sub>2</sub> -H <sub>2</sub> O Equilibrium at 25° C.	14
3	Analysis of the Liquid Phase of the System MgO-SO <sub>2</sub> -H <sub>2</sub> O Equilibrium at 15° C.	16
4	Composition of the Liquid Phase of the System MgO-SO <sub>2</sub> -H <sub>2</sub> O	20

SOME EQUILIBRIUM RELATIONS IN THE SYSTEM MAGNESIUM OXIDE-  
SULFUR DIOXIDE-WATER (ACID REGION) AT  
PRESSURES BELOW ATMOSPHERIC

I. INTRODUCTION

This thesis describes the system Magnesium Oxide-Sulfur Dioxide-Water when brought to equilibrium at various pressures of sulfur dioxide plus water vapor, ranging from the vapor pressure of water at the temperature in question to atmospheric pressure.

This system is of significance because it is being used more and more in the "Sulfite Process" in the manufacture of wood pulp and is replacing calcium oxide or a mixture of magnesium and calcium. The solution as it comes from the absorption towers is essentially such a system. Numerous investigators have done work on the system sulfur dioxide and water and the work of Conrad and Beuschlein (1) on the similar system  $\text{CaO-SO}_2\text{-H}_2\text{O}$  is complete. Their procedure was applied to this system of which there are no data available in the literature.

The only mention of this system in the literature was that by O. Maass et al. (2) who mentioned that preliminary work by King (2) showed that the partial pressure of sulfur dioxide over magnesium base liquors differs considerably from that over calcium base liquors of the same mole percentage composition. The data obtained by this investigator agree. The magnesium bisulfite was found to be more soluble and equilibrium curves represented more sulfur dioxide dissolved per given quantity than calcium (1).

The system  $\text{MgO-SO}_2\text{-H}_2\text{O}$  is one of three components. By working at constant temperature, such a system may be made univariant, in which case, the existence of a single solid phase is indicated by a variation in the pressure, hence in the composition of the solution. For this investigation only those conditions under which at least three phases -- gas, solid, and solution -- exist in equilibrium were of interest and the isotherms at  $15^\circ$  and  $25^\circ$  C. were determined.



## II. THE EXPERIMENTAL PART

### 1. MATERIALS USED

The materials used were "C.P. Analyzed" magnesium oxide containing negligible quantities of sulfates and calcium.

The sulfur dioxide was commercial grade, tested for sulfur trioxide by bubbling through an acidified solution of barium chloride which failed to show a precipitate of barium sulfate after thirty minutes. Absorption of the sulfur dioxide with strong alkali gave a residue of 0.30%. Inerts were removed by withdrawing a quantity of gas equal to the size of the equilibrium flask after the materials were prepared for a run.

Freshly boiled distilled water was used.

### 2. APPARATUS

The apparatus was of Pyrex glass and consisted of an equilibrium flask "A" and weighing pipette "B" as shown in Figure 1. The equilibrium flask was approximately 33 cc. in volume. The opening fitted with a ground glass connection (2), was used to introduce the magnesium oxide and water. The two-way stopcock (3) was for the four-fold purpose of evacuating the flask to remove dissolved gases and inerts, introducing the sulfur dioxide, evacuating the manometer by which the pressures were measured, and removing the sample for analysis.

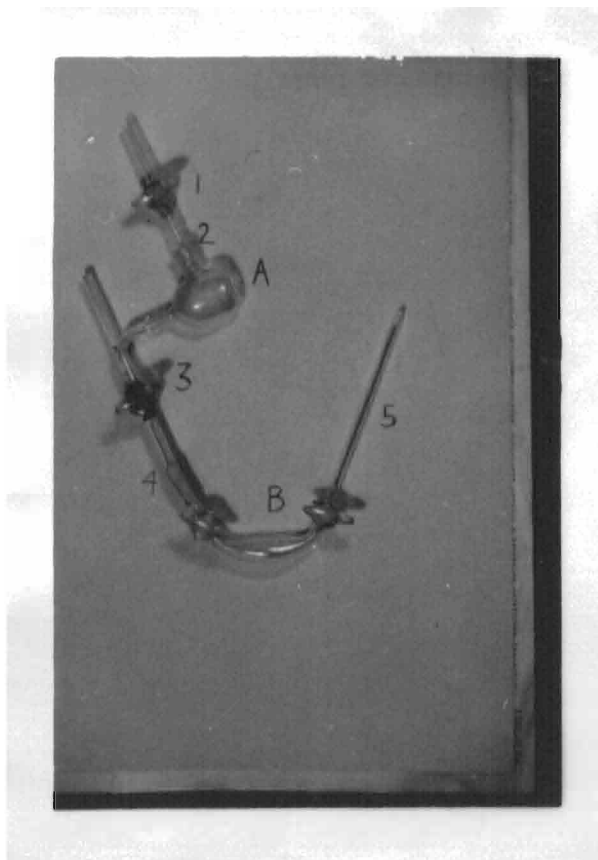


FIGURE 1

THE EQUILIBRIUM FLASK AND WEIGHING PIPETTE

The apparatus, as shown, is connected in position for the removal of a sample of saturated liquid. A slight pressure was applied through stopcock (1) just before the removal of the sample into the weighing pipette (B). The bore of all tubing connected to the equilibrium flask (A) was 1.5 mm. which reduced the volume of expansion of the gas. The pipette extension (5) served a two-fold purpose in allowing the air to escape above the surface of the water of the thermostat during sampling and to transfer the solution to a volumetric flask for dilution and subsequent analysis.

### 3. PREPARATION OF EQUILIBRIUM MIXTURES

The equilibrium mixtures were prepared by introducing the magnesium oxide and the water to the equilibrium flask. The flask was then connected to a Hyvac pump to remove all air and any dissolved gases present in the water. The flask was then ready for the introduction of the  $\text{SO}_2$  which was added to the flask from a gas burette. The gas burette was first evacuated before it was filled with  $\text{SO}_2$ . Sufficient sulfur dioxide was introduced to combine with all the magnesium oxide plus an additional amount to give the desired pressure reading for the run in question. A volume of gas of approximately 40 cc. was then removed to insure no inerts present in the equilibrium flask. Solid was present in all experiments. After this procedure the flask was placed in a water bath and agitated for a period of twelve hours or more. The temperature of the water bath was controlled to  $0.1^\circ \text{C}$ .

Pressure was read by connecting the flask while still in the water bath to a mercury manometer and allowed to remain attached to the manometer for at least one hour before readings were taken. This time was in all cases sufficient to obtain constant readings. Pressures were then determined by noting the difference between this reading and that of a corrected barometer. Readings were taken to the nearest millimeter.

After the pressure readings were made the sample was immediately withdrawn to a weighing pipette and weighed.

#### 4. METHODS OF ANALYSIS

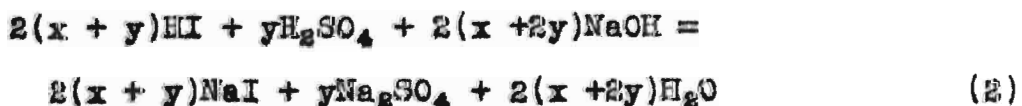
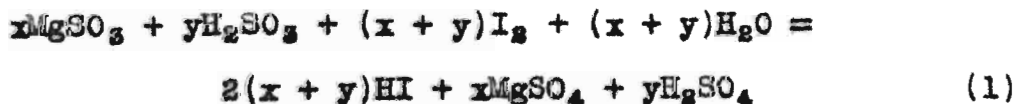
After the saturated solution was removed to the volumetric flask it was analyzed by the Hohn method, the essentials of which are given by Birchard (3). The standard solutions used in this analysis were sodium thiosulfate and iodine of approximately 0.1N and sodium hydroxide of approximately 0.2N. Standardizations were made by the appropriate use of sodium oxalate and potassium permanganate for the iodine and thiosulfate solutions. The sodium hydroxide was standardized by the use of potassium acid phthalate.

The sample (9 to 12 grams) was drained and washed into a volumetric flask nearly full of water. The tip of the weighing pipette was kept below the surface of the water to prevent the loss of any sulfur dioxide in the transfer. The flask was then filled to volume and the aliquots were withdrawn in a similar manner to that from which water is re-

moved from a wash bottle. This method of removal was to avoid the loss of any sulfur dioxide.

Aliquots were analyzed for total, free and combined, sulfur dioxide and separate titrations were made with the sodium hydroxide to determine free sulfur dioxide. This extra titration was used only as a check as the Hohn method is considered more accurate for this determination. The terms total, free and combined, sulfur dioxide as used in this paper are defined by the Technical Association of Pulp and Paper Institute (4). The free sulfur dioxide is the actual free sulfur dioxide plus half of the sulfur dioxide in the bisulfite of magnesium, and is more properly called the 'available sulfur dioxide' as it indicates the sulfur dioxide in excess of that required to form the monosulfite. The combined sulfur dioxide as above calculated represents that required to form the monosulfite.

The equations listed below were used to determine the combined sulfur dioxide. These equations are similar to those of Conrad and Beuschlein (1).



where  $x, y = \text{moles.}$

Let,  $I = \text{cc. of iodine consumed by equation (1)}$

$N = \text{cc. of alkali consumed by equation (2)}$

And when the equivalent concentration of the iodine and

alkali solutions are equal, then the combined sulfur dioxide is given by the expression:

$$\left( \frac{2I - N}{I} \right) \left( \begin{array}{l} \text{Grams Total SO}_2 \\ \text{in Sample} \end{array} \right) - \text{Grams Combined SO}_2 \text{ in Sample}$$

## 5. PROOF OF METHOD

The vapor pressure of water was measured with the apparatus described. Two separate determinations were made, one at 24.40 degrees C. and the other at 24.60 degrees C. In the former a value of 22.4 mm. of mercury was obtained. The "International Critical Tables" (5) list the value as 22.922 mm. In the latter a value of 23.0 mm. was recorded against the Critical Tables (5) value of 23.198 mm.

To further check the apparatus it was decided to determine the pressures of various solutions of sulfur dioxide in water at 25° C. Water and sulfur dioxide were placed in the flask, treated in the manner described and after shaking in the thermostat for sufficient time to allow equilibrium to be reached, the flask was connected to the manometer. The flask was allowed to remain in this position for one and one half hours to insure equilibrium had been obtained. It was noted that after two or three minutes the pressure would remain constant.

The data obtained for the solubility of sulfur dioxide in water are shown in Table I.

TABLE I  
SOLUBILITY OF SULFUR DIOXIDE IN WATER (25° C. )

Expt.	Partial Pressure SO <sub>2</sub> mm. Hg	Grams SO <sub>2</sub> per 100 Grams of H <sub>2</sub> O
1	381.9	4.60
2	756.4	8.71
3	246.0	3.05
4	543.6	6.35
5	151.7	1.97

The partial pressure of water above various sulfur dioxide solutions, obtained by graphical interpolation of the Critical Table data, was subtracted from the total corrected pressure to give the partial pressure of the sulfur dioxide.

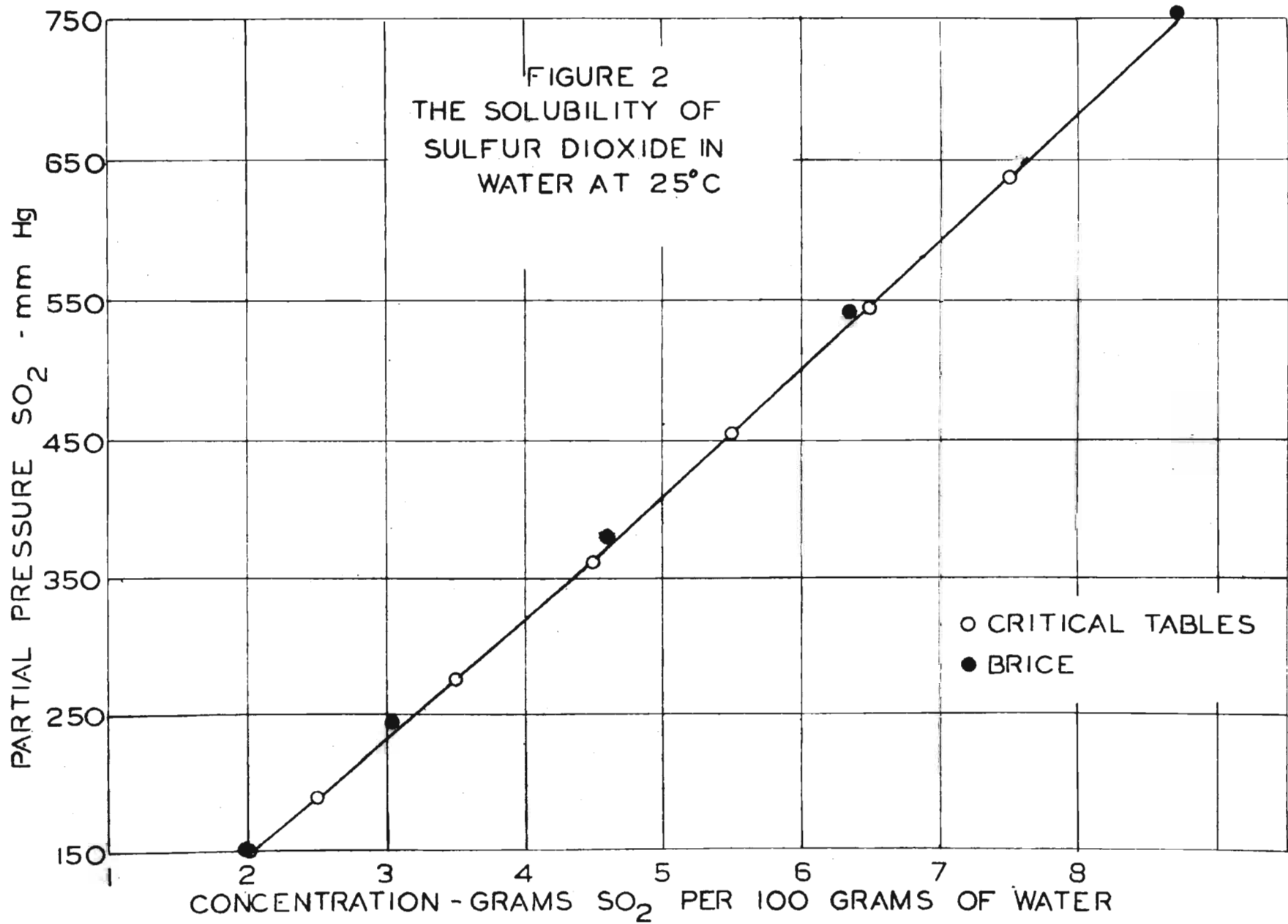
The values given in Table I are shown graphically in Figure 2 and are compared with the values obtained from the Critical Tables (6).

The data of Table I lie consistently to the left of the curve drawn through that of the "International Critical Tables." The maximum deviation of any one point was 0.1 g. per 100 g. water.

All experiments described approached equilibrium from a supersaturated liquid phase since sulfur dioxide was absorbed at a temperature below 25° C. and the pressure in the flask after evacuation to remove inerts was less than the final pressure. If equilibrium had not been reached

the measured pressure should have been low and the analysis of the solution correspondingly high. Examination of the data of this research in Figure 2 shows the converse.





### III. EXPERIMENTAL RESULTS

It was possible to remove only one sample without disturbing the equilibrium. Duplicate determinations were made on some samples. The results checked to within 0.6 grams  $\text{SO}_2$  per 100 grams of water. A separate titration was made on each sample to determine the free sulfur dioxide.

Results of analysis of the liquid phase at  $25^\circ \text{C}$ . and at  $15^\circ \text{C}$ . are given in tabular form in Tables II and III, respectively, and are shown in graphical form in Figures 3 and 4.

Saturation of the liquid phase, with respect to both gas and solid, was approached from both the supersaturated and unsaturated conditions. In all experiments at  $25^\circ \text{C}$ . except those at atmospheric pressure the temperature at which the gas was admitted was three to five degrees below the final equilibrium temperature. Also, in order to remove inerts admitted with the sulfur dioxide, solutions were boiled at reduced pressure. As sulfur dioxide is more soluble at low temperatures and high pressures these experiments were approached from supersaturation with respect to the gas.

Equilibrium at  $15^\circ \text{C}$ . was approached from the unsaturated state with respect to both gas and solid. The temperature at which the gas was admitted was five to eight degrees higher than the equilibrium temperature. The pressure was greater when the flask was placed in the thermostat than at the final equilibrium. Thus these experiments

were approached from unsaturation with respect to the gas.

In experiments 11 and 12 of Table II sulfur dioxide was added until all the solid phase was dissolved. After the solid phase was dissolved the solution was subjected to vacuum until solid phase again reappeared. After the solid phase appeared the flask was placed in the thermostat and treated in the same way as in other experiments. Experiments 11 and 12 Table II thus were approached from the supersaturated condition with respect to both gas and solid.

The curves of Figures 3 and 4 have been constructed from data obtained by approaching equilibrium from the supersaturated and unsaturated condition. The correlation of these data by smooth curves is good.

In order to show the effect of temperature upon the concentration of sulfur dioxide experiment "A" (Table II) was made at 35° C. and atmospheric pressure ( in this case 728 mm. Hg). The results of this experiment and the corresponding values at the same pressure ( the 15° C. run was at 727 mm. Hg), read from curves in Figures 3 and 4 are plotted in Figure 5. Beuschlein and Conrad (1) found that with the system  $\text{CaO-SO}_2\text{-H}_2\text{O}$  in the same temperature range as this research that the solubilities of total and of free sulfur dioxide increases with decreasing temperature at approximately constant and equal rates and the solubility of combined sulfur dioxide increases at a much slower rate. Their curves also showed more free than combined sulfur dioxide was associated with each solution. In this investigation the rates

TABLE II  
ANALYSIS OF THE LIQUID PHASE OF THE SYSTEM  $\text{MgO-SO}_2\text{-H}_2\text{O}$   
EQUILIBRIUM AT 25° C.

Expt.	Total Pressure mm. Hg	Grams per 100 Grams of Water		
		Total $\text{SO}_2$	Free $\text{SO}_2$	Combined $\text{SO}_2$
1	288.0	37.5	18.75	18.75
2	213.2	35.6	17.4	18.2
3	410.9	42.1	20.8	21.3
4	560.7	50.3	24.9	25.4
5	130.2	28.2	14.0	14.2
6	154.4	28.0	13.15	14.85
7	638.4	51.6	25.3	26.3
9	726.8	50.7	24.85	25.85
10	728.4	52.0	25.8	26.2
11	264.3	35.2	17.3	17.9
12	326.5	40.7	20.35	20.35
†A	728.7	50.1	24.4	25.7

† Experiment A made at 35° C.

FIGURE 3  
 PRESSURE-CONCENTRATION CURVES FOR LIQUID PHASE  
 OF SYSTEM  $\text{MgO} - \text{SO}_2 - \text{H}_2\text{O}$ . TEMPERATURE  $25^\circ \text{C}$

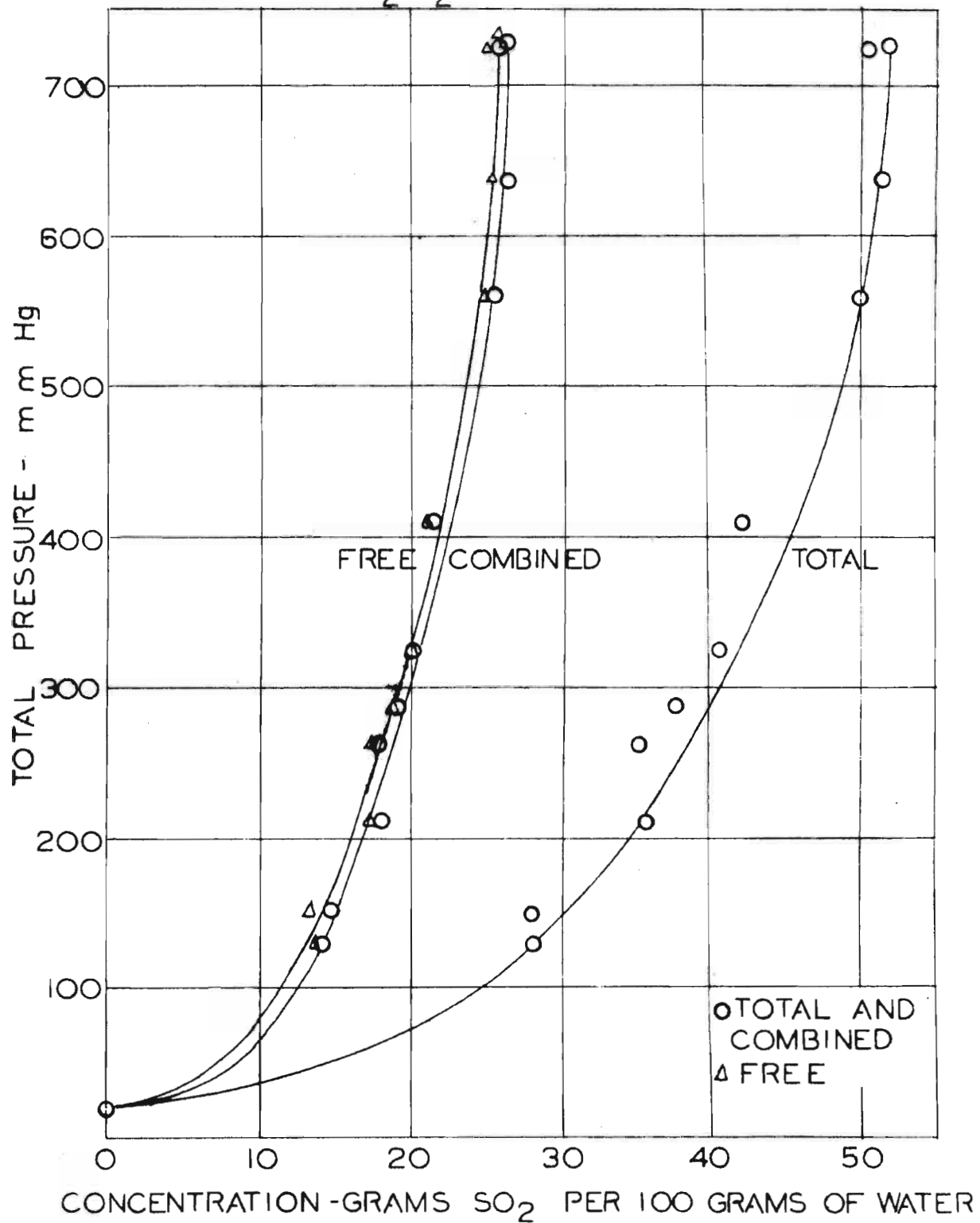
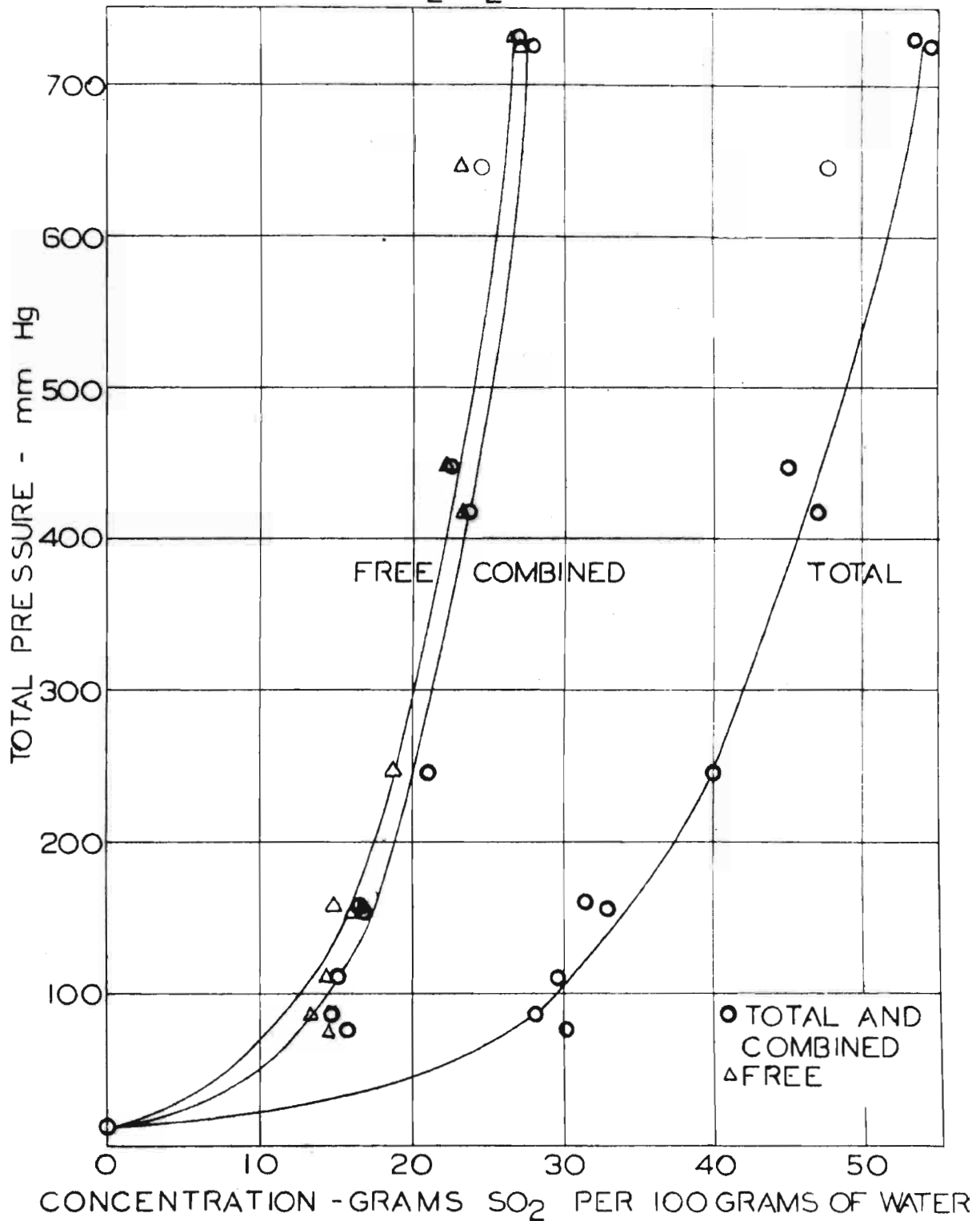


TABLE III  
ANALYSIS OF THE LIQUID PHASE OF THE SYSTEM  $\text{MgO-SO}_2\text{-H}_2\text{O}$   
EQUILIBRIUM AT  $15^\circ \text{C}$ .

Expt.	Total Pressure mm. Hg	Grams per 100 Grams of Water		
		Total $\text{SO}_2$	Free $\text{SO}_2$	Combined $\text{SO}_2$
1	448.7	44.8	22.4	22.4
2	419.3	46.9	23.35	23.55
3	162.3	31.4	14.85	16.55
4	245.5	39.9	18.9	21.0
5	75.5	30.4	14.7	15.7
6	87.5	28.05	13.3	14.75
7	110.7	29.65	14.6	15.05
8	156.8	32.9	16.0	16.9
9	647.6	47.55	23.05	24.5
10	726.8	54.6	26.8	27.8
11	730.3	53.3	26.55	26.75

FIGURE 4  
 PRESSURE-CONCENTRATION CURVES FOR LIQUID PHASE  
 OF SYSTEM  $\text{MgO} \cdot \text{SO}_2 \cdot \text{H}_2\text{O}$ . TEMPERATURE  $15^\circ \text{C}$



of decrease of solubility total, free and combined sulfur dioxide with temperature increase were all approximately constant and equal. This being different for the combined sulfur dioxide. Also it was found that the amount of sulfur dioxide in a solution with the same pressure was much greater for the MgO system than the CaO system. The amount of combined sulfur dioxide was always greater than the free for this system in contrast to that for the CaO system. The amounts of combined and free were very nearly equal, the combined being always greater representing slightly greater than 0.5 of total. The combined was never more than 0.52 of the total. This difference in the two systems is attributed to the greater solubility of the bisulfite of magnesium. Also the solubility of magnesium sulfite in cold water is 1.25 grams per 100 cc. of water compared with 0.0043 grams per 100 cc. of water for calcium sulfite. This would help to explain why at the pressures investigated the "combined SO<sub>2</sub>" is always greater than the "free SO<sub>2</sub>" in the MgO system.

Table IV was compiled from data of Tables II and III plotted to large scale and shows values of total, free and combined sulfur dioxide at 50 mm. intervals below atmospheric pressure.



FIGURE 5  
TEMPERATURE - CONCENTRATION CURVES  
FOR LIQUID PHASE OF THE SYSTEM  $\text{MgO} \cdot \text{SO}_2 \cdot \text{H}_2\text{O}$   
TOTAL PRESSURE 728 mm Hg

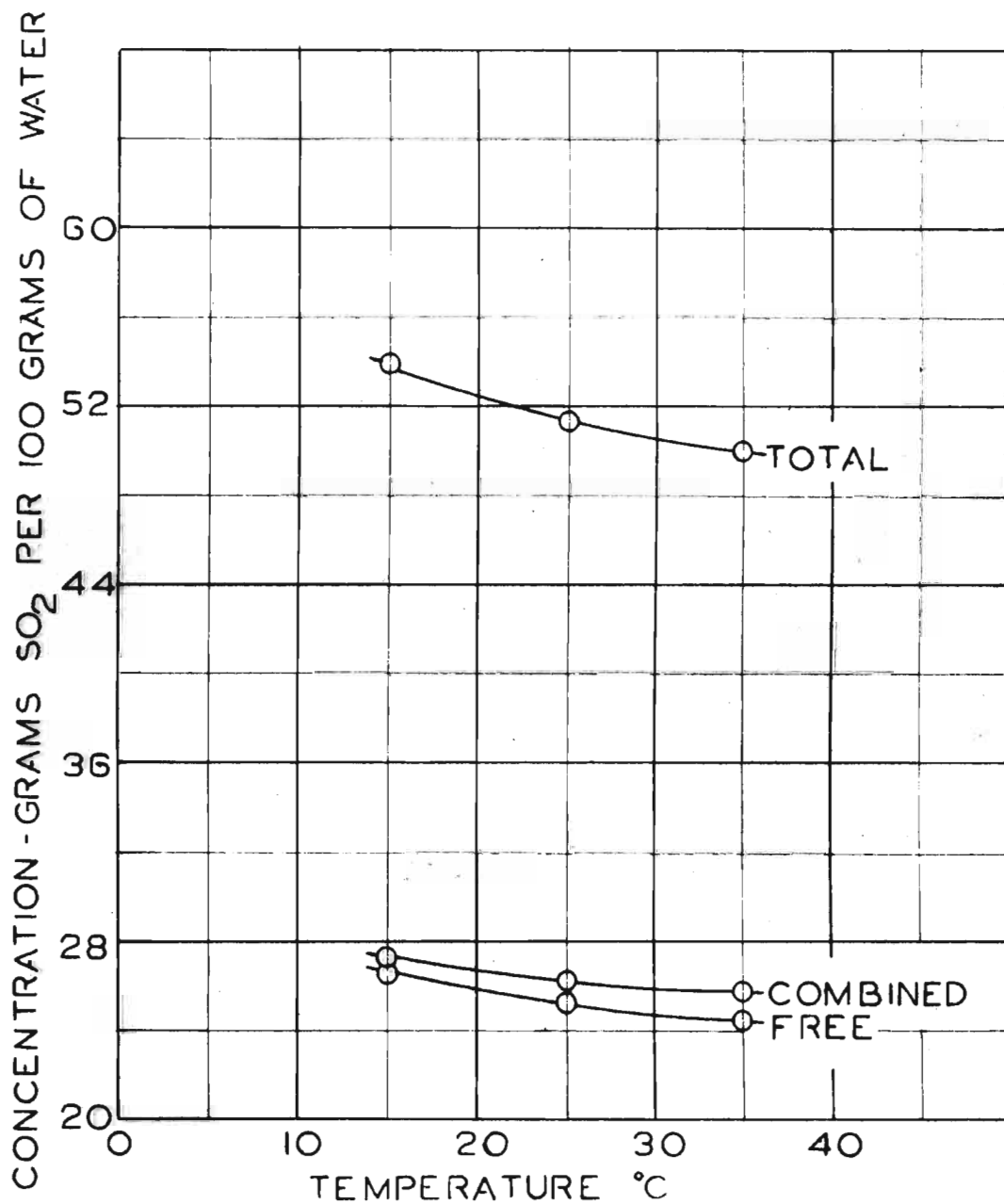


TABLE IV  
COMPOSITION OF LIQUID PHASE OF THE SYSTEM  
MgO-SO<sub>2</sub>-H<sub>2</sub>O

Total Pressure mm. Hg	Concentration of Sulfur Dioxide at 15° C. Grams per 100 Grams Water			Concentration of Sulfur Dioxide at 25° C. Grams per 100 Grams Water		
	Total	Com- bined	Free	Total	Com- bined	Free
50	16.0	10.0	6.0	9.2	5.2	4.0
100	29.2	16.2	13.0	20.8	11.4	9.4
150	34.6	18.1	16.5	30.0	15.8	14.2
200	37.8	19.5	18.3	34.5	17.8	16.7
250	40.0	20.5	19.5	37.6	19.1	18.5
300	42.1	21.6	20.5	40.0	20.5	19.5
350	44.0	22.5	21.5	43.0	21.9	21.1
400	45.9	23.4	22.5	44.9	22.8	22.1
450	47.7	24.3	23.4	46.4	23.5	22.9
500	49.5	25.2	24.3	48.4	24.5	23.9
550	51.1	25.9	25.2	50.0	25.3	24.7
600	52.4	26.5	25.9	51.0	25.9	25.1
650	53.5	27.1	26.4	51.7	26.2	25.5
700	54.3	27.5	26.8	52.0	26.3	25.7
750	54.7	27.7	27.0	52.1	26.3	25.8

## SUMMARY

1. The total pressure-composition relationships have been determined for the system  $\text{MgO-SO}_2\text{-H}_2\text{O}$  in the acid region up to atmospheric pressure at  $15^\circ$  and  $25^\circ$  C.
2. The total, free and combined sulfur dioxide, has been determined for saturated solutions in equilibrium with solid magnesium monosulfite at total pressures of sulfur dioxide and water vapor from the vapor pressure of water to atmospheric pressure for the temperature  $15^\circ$  and  $25^\circ$  C.
3. The temperature-composition relationship has been determined for the total pressure of 728 mm. at temperature of  $15^\circ$ ,  $25^\circ$  and  $35^\circ$  C.

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## INDEX

	<u>Page</u>
Analysis, Method	6
Apparatus	3
Bibliography	23
Burette, Gas	5
Combined Sulfur Dioxide	7
Equilibrium Flask	3
Flask, Equilibrium	3
Free Sulfur Dioxide	7
Gas Burette	5
Hohn Method	6
Illustrations	1
Introduction	1
Iodine	6
Literature Cited	22
Magnesium Oxide	3
Materials Used	3
Methods of Analysis	6
Phase, Solid	2
Pipette, Weighing	3
Preparation of Equilibrium Mixture	5
Pressure, Vapor of Water	8

	<u>Page</u>
Proof of Method	8
Results	12
Sodium Hydroxide	6
Sodium Thiosulfate	6
Solid Phase	2
Solubility of Calcium Sulfite	18
Solubility of Magnesium Sulfite	18
Sulfite Process	1
Sulfur Dioxide	3
Summary	21
Supersaturated Solution	12
Tables	11
Total Sulfur Dioxide	7
Unsaturated Solution	12
Vapor Pressure of Water	8
Weighing Pipette	3