The Equilibria Existing
In The Three Component System
MAGNESIUM OXIDE - SULPHUR DIOXIDE - WATER
Over The Temperature Range
25°C. To 130°C.

T H E S I S

Submitted to

The Faculty of Graduate Studies and Research

of McGill University

In Partial Fulfillment of the Requirements

for the Degree of

Doctor of Philosophy.

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by

Thomas E. King.

McGill University September 1939.

ACKNOWLEDGMENTS

The author takes pleasure in expressing his thanks:

To Dr. O. Maass, as director of this research, for invaluable advice and continued encouragement throughout the duration of the investigation.

To Dr. W. Boyd Campbell for his helpful suggestions and constructive criticism.

To the Canadian Pulp and Paper Association for a scholarship, and to the National Research Council of Canada for a Bursary, held during the course of this research.

To the Forest Products Laboratories of Canada for certain equipment and the use of their laboratories.

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INTRODUCTION

The work to be described in this thesis forms part of a comprehensive research which is being carried out in this laboratory on the properties of sulphite systems. This general investigation was instituted when it was found that there were little available data on sulphur dioxide, sulphurous acid solutions and its salts. Furthermore the data recorded in the literature were not of great value since experimental results had been obtained over only small ranges of temperature and concentration.

In 1923 Dr. O. Maass and Dr. W. B. Campbell with their co-workers undertook a series of primary investigations on pure sulphur dioxide and this formed the nucleus for the systematic investigation of sulphite systems in this laboratory which has been in progress for the last twelve years. First of all the physical properties of aqueous solutions of sulphur dioxide were carefully determined and theoretical deductions made in regard to the equilibria existing in such a system. Then it was found desirable to examine the physical properties of the three component systems, namely the systems including a base as well as sulphur dioxide and water. The data determined for such three component systems, apart from their purely scientific interest were expected to be of practical

interest to the manufacturer of wood pulp using the sulphite process.

The properties of the three component system calcium oxide - sulphur dioxide - water were thoroughly investigated. Conductivities and vapour pressure measurements were carried out over large ranges of temperature and concentration, and from the resultant information, theories were developed which have been of great use in the elucidation of the equilibria existing in this system. The practical value of this particular investigation was made apparent by the interest taken by those engaged in the manufacture of sulphite pulp. The results have been of assistance to them and they have expressed the desire that work of this nature be continued.

It is not the intent of the writer to unduly stress the practical importance of such investigations but rather to indicate that in this work practical and academic interests run parallel. The equilibria shown to exist between sulphur dioxide and water proved that the amount of free sulphur dioxide increased with rise in temperature, taking into account the amount of uncombined sulphur dioxide, sulphurous acid was shown to be a relatively stronger acid than would be given by its apparent dissociation constant; the investigation of the three component system proved that with the calcium oxide as a base, variation in concentration gave a buffer solution

as far as sulphite ions are concerned; it was made possible to calculate hydrogen ion concentrations from conductivities and vapour pressures; etc. - all these points are definitely of fundamental interest from a scientific point of view as well as having practical repercussions.

This thesis describes an investigation of the equilibria vapour pressures of the three component system magnesium oxide - sulphur dioxide - water. Magnesium oxide was the third component chosen since in contrast to calcium sulphite, the magnesium sulphite is very soluble and is relatively much more stable at high temperatures.

Therefore by substituting magnesium oxide for calcium oxide the equilibria existing in such a three component system could be examined at lower sulphur dioxide concentrations and over a larger temperature range as a two phase system, and the complexity introduced by a heterogeneous phase would be eliminated.

The apparatus used throughout this investigation was constructed so that accurate weights of the reactants, free from all possible impurities could be introduced into the reaction cell. The cell was of Pyrex glass equipped with an all glass magnetic stirrer, this assured adequate stirring

of the solutions under investigation. The cell was connected to a manometer capable of registering pressures up to five atmospheres.

The problem involved the measurement of the vapour pressures of solutions of known weights of magnesium oxide, water and sulphur dioxide, the determinations being made at appropriate temperatures between 20°C. and 130°C. The concentrations of magnesium oxide used were approximately 0.6%; 1%; 1.4% and 1.8%, while the sulphur dioxide concentrations were made to range from 1% to 7%.

The results obtained from this investigation are tabulated by extrapolation to show the total vapour pressure of this system from 0% to 1.8% magnesium-oxide over a range of sulphur dioxide concentrations from 1% to 6% in 1% steps.

As mentioned before the interesting property of the magnesium system as contrasted to the calcium system is the great solubility of the magnesium sulphite. It was found that even at high temperatures precipitation never occurred, although it was evident from the pressure curves that as the temperature increased more and more magnesium bisulphite was transformed into the mono sulphite. It has been recognized that this property should be of commercial importance since the so-called "liming up" of digesters which is so often encountered in the industrial process due to the precipitation of calcium sulphite, would be eliminated if magnesium sulphite

solutions were used.

The results obtained from this investigation are discussed by comparing the properties of the magnesium oxide system to those of the calcium oxide system, and inferences are drawn in regard to the equilibria existing in the system magnesium oxide-sulphur dioxide-water.

H I S T O R I C A L

HISTORICAL

To investigate the equilibria existing in the three component system magnesium oxide - sulphur dioxide - water, it was necessary to have reliable data in regard to the physical properties of the individual components and also those two component systems that make up this system.

As has been previously indicated, the available data on sulphur dioxide solutions and such solutions in the presence of a base prior to 1923 were very limited and the nature of the results left question as to their value. Realizing the need for reliable physical data, both on aqueous solution of sulphur dioxide and the three component systems, Dr. O. Maass, Dr. W.B. Campbell and their co-workers instituted their extensive series of investigations on the properties of these sulphite solutions.

As a result the physical properties of the three component system, calcium oxide - sulphur dioxide - water, have been thoroughly examined over large ranges of temperature and concentrations by several workers in this laboratory (1, 2, 3, 4); but the properties of the three component system magnesium oxide - sulphur dioxide - water, have not been previously investigated.

This investigation was undertaken in order to study the equilibria existing in this latter three component system. For convenience of discussion the investigations of previous

workers will be summarized under the following headings.

(a) The system sulphur dioxide - water.

(b) The system magnesium oxide - water.

(c) The system magnesium oxide - sulphur dioxide - water.

(a) The System Sulphur Dioxide - Water

In recent years Maass and co-workers (5, 6, 7) carried out an exhaustive investigation on the properties of this system, and the resultant data due to the greater accuracy attained supersedes that of previous investigators.

The literature survey carried out in 1923 revealed that there was surprisingly little data available on the aqueous solution of sulphur dioxide. Sims (8) determined the vapour pressure of this system with a fair degree of accuracy over a range of pressures up to 200 cms.; and temperatures up to 50°C. Shiff (9), Gerlach (10) as well as Giles and Shearer (11) gave values for the density of these solutions at relatively low temperatures, the values of the latter are more reliable. Ostwald (12) and Barth (13) investigated the conductivity of sulphur dioxide - water solutions, McCrae and Wilson (14) have determined partition co-efficients of sulphur dioxide between water and chloroform, Walden and Centnesszwer (15) determined the freezing points. From the combined results of the last four investigators Drucker (16) calculated the dissociation constant. Kerp and Bauer (17) made conductivity

and freezing point measurements. Fulda (20) calculating from the heat of dissociation data of Thomsen (18) and Berthelot (19) gave figures for the dissociation constant at temperatures from 7°C. to 50°C. Foerster, Lang, Drossback and Seidel (21) carried out an extensive investigation on the decomposition of sulphur dioxide and its salts in aqueous solutions, proving the existence of many complex sulphur compounds. Wright (22) by absorption spectra showed that sulphur dioxide existed as such in solution. Oman (23), Hudson (24) and Enckell (25) determined the solubility of sulphur dioxide in water up to 90°C. The values of Oman are the more accurate. Davis (26) published a monograph on the solubility of sulphur dioxide in water. Tesees and Rühl (27) developed a phase rule diagram for the sulphur dioxide - water system.

All this may serve as an indication of an exhaustive search of the literature. The conclusion reached by Campbell and Maass that no definite theories could be drawn from the investigations quoted led to a far more systematic and comprehensive investigation of the properties of the sulphur dioxide - water system. Maass and Maass (5) measured vapour pressure and conductivities of aqueous solutions of sulphur dioxide at temperatures below 27°C. Campbell and Maass (29) determined the densities, vapour pressures and conductivities of sulphur dioxide - water solutions at concentrations up to 8% and over a temperature range from 20°C. to 130°C. Morgan and Maass (30) made precision measurements of the vapour pressures and

conductivities of sulphur dioxide solutions at the lower temperature range of 0°C. to 25°C., and pressures up to one atmosphere.

The important conclusions drawn from their work listed above were that in the equilibrium

$$H_2O + SO_2 \rightleftharpoons H_2SO_3$$

a rise in temperature causes the equilibrium to shift to the left and that the partial vapour pressure of the sulphur dioxide is a measure of the free sulphur dioxide in solution. Consequently sulphurous acid solutions at high temperatures give rise to only a small hydrogen ion concentration, not because sulphurous acid is such a weak acid but because there is so little of it in solution to dissociate. Furthermore, the hydrogen ion concentration over the range of sulphur dioxide concentrations 1% to 8% and over the temperature range 0°C. to 140°C. were calculated. This will be gone into more fully under "Discussion of Results".

(b) The System Magnesium Oxide - Water

Magnesium oxide has the property of being sparingly soluble in water and consequently very little data were available on this two component system. This is partly due to what might be called the "indeterminacy" of the nature of magnesium oxide itself. A considerable amount of work has been carried out investigating both the physical and chemical properties of magnesium oxide. As magnesium oxide is the "base" component it may be well advised to enumerate the more important known

facts in regard to its nature.

Magnesium oxide differs from the calcium oxide in that it has two oxides differing in their physical properties. The magnesium oxide used throughout this investigation was the high specific gravity or β- oxide.

Mention will be made of a few who investigated the properties of magnesium oxide. Goodwin and Mailey (31) determined the specific gravity of the national crystal of magnesium oxide. Ditte (32) showed that the specific gravity of the amorphous form increased on calcination. Rose (33) showed that by calcination over a period of several hours the specific gravity approached that of the crystaline form. Mellor (34) investigated the rate of transformation of the α-magnesium oxide to the β form with temperature. Richards and Rogers (35) measured the amount of occluded gas in metallic oxides, and showed that it was negligible in the case of β-magnesium oxide. Anderson (36), Campbell (37) and Ditte (32) showed that β-magnesium oxide was very resistant to moisture, mineral acids and was practically unacted upon by water. Davy (38) noted the inertness of calcinated magnesium oxide.

By means of X-ray Hull (40),,Gerlach and Pauli (41), Hedvall (42), Giague and Archibald (43) studied the crystal structure of both the α and β oxides and found they were the same. According to Taylor and Wells (44) the particle size changed but not the crystal structure when the oxide was heated.

Several investigators studied the solubility of magnesium oxide in water. There is great disagreement among their results. In most cases they do not stipulate which oxide was used (α or β) so these variations in the results may be due to this or to experimental error. Mellor (39) gives a representative value for the solubility of the magnesium oxide in water as 10 mgm. per litre at 20°C. According to this the solubility of magnesium oxide is less than one hundredth of that of calcium oxide.

(c) The System Magnesium Oxide - Sulphur Dioxide - Water

If little is known of the magnesium oxide - water system it is not surprising to find that even less reliable data have been published on the three component system magnesium oxide - sulphur dioxide - water. An explanation for the lack of accurate data is that those workers investigating this system were interested in the industrial application of their results, rather than in theoretical conclusions, and that therefore they did not take the necessary precautions to assure accurate results. Perhaps the only publication worth mentioning at all is that of Smith and Parkhurst (45) who measured the vapour pressures and the solubility of sulphur dioxide in aqueous solutions containing varying amounts of magnesium oxide, over very small ranges of temperature.

It is evident from what has just been said that there is need for a thorough investigation of the magnesium oxide - sulphur dioxide - water system. This is particularly so because of concurrent investigations by Calhoun (46) and Cannon (47) in this laboratory on the rate of delignification of wood when the calcium base is replaced by the magnesium base.

The equilibria existing in the magnesium base system may be expected to be similar to those existing in the calcium base system. In so far as vapour pressure determinations can be used to compare these equilibria with one another, this will be done at the same time.

E X P E R I M E N T A L

A. Experimental Section.

1. General
2. Detailed Description of Apparatus.
   - (a) Gas Purification System.
   - (b) Gas Measuring System.
   - (c) Gas Introduction System.
   - (d) The Reaction Cell-Manometer System.
   - (e) The Oil Bath, Heaters, etc.

1. General:

The apparatus was primarily designed, so that known weights of magnesium oxide, sulphur dioxide and water could be brought together in the absence of all impurities. It provided a means of bringing together air free water, pure sulphur dioxide and magnesium oxide free of carbon dioxide and any occluded gases.

Gas from a supply cylinder, was dried and then purified by several fractional distillations, the middle fraction being kept in each case. By means of the gas measuring system the accurate weight of the gas was determined, this was introduced by means of a mercury seal into the cell containing the magnesium oxide and water.

The cell was connected by lagged pyrex tubing to the pressure manometer. The lagged tubing was always at a higher temperature than the cell thus preventing condensation.

The cell was immersed in a thermostated oil bath containing the heaters, cooling coil, and stirrers.

By means of an all glass magnetic stirrer the reagents were thoroughly mixed and equilibrium was thus assured.

2. Detailed Description of Apparatus

(a). Gas Purification System

This section will be devoted to a description of the apparatus. The apparatus as a whole may be considered as made up of several separate units, and for ease of discussion a detailed description of each will be given. The functions of each unit will be thoroughly explained in the section on experimental technique.

A diagram of the gas purification and measuring systems will be found in Fig. 1. The gas purification system is that section left of stopcock "S_1", as shown in the diagram. This section was constructed of soft glass and connected to the sulphur dioxide cylinder by means of pressure tubing, the joints were covered with DeKhotinsky cement. The sulphur dioxide was dried by means of the phosphorous pentoxide tube. A mercury exhaust trap "O" permitted the rejection of excess sulphur dioxide.

The evacuation system consisted of a water pump, a Cenco Hyvac pump, and a Langmuir diffusion pump backed by a Hyvac, these were protected by another phosphorous pentoxide tube. The apparatus was so designed that the whole or any part could be evacuated by the pumping system.

Also included in this section are an open air monometer "D" this was of two fold value, for rough pressure measurements and it acted as a safety valve should the gas pressure become too

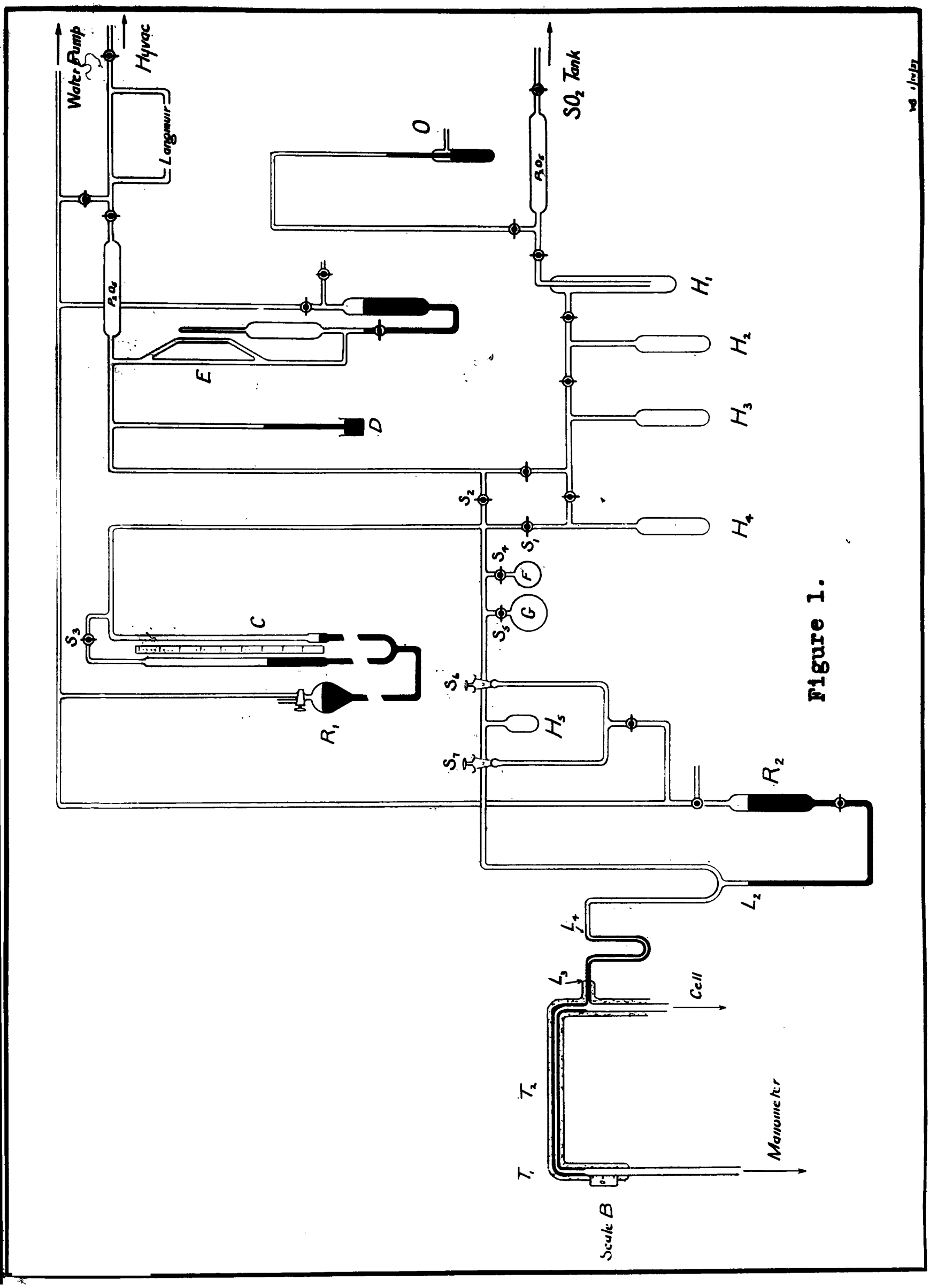

Water Pump
Hyvac
Langmuir
SO_2 Tank
O
E
D
C
R_1
R_2
H_1
H_2
H_3
H_4
H_5
S_1
S_2
S_3
S_4
S_5
S_6
F
G
L_1
L_2
L_3
L_4
T_1
T_2
Cell
Manometer
Scale B

Figure 1.

become too great, a McLeod Guage "E" used to measure pressure on evacuation.

The bulbs "H_1", "H_2", "H_3" were used to purify the sulphur dioxide by fractionation, the purified gas was stored in "H_4".

(b). Gas Measuring System

This system as shown in Fig.1 consisted of the calibrated volumes "F" and "G" the connecting tubing limited by the stopcocks "S_1", "S_2", "S_3", "S_7", and the 10 cm. mark on the right hand arm of the manometer "C".

The 10 cm. mark on the manometer "C" was arbitrarily chosen and the volume of the connecting tubing was determined up to this mark. In all measurements made with the manometer the mercury in the right arm was brought to the 10 cm. mark by applying either vacuum or pressure to the mercury reservoir "R_1", otherwise the volume of the connecting tubing would not be constant and would vary with changing mercury level. The left hand side of manometer "C" was evacuated by the diffusion pump backed by the Hyvac. The pressure of the gas in this system was measured by taking the difference in mercury level of the two arms and applying the necessary glass scale temperature corrections.

The volumes "F" and "G" were calibrated, by weighing them empty and then full of water, applying the necessary corrections. The volume of the connecting tubing was determined

using the values of "F" and "G" and applying the gas law

The temperature of the gas in the connecting tubing was determined by two calibrated thermometers hung at suitable points. The volumes "F" and "G" were immersed in a water bath, thus insuring the same temperature of both and providing protection against any sudden variations in (room) temperature The bath was equipped with a calibrated thermometer.

(c). Gas Introduction System

This system consisting of the two vacuum stopcocks, "S_6", "S_7", the bulb "H_5" and the connecting tubing limited by "S_7" and the points "L_2", "L_3", is connected to the gas measuring system through stopcock "S_6".

The bulb "H_5" was used as a final storage for the pure sulphur dioxide. The gas in "H_5" was warmed slightly just before injection into the cell, and to prevent the plugs of the stopcocks "S_6" and "S_7" from being blown out of their seats by the pressure generated, it was necessary to employ vacuum stopcocks.

The connecting tubing above "L_2" includes a mercury cut off, this permitted the purification of the water by evacuation. The soft glass section of apparatus was joined to the Pyrex section by a Pyrex to soft glass graded seal, located just above the right hand side of the mercury cut off. A small

"U" tube made of Pyrex capillary was sealed to the cut off at "L_4". This capillary functioned as a frozen mercury seal. The mercury in the cut off and frozen seal could be raised or lowered by applying pressure or vacuum to the mercury reservoir "R_2".

The frozen mercury seal will be described in detail. It was necessary to isolate the cell-manometer system during a run from the rest of the apparatus. At the same time a means had to be provided by which more sulphur dioxide could be injected into the cell at the completion of a run so that a series of runs could be carried out at the same magnesium oxide and water concentrations, but with increasing amounts of sulphur dioxide. A stopcock could not be used since it would not withstand the pressure developed during a run. The frozen mercury seal was ideal, since it could be opened or closed by applying vacuum or pressure to "R_2" and once the mercury was frozen it could withstand any pressure.

(d). The Cell-manometer System

Since the cell was to be subjected to large temperature variations, the cell-manometer system was constructed of Pyrex glass. The reaction cell is shown in detail in Fig. 2. The volume of the cell was approximately 100 cc. The magnesium oxide was introduced through the side arm "V". A flask was sealed onto "W", after which a known weight of water was transferred into it from a pipette.

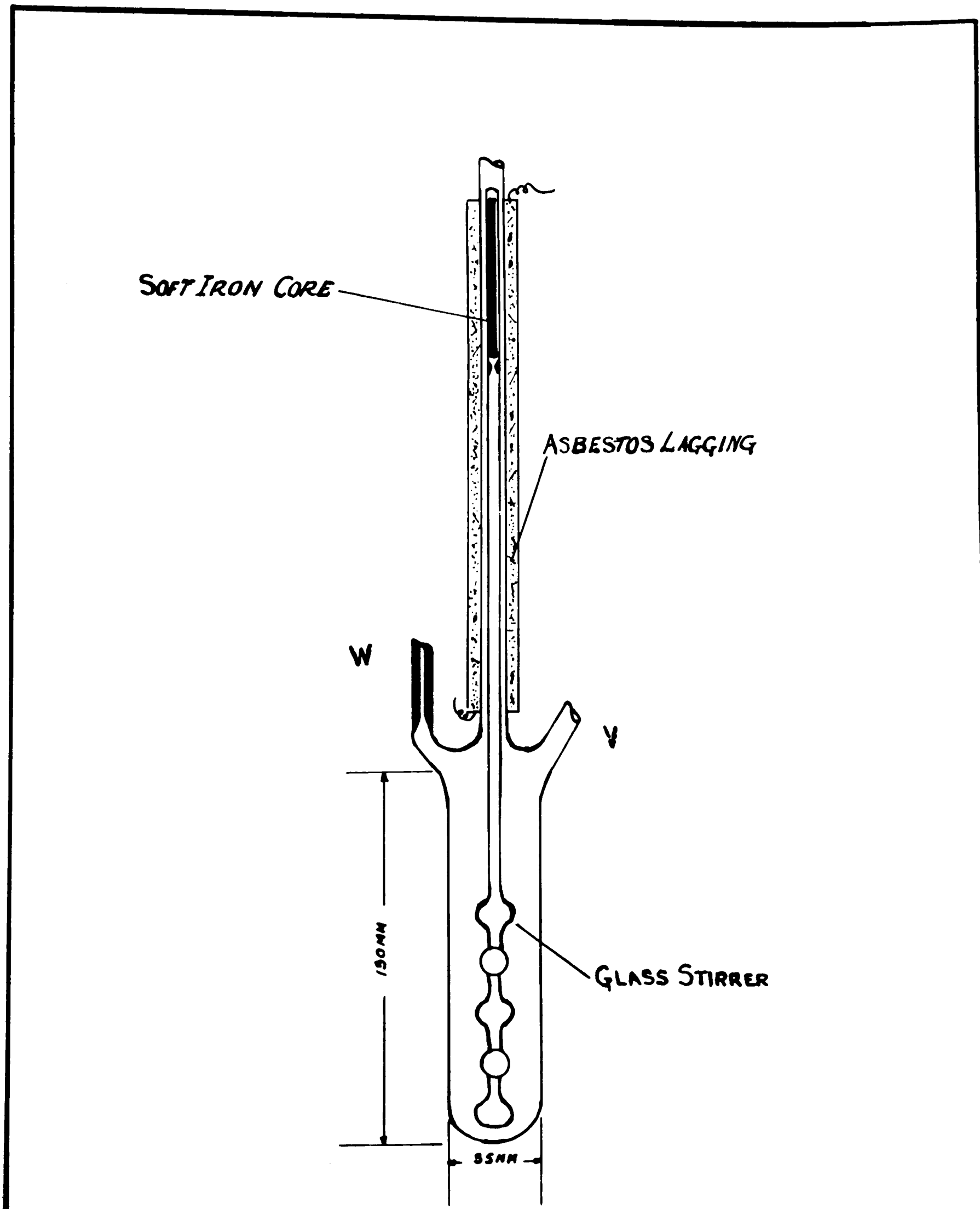

SOFT IRON CORE
ASBESTOS LAGGING
W
V
150MM
GLASS STIRRER
55MM

Figure 2.

Stirring was effected by means of an all glass electro-magnetic stirrer, this was necessary to assure true equilibrium. The stirrer consisted of a glass tube which extended to half way up the shaft of the cell. A soft iron bar approximately 7 cm. long and 4 mm. in diameter was sealed into the top of the stirrer, permitting the raising and lowering of the stirrer by the electro-magnet. The diameter of the shaft connecting the cell to the rest of the apparatus was large enough to allow the stirrer to move up and down freely, at the same time the volume of the gas space above the liquid in the cell had to be kept at a minimum. For the same reason all the tubing of this section was of small bore. The lower part of the stirrer had several spheres blown on it, these broke the surface of the liquid with each oscillation of the stirrer.

The glass tubing connecting the cell with manometer and the gas introduction system had to be kept at a temperature above that of the oil bath to prevent condensation of water. The tubing was first covered with a layer of asbestos paper, the heating element consisting of thin Nichrome wire was wound over the asbestos layer, then a thick coating of asbestos cement was applied acting as a heat insulator. The cell shaft was covered with several layers of asbestos paper instead of the asbestos cement, this facilitated the adjustment of the electro-magnet. The heating element was in series with a variable resistance, the temperature of the tubing could be controlled by varying the

current flow by this resistance. The temperature was read from two thermometers "T_1", "T_2" which were imbedded in the lagging, the mean of which was taken as the temperature of the gas phase.

A portion of the lagging was removed from scale "B", permitting the setting of the mercury level at the zero mark. This was necessary to keep the cell system one of constant volume. The mercury in scale "B" was heated several degrees above that of the oil bath to prevent condensation from the solution on the mercury surface. A scale reading correction had to be applied to account for the density change of this column of mercury.

During a run the pressures developed were often several atmospheres. The manometer used was of the closed end type capable of measuring pressures up to 7 atmospheres, it was constructed and calibrated by Gurd (2). (Please refer to Fig. 3).

The manometer was constructed of Pyrex tubing 1 cm. in diameter and approximately four metres long. Throughout its length the manometer was surrounded by a soft glass tube 2.5 cm. in diameter. This outer tubing protected the manometer from any sudden changes in room temperature that might occur during a run. The temperature of the air above the mercury surface in the manometer was determined by three thermometers hanging between the outer and inner tubes, one was placed at the top, one at the centre and one at the bottom, the mean of the three was taken as

the temperature of the entrapped air. The pressure was read from a scale consisting of four wooden metre sticks placed parallel to the manometer. The whole was securely fastened to a solid wooden support, which was rigidly held in place by brackets screwed into the floor and ceiling.

The base of the manometer was in the form of a "T" one arm was connected to the lower part of scale "B", this tube was protected by means of a removable wooden frame. The other arm was connected by several feet of rubber pressure tubing (7 ply oxygen hose) to the one litre mercury reservoir "R_3". This reservoir was set in a wood support, this could be raised or lowered by a system of pulleys. A wheel with a spinner was mounted close to scale "B", this was connected to the pulley by a chain. It was essential to have the levelling control close to scale "B" so that the scale could be observed, and the final adjustment of the mercury surface could be made accurately. The greatest care was taken during the process of raising the mercury to the zero mark, to prevent the mercury from flowing over into the cell. The chain connection to the pulley was very helpful when making the final adjustments since it prevented slipping which was the trouble encountered when belt connections were used.

It was found that at high temperatures even when the reservoir was at the top, the column of mercury would not balance the pressure developed in the cell. It is evident that additional pressure had to be applied to the mercury surface. This was

accomplished, by a copper tube sealed into the top of reservoir by sealing wax, to this was soldered a bicycle valve seat and a valve was inserted. By pumping air into the reservoir it was possible to obtain the necessary pressure.

The electro-magnet (for detailed description see thesis of Beazley (4)) which activated the stirrer, had to be rather large due to the weight of the stirrer. This was constructed as follows: a Pyrex tube 15 cms. long just larger than the lagged shaft of the cell, was wound with a copper cooling coil. This was covered with a layer of asbestos, three pounds of double cotton covered annunciator wire and the whole surrounded by a galvanized protective casing.

The current flow through the solenoid was controlled by a lamp bank of carbon filament lamps. This was divided into two parts, one supplying the direct current consisting of 6 lamps, the second consisting of two lamps of 100 W. and 200 W. respectively, supplied the intermittent current. By means of the lamps the steady current was adjusted so that the stirrer was just supported above the bottom of the cell. The second lamp bank was wired in series with an interrupter (Cenco Mercury Switch), the pitch of the stirrer stroke was governed by the number of lamps in this bank. The interrupter was fastened to a lever arm which was connected to an escentric, which was connected by a belt to an electric motor. The number of strokes per minute could be regulated by varying the speed of the motor.

The solenoid heated up due to the heat energy from the current flow and that given off by the heating element around the shaft of the cell. This was counteracted by allowing water to flow slowly through the cooling coil. Care had to be taken in adjusting this flow to prevent condensation in the cell shaft.

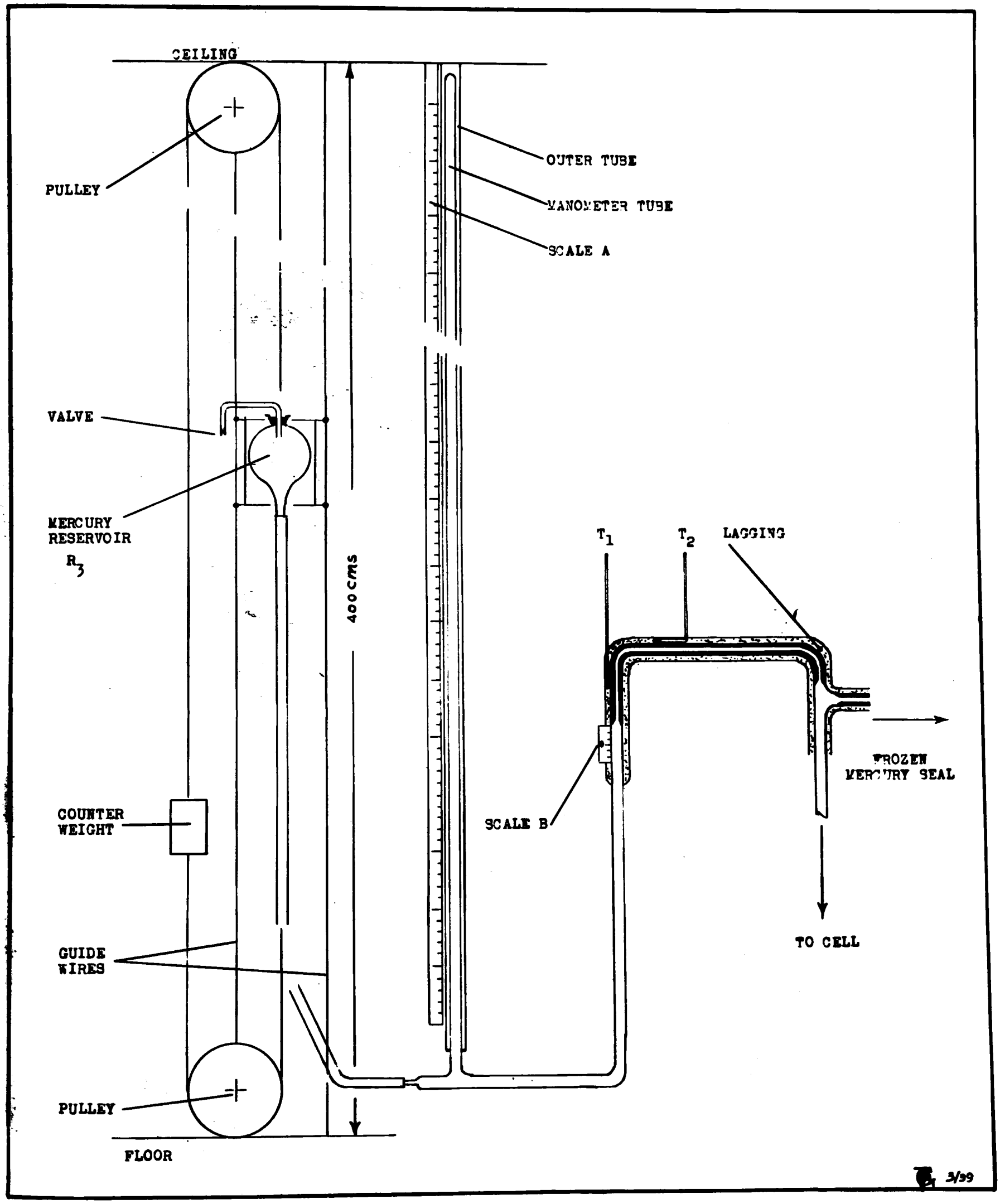

CEILING
PULLEY
OUTER TUBE
MANOMETER TUBE
SCALE A
VALVE
MERCURY RESERVOIR
R_3
400 cms
T_1
T_2
LAGGING
SCALE B
FROZEN MERCURY SEAL
TO CELL
COUNTER WEIGHT
GUIDE WIRES
PULLEY
FLOOR

Figure 3.

The volume of the entrapped air within the manometer corresponding to any scale reading was found by interpolation between the values below. (The values are those of Gurd (2)).

Scale Reading	Corrected Volume in cc.
3.90	3.03
7.85	6.124
36.15	27.884
65.05	49.734
87.85	67.493
92.38	71.275
120.30	93.210
148.50	115.21
178.00	138.02
180.50	139.96
183.25	142.21
211.50	164.11
240.45	186.26
271.15	209.52
273.82	211.83
301.25	233.91
328.63	255.63
360.90	281.58
363.43	283.92
364.61	284.91
370.49	289.35

(e). The Oil Bath, Heaters, etc.

The reaction cell was immersed in a bath filled with diethylene glycol, the surface of which just covered the side arms "V" and "W". This bath consisted of a Pyrex jar 16 inches deep and 8.5 inches in diameter. It was covered with several layers of heat insulation material, and then placed in a wooden box. A section of the box was cut away so that the cell was visible.

The heating system consisted of three bare nichrome wire coils arranged as follows: the first had a capacity of 1200 watts, which was in series with a system of external variable resistances so that the current could be varied as required. This heater was activated by the thermoregulator through the relay. The second heater was supplied with a 400 watt coil, this was in series with an external resistance. This heater was used at high temperatures to balance the heat lost due to radiation. The third heating coil of 800 watts was employed to raise the bath temperature rapidly, it was connected directly to the 110 volt A.C. line.

The bath was equipped with a cooling coil, providing a means to cool the bath rapidly. It was built by coiling 12 feet of copper tubing inside the bath. The cooling system was arranged so that the bath could be cooled by either water or brine solution. During the summer the tap water at times reached 26°C., and as it is often necessary to keep the bath at much lower temperatures, a

circulating system was built, consisting of an automobile water circulating pump driven by an electric motor.

This brine at -10°C. was pumped through the cooling coils, by controlling the brine flow by means of a valve, any desired bath temperature down to 0°C. could be attained. By using two, two-way stopcocks it was a simple matter to change from the water to the brine cooling systems.

The temperature of the bath was controlled to within ± 0.05°C. by an all mercury thermoregulator which activated a mercury switch relay. The thermoregulator was made of Pyrex, consisting of a centre tube 1 cm. in diameter and one foot long, around this was spiralled several feet of 7 mm. tubing. This design ensured compactness and quick establishment of equilibrium owing to the large surface-volume ratio. The platinum contact wire was soldered to a screw which permitted the adjustment of the temperature, this had one inconvenience, that was, the mercury surface became dirty owing to the amalgam formed with the solder. By replacing the solder by a small steel chuck the mercury surface remained free from contamination.

The relay was of the mercury switch type (Amer. Instr. Co.). This was very satisfactory since it was activated by a very small current supplied from rectifying transformer (Amer. Inst. Co.), This prevented oxidation of mercury surface in thermoregulator, at the same time breaking a large current on the power side without burning of contact points because the circuit

is completed by mercury in the switch. The relay was enclosed in a dust proof glass casing.

The stirring was accomplished by a motor driven stirrer, equipped with four, three inch paddles.

The pressures developed during a run were often of several atmospheres, since no pressure tubing was used in the construction of the apparatus, there was the possibility of an explosion. Therefore this section of the apparatus was surrounded by a wooden shield. Where it was necessary to make observations, shatterproof glass was employed.

B. Experimental Technique

1. Preparation and Purification of Materials.
   - (a) Water
   - (b) Sulphur dioxide.
   - (c) Magnesium oxide
2. Preparation of Solutions.
3. Operating Technique

Experimental Technique

This section will be devoted to a detailed account of the purification of the reactants and the technique involved in manipulating the apparatus during the vapour determinations.

1. Preparation and Purification of Materials

The purity of the reagents was an important factor in this investigation. For this reason all the glass used in building the apparatus was thoroughly cleaned with hot chromic acid, washed several times with distilled water, with alcohol and finally with ether.

The mercury used in the manometer system etc., was cleaned by allowing a fine spray to fall through a 15% nitric acid solution in a cleaning tower and washed twice with distilled water, dried by pouring through a filter of cotton gauze and stored in a clean flask.

The three components water, magnesium oxide and sulphur dioxide were purified as follows.

(a). Water

Distilled water was used and the only impurities present were dissolved gases. These were removed by alternate freezing and melting with evacuation.during the frozen stage. The process of out-gassing was continued until no bubbles were seen rising from the water.

(b). Sulphur Dioxide

The sulphur dioxide was purified by fractional distillation. After preliminary evacuation of the system, gas from a supply cylinder was dried by passing through a phosphorous pentoxide drying tube and condensed in bulb "H_1" surrounded by carbon dioxide - acetone freezing mixture. The freezing mixture was removed and the lower boiling point fraction was allowed to escape, the centre fraction was distilled to a second bulb "H_2" and the final fraction was discarded. This procedure was carried out three times, thus assuring pure sulphur dioxide free from water and any sulphur trioxide.

(c). Magnesium Oxide

Pure magnesium oxide is perhaps more difficult to obtain. The most objectionable impurities are the carbonate and occluded gases. When the oxide is dissolved both the combined carbon dioxide and the other gases are liberated, and cause the vapour pressures as read to be too high. The purity of magnesium oxide from different sources was determined and it waw found that chemically pure magnesium oxide would be quite satisfactory. C.P. magnesium oxide as supplied by J.T. Baker Co. Ltd. was used throughout this investigation. The oxide was placed in a porcelain boat and heated at 950°C. in an electric muffle furnace for ten days in the presence of a current of dry carbon dioxide free air, obtained by circulating air through a concentrated

solution of potassium hydroxide, a soda lime tower and finally through a calcium chloride drying tower. The porcelain boat containing the oxide was transferred quickly from the muffle to a vacuum desiccator containing phosphorous pentoxide and small fragments of sodium hydroxide to remove water vapour and carbon dioxide. The desiccator was evacuated and the oxide was allowed to cool.

Before the weighing out of the oxide, the desicoator was filled with air circulated through a solution of potassium hydroxide and soda lime and calcium chloride towers. In each separate purification the air flow was regulated so that it took about two hours to fill the desiccator. The oxide was weighed as rapidly as possible to avoid contamination by carbon dioxide or water from the air.

The oxide calcinated as above, was the heavy inert variety, but an additional precaution was taken to be certain that all the carbonate had been converted into the oxide and that all the occluded gas was expelled. Before a run was started each sample of oxide was tested for gas content by the method of Richards and Rogers (35). A pipette in the shape of a U was constructed with one side arm graduated in tenths of a cubic centimetre. This was filled with air-free water, a known weight of the oxide was inserted through the open arm, when this had settled, a few cubic centimetres of concentrated hydro-

chloric acid were added, the magnesium oxide was dissolved and any gas liberated entered the graduated arm of the pipette, where its volume was measured. In every case the amount of gas given off was negligible, 0.025 cc. per gram of magnesium oxide.

On account of hygroscopicity of magnesium oxide, it was found advisable to verify the weights of the oxide used by analysing the solution at the completion of a series of runs. After several methods were tried, the one finally adopted was that suggested in J.H. Mennie's Elementary Quantitative Analysis.

The magnesium was weighed as magnesium ammonium phosphate hexahydrate. The values found by analysis agreed to within 0.7% with the original values In view of all the precautions taken it is apparent that impurities were present in such small amounts as to have an entirely negligible influence on the results.

2. Preparation of Solutions

The procedure followed and the precautions taken in preparing the solutions will be described in detail.

The cell was thoroughly cleaned, the side arm "V" was sealed off and the distilling bulb was sealed on to the side arm "W". The distilling bulb was constructed of three cm. Pyrex tubing with a volume of approximately 100 cc. The side arm "W" was so arranged that when the cell was in place the distilling bulb was completely outside the bath and that part of the arm close to the cell was of medium capillary bore to permit selaing off under vacuum.

The solenoid was slipped over the cell shaft and the cell was sealed to the rest of the apparatus. Before the evacuation pumps were started it was necessary to lower reservoir "R_3" to prevent mercury from being sucked into the cell. Evacuation was continued for several hours to remove any moisture and the apparatus was left under vacuum overnight to test for leaks. At this stage the length of the stirrer stroke was determined by adjusting the height of the solenoid. The join, where the cell is sealed to the apparatus, was covered with a layer of asbestos, wound with nichrome wire, and finally covered with another layer of asbestos.

The apparatus was next filled with dry carbon dioxide - free air by slowly admitting it from a soda lime tower and a phosphorous pentoxide drying tube.

The side arm "V" and the neck of the distilling bulb were blown open to admit the magnesium oxide and the water. The magnesium oxide was rapidly weighed on glazed paper and introduced into the cell through a burette funnel. The oxide tended to clog in the funnel but this was overcome effectively by gentle tapping. The side arm "V" was now sealed off close to the cell.

The water was boiled to remove a portion of the dissolved gases, cooled, weighed in a special pipette and transferred to the distilling bulb, the neck of which was then sealed off. The pipette was again weighed and the difference found gave the weight of the water in the distilling bulb. The water was frozen from the bottom of the bulb upwards by slowly raising a Dewar flask containing carbon dioxide - acetone freezing mixture around the bulb, greatest care had to be taken during this process, to be certain that the water surface did not freeze over before the main body of water was frozen, otherwise the bulb would burst. Once the water was frozen the apparatus was exhausted by the evacuation pumps. Because of the low vapour pressure at -78°C, no appreciable amount of water vapour was lost during evacuation.

The mercury was raised in the U-shaped cut off by applying pressure to "R_2" and the ice was allowed to melt. It was necessary to exercise great care during this process

to prevent the bulb from breaking, as would result if a layer of water formed between the glass wall and the ice and then froze again. Of the different methods tried, the one finally adopted was to cover the bulb with several layers of cloth immediately after the removal of the freezing mixture

The water was again frozen in the same manner. Because of the reduced air pressure over the water surface, very little gas was dissolved on the second freezing. When the water was completely frozen, a period of at least fifteen minutes was allowed for the water vapour in the system to condense and freeze before the mercury was withdrawn from the cut off and the apparatus evacuated for the second time. The procedure was carried out until no air bubbles were seen to rise from the water as the ice melted. When the water was completely free of air the mercury was raised in the shut off and the stop-cock "S_7" was closed.

The water in the distilling bulb was gradually warmed until a temperature was reached at which it began to distill into the cell. During this process the bath was cooled to about 5°C. either by circulating water or lime solution through the cooling coils to accelerate the distillation.

When all the water had distilled over into the cell, the distilling bulb and the connecting tubing were flamed to expel the remaining water vapour from the bulb and the side arm "W" was sealed off at the capillary section of the side arm.

This completed the formation of the water - magnesium

oxide mixture and everything was now ready for the introduction of the desired amount of sulphur dioxide.

Pure sulphur dioxide after three fractional distillations was stored in the solid state in the bulb "H_4". Prior to measuring out the sulphur dioxide, any air that may have come over from the supply cylinder was removed by closing stop-cock "S_2" and opening "S_1" for a few seconds, then closing "S_1", opening "$S_{2_{out}}$" and evacuating the system. This operation was carfied/several times to assure the removal of the last trace of air. The stop-cocks "S_4", "S_5" and "S_6" were now opened and this section of the apparatus was flushed out several times with pure sulphur dioxide from "H_4". The stop-cock "S_1" was then shut and the apparatus evacuated until the pressure as read from the McLeod Guage was reduced to at least 10^{-3}mm., and the stop-cock "S_2" was closed.

The stop-cock "S_1" was now opened, the freezing mixture was removed from around the bulb "H_4" and the pressure of the gas was followed on the manometer "C". When the desired pressure was reached, "S_1" was closed and the liquid sulphur dioxide that remained in the bulb "H_4" was allowed to evaporate through the mercury valve "O" to the fume cupboard.

A period of at least fifteen minutes was allowed to elapse before any readings were taken, to permit the gas to reach temperature equilibrium with the tubing. The mercury was raised to the 10 cm. on the right hand side of manometer "C",

by applying either pressure or vacuum to the mercury reservoir "R_2". Both temperature and pressure were recorded.

The gas in the calibrated volumes "F" and "G" and connecting tubing was condensed into "H_5" by surrounding it with a Dewar flask containing the freezing mixture and the stop-cock "S_6" was closed.

The sulphur dioxide was transferred from "H_5" to the cell in the following manner. The mercury was withdrawn from the cut off, the carbon-dioxide - acetone freezing mixture was removed from around "H_5", the liquid sulphur dioxide was allowed to warm up for a few minutes and the stop-cock "S_7" was opened. The pressure which had developed during the warming up caused the gas to rush through the connecting tubing and into the cell where it rapidly dissolved in the water. The rate at which the gas dissolved, could be determined by watching the level of the mercury in scale "B", if the pressure developed became too great, that is, if the liquid sulphur dioxide evaporated at a greater rate than that at which the gas was dissolved in the water, bulb "H_5" was surrounded momentarily by the freezing mixture to decrease the rate of evolution of the gas. To increase the rate of solution of the sulphur dioxide, the temperature of the bath was held as low as possible and the magnetic stirrer was started and adjusted to assure adequate stirring of the magnesium oxide-water mixture in the cell.

When all the liquid sulphur dioxide had evaporated

from bulb "H_5" and the gas in the tubing was in equilibrium with that of the system magnesium oxide - sulphur dioxide - water in the cell, the mercury was raised into the cut off, and the mercury-seal capillary to "L_3" and the capillary U-tube surrounded by a Dewar flask containing the freezing mixture. The gas that remained in the connecting tubing was condensed back into the bulb "H_5" by replacing the carbon-dioxide - acetone freezing mixture. The stop-cock "S_7" was closed, "S_6" was opened and the freezing mixture removed from around the bulb "H_5". The pressure of the residual gas was measured on manometer "C". A correction had to be applied for that fraction of the gas remaining in the tubing between "S_7" and the mercury in the cut off arm at the gas pressure of solid sulphur dioxide at -78°C. In both pressure measurements the following readings had to be taken and recorded.

1. The pressure as read from the manometer "C".
2. The temperature of the mercury in the manometer.
3. The temperature of the connecting tubing.
4. The temperature of the water bath surrounding the calibrated volumes "F" and "G".

From the above readings, it was possible to calculate the exact weight of the sulphur dioxide injected into the cell. The method of calculating the weight of the sulphur dioxide will be discussed in detail in the section dealing with calculations.

A run was then made in the manner described below. At

the completion of the run the bath was cooled to room temperature, the freezing solution removed from around the U-capillary and the mercury drawn down into the reservoir "R_2". Any mercury remaining in the capillary was expelled by careful flaming with hand torch. The amount of sulphur dioxide which was desired to be added for the second run was weighed, condensed into bulb "H_5" and injected into the cell as described before; the mercury was raised into the capillary, the seal frozen and the run started.

When a series of runs had been completed covering the desired sulphur dioxide concentration range for a definite magnesium oxide concentration, the cell was cut out and the liquor filtered and kept for analysis. The cell was thoroughly cleaned, dried and the complete procedure of preparing the solution repeated, using a different ratio of magnesium oxide to water.

3. Operating Technique

Prior to making a run, the stirrers, thermoregulator circuit and heating units were examined and final adjustments made. The temperature of the oil bath was raised to the temperature at which the first vapour pressure-measurement was to be made. The thermoregulator was set and the heater was adjusted to give the proper amount of heat. As the temperature increased the mercury level was kept at the zero point on scale "B" by raising the mercury reservoir "R_3" and it was necessary at all times during a run to keep the mercury level within the lagged section of scale "B" to prevent condensation of water vapour on the surface of the mercury.

When making a run with a low sulphur dioxide concentration, it was necessary to allow sufficient time for all the sulphur dioxide to combine with the magnesium oxide. In certain instances it was necessary to wait three days before starting a run, this was caused by the very slow rate at which the magnesium oxide dissolved. In general, two hours were found to be sufficient time for a two phase system to come to equilibrium.

When equilibrium was finally reached, as indicated by the constancy of the mercury level in scale "B" over a period of an hour, the following readings were recorded:

1. The temperature of the oil bath.
2. Height of mercury in large manometer.
3. Temperature of the large manometer (top, middle and bottom).

4. Temperature of the lagged tubing connecting the cell to the large manometer.

This completed, the temperature of the oil bath was increased and the next reading taken. In most cases the vapour pressures were determined at ten degree intervals either up to 130°C. or until the pressure had increased to approximately four atmospheres. The pressure was not raised above four atmospheres because the danger of the cell bursting was rather great.

If it was found necessary to have values corresponding to higher temperatures, these were obtained by extrapolation, these values were quite accurate since a straight line relationship was obtained when the logarithm of the total vapour pressures was plotted against the reciprocal of the absolute temperature.

Check points were made with descending temperature and the values agreed with the former values to within experimental error. These check values showed that the phenomenon of hysteresis was absent.

For several runs it was observed that the slope of the line changed, indicating the presence of a transition point It was advisable to investigate this region to determine whether the change in slope was gradual or at one particular temperature. In several cases the vapour pressure was determined at one degree intervals on either side of this point over a temperature range of ten degrees. Plots of the data showed that the slope changed gradually.

At higher temperatures it was necessary to include the

auxiliary heater to maintain temperature limits controllable by the thermoregulator. As the higher pressures were developed in the cell, it was necessary to pump air into the reservoir "R_3" with a bicycle pump in order to keep the mercury in scale "B" at the zero mark.

The greatest precaution had to be taken throughout a run to keep the mercury at the zero mark on scale "B". On cooling the oil bath it was necessary to lower the mercury in scale "B" constantly, otherwise the mercury was forced over into the cell from scale "B".

C. Factors to be Considered in the Calculation of the Results

1. Calculations on the Apparatus.
2. Calculations on the Introduction of the Reagents.
3. Calculations Necessary to Place the Data in a Useful Form

1. Calculations on the Apparatus

Considerable time was spent on the calculations as they were quite complicated though not difficult. The procedure followed will be explained and for the sake of clarity type calculations will be included.

The volume of the gas measuring system was accurately determined. The volumes "F" and "G" from which the other volumes were determined, were calibrated up to the stop-cocks by weighing them full of water and then empty and applying the necessary density corrections.

The gas measuring and the introduction systems including the cell were divided into four sections, the volume of each being measured separately (Fig. 1). The sections are as follows:

Section A:

The connecting tubing limited by the stop-cocks "S_1", "S_2", "S_3", "S_4", "S_5", "S_7" and the 10 cm. mark on manometer "C".

Section B:

The connecting tubing limited by stop-cock "S_7", the mark "L_2" and "L_4".

Section C:

The capillary tubing between "L_3" and "L_4".

Section D:

The tubing including the cell bounded by "L_3" to the zero mark on scale "B".

The volume of sections A, B and D was determined in the same manner, as follows. The calibrated volumes, "F" and "G" were filled with dry air at a known pressure and temperature. This air was allowed to expand into the evacuated volume to be measured, the resultant pressure was read from the manometer and the temperature of the gas recorded. The glass scale correction was applied to the pressure readings (49) and the unknown volume was determined by applying the gas laws.

The value of the unknown volume was obtained by substituting the known values in the following equation.

$$P_1V_1T_2 = P_2V_2T_1$$

where:

P_1 = Pressure of air in calibrated volumes (usually atmospheric)

V_1 = Calibrated volume ("F" + "G").

T_1 = Absolute temperature of air before expansion.

P_2 = Pressure of air after expansion.

V_2 = Total volume after expansion.

T_2 = Absolute temperature of air after expansion.

To evaluate the volume of section B the tubing at the point "L_4" was sealed shut, the mercury in the reservoir "R_2" was brought to the reference mark "L_2", and air was expanded into the evacuated tubing. Once the volume was determined the tubing was blown open and sealed to the capillary at "L_4".

The volume of the capillary tubing, section C was

determined in a different manner. Its length was measured, and the amount of mercury contained by a piece of capillary of the same length and bore was weighed. This weight divided by the density of the mercury gave the volume.

The total volume represented by the sections B, C and D, was determined by raising the mercury to the zero mark in scale "B" and expanding air from the known values (Section A, "F" and "G") into it.

The volume of section D had to be known in order to make corrections for the amount of sulphur dioxide that existed in the gas phase during a run. This volume was found by subtracting the sum of the volumes of sections B and C from the value representing the total volume of section B, C and D.

Manometer Constant

The high pressure manometer was of the closed end type, a manometer constant had to be determined, so that the scale readings could be expressed in terms of pressure in centimeters of mercury. This constant was determined before the cell was sealed into place, consequently the air pressure above the mercury surface in scale "B" was atmospheric. A point on scale "A" exactly level with the zero mark on scale "B" was determined with a large cathetometer. The mercury was now raised up to the zero mark on scale "B", the barometric pressure recorded and the level of the mercury in the manometer was

read on scale "A". The temperature of the entrapped air in the manometer was read from three thermometers spaced along its length. The manometer constant was calculated from the above data.

The procedure described above will be better understood by including the calculations for an actual determination.

Observed Values

Barometric pressure:	75.12 cm. (24.2°C.)		
0 scale "B" corresponds to	280.82 cm. on scale "A".		
Pressure on scale "A"	304.82 cm.		
	Bottom	Middle	Top
Manometer temperatures	24°C	24.8°C.	26°C.

Corrected barometric pressure (50) = 74.83 cms.

Difference between mercury level on scale "B" and scale "A"

304.82 cm.
280.82 cm.
24.00 cm.

This figure was corrected to the corresponding figure at 0°C. by multiplying the density of mercury at the temperature of the manometer and dividing by the density of mercury at 0°C.

$$\frac{24.00 \times 13.536}{13.596} = 23.89 \text{ cm.}$$

From the data of Gurd (2) for the calibration of the manometer, the volume of the trapped air above the 304.82 cm. division was determined as follows:

Volume cc.	Scale reading cm.	Difference cm.
255.63	328.63	304.82
233.91	301.25	301.25
21.72	27.38	3.57

$$\text{Volume correction} = \frac{3.57 \times 21.72}{27.38} = 2.83 \text{ cc.}$$

Volume of trapped air = 233.91 + 2.83 = 236.74 cc.

The pressure exerted by the enclosed air is equal to the atmospheric pressure plus the corrected difference between the mercury levels, i.e.

Pressure = 74.83 + 23.89 = 98.72.

From the gas laws;

$$PV = KT$$

$$\text{or,} \quad K = \frac{PV}{T}$$

Where: K = A constant.

P = Pressure of the trapped air.

V = Volume of the trapped air.

T = Absolute temperature of the trapped air.

By substituting the values obtained into the above equation, the manometer constant was found to be:

$$\frac{98.72 \times 236.74}{298.4} = 78.32 \text{ cm}^4/^\circ\text{K.}$$

The manometer constant was determined several times during this investigation and the values found agreed to within one part in five hundred.

2. Calculations on the Introduction of the Reagents

It was not necessary to apply corrections for the weight of water or magnesium oxide introduced into the cell. The bulb from which the water was distilled into the cell was flamed by a hand-torch, and immediately sealed off. The volume of this bulb was approximately 100 cc. and therefore the weight of the water vapour that remained was negligible in comparison to the weight of the water in the cell.

The weight of the sulphur dioxide introduced into the cell had to be calculated. The gas was expanded into a known volume at a known temperature, and the pressure exerted by the gas was recorded, and the glass scale corrections were applied. The weight of the sulphur dioxide was calculated from the equation of Maass and Maass (5).

$$m = \left[64.06 + (M - 64.06)\,P\right] \times \frac{PV}{RT}$$

where m = mass of the sulphur dioxide in grams.

P = Pressure in atmospheres.

T = Absolute temperature.

V = Volume in litres.

R = Gas constant

M = Molecular weight of sulphur dioxide at temperature T.

Since sulphur dioxide exhibits the property of association, the molecular weight varies with the temperature. The

molecular weight of the sulphur dioxide is given from a curve constructed from the following data.

t°C.	M.
38.05	65.20
22.90	65.27
10.35	65.42
1.40	65.60
0.80	65.61
-6.55	65.76

A final connection had to be applied to the weight of sulphur dioxide injected into the cell, this was the weight of the gas which occupied the connecting tubing between stop-cock "S_7" and the level of the mercury in the right hand arm of the mercury cut off. This could be evaluated because the pressure of the gas at -78°C. and the volume of the tubing were known.

With these values, the weight of the gas calculated from the gas laws was found to be 0.0010 gms.

Below are shown the calculations necessary to determine the weight of the sulphur dioxide injected into the cell, the values chosen were those for run No. 2G.

	Press. cm.	Press. corr. cm.	Bath Temp. °C.	Tube Temp. °C.	Man. Temp. °C.	Vol. Tube cc.	Vol. F+G cc.	Mol. Wt. SO_2
Before SO_2 injected	34.83	346.9	24.0	24.0	24.0	103.2	646.2	65.26
After SO_2 injected	13.2	13.2	24.4	24.3	24.0	103.2	646.2	65.26

By substituting the above values in the following equation,

$$m = \left[64.06 + (M - 64.06)\ P\right] \times \frac{PV}{RT}$$

therefore:

$$m = \left[64.06 + x\ \frac{346.86}{760}\right] x\ \frac{346.86 \times 749.41}{760 \times 1000 \times .08207 \times 297}$$

$$-\left[64.06 + 120 \times \frac{13.2}{760} \times \frac{13.2 \times 646.2}{760 \times 1000 \times .08207 \times 297.3}\right]$$

$$-\left[64.06 + 120 \times \frac{13.2}{760} \times \frac{13.2 \times 103.2}{760 \times 1000 \times .08207 \times 297.15}\right]$$

$$= 0.9067 - (0.02947 + 0.004709)$$

$$= 0.8725 \text{ gm.}$$

Correction for SO_2 trapped in tubing = 0.0010 gm.

Total weight of SO_2 injected into cell = 0.87152 gm.

3. Calculations Necessary to Place the Data in a Useful Form.

It was necessary to carry out a series of calculations for each reading before the data could be presented in the desired form. The observed and calculated values were tabulated for each run. An explanation of the headings of each column will show how the final values were obtained.

Time: Sufficient time, in general two hours, was allowed for equilibrium to be reached before a reading was taken. Relative times were used because the time factor does not influence the results.

Temp: The temperature of the thermostatically controlled oil bath surrounding the cell.

Corrected Temp: The temperature of the oil bath after thermometer corrections had been applied.

$\frac{1}{T}$: The reciprocal of the corrected temperature.

Scale: The values as read on scale "A".

Height of Mercury Column: This is the pressure exerted by a column of mercury the height of which is the difference in level between the zero mark on scale "B" and the value as read from scale "A". Consequently the pressure is the difference between the reading on scale

"A" and 280.81. This difference is either positive or negative, depending on the height of mercury in scale "A". Scale "A" was graduated in centimetres reading from the top to the bottom. The pressure exerted by this column of mercury is obtained by subtracting 280.81 from the reading of scale "A" if the latter is numerically greater than 280.81, the pressure in such a case is negative. If the reading of scale "A" is numerically less than 280.81, the reading of scale "A" is subtracted from 280.81 and the pressure is positive. As was mentioned previously, the zero mark on scale "B" corresponds to the 280.81 mark on scale "A".

Corrected Height of Mercury Column: This value was obtained by correcting the length of mercury column to the corresponding length at 0°C.

Volume: The volume of the enclosed air above the mercury surface in the manometer.

Manometer Temp: The average manometer temperature in degrees Absolute.

Air Pressure: The pressure exerted by the air above the mercury surface in the manometer was calculated with the aid of the formula $P = \frac{KT}{V}$, by substituting therein the values of the manometer constant, the

temperature and volume occupied by the air.

Total Pressure: The sum of the air pressure and the pressure corresponding to "Height of Mercury Column" plus a small density correction to the six centimetres of hot mercury in scale "B".

Log Pressure: The logarithm corresponding to the total pressure.

Partial Pressure of Water: The partial pressure of water vapour, at the corrected temperature of the oil bath.

Times Mole Fraction: The total vapour pressure of the water was multiplied by the mole fraction of water present in the solution, to correct for the lowering of the vapour pressure by the addition of the solutes. The mole fraction of water was calculated as follows:

$$\frac{\frac{\text{Weight of } H_2O}{18}}{\frac{\text{Weight MgO}}{40.3} + \frac{\text{Weight } SO_2}{64} + \frac{\text{Weight } H_2O}{18}}$$

Partial Pressure of Sulphur Dioxide: The partial pressure of sulphur dioxide at the corrected temperature, was obtained by subtracting the value of "Times Mole Fraction" from the value of "Total Pressure",

Temp. of the Gas Phase: The mean temperature of the lagged tubing of the cell-manometer system, as read from the thermometers T_1 and T_2 respectively.

Weight of Sulphur Dioxide in the Gas Phase: To determine the weight of sulphur dioxide in the gas phase, the volume occupied by the gas above the surface of the solution in the cell to the zero mark on scale "B" had to be known. The gas volume was divided into two sections, that in the cell directly above the solution, at the temperature of the bath and that in the heated tubing at a much higher temperature. Knowing the volumes, the temperature, and the partial pressures, the weight of sulphur dioxide in each section was calculated from the gas laws. The sum of the two gave the total weight of the sulphur dioxide in the gas phase.

Weight of Sulphur Dioxide in the Liquid Phase: These values were obtained by subtracting the weight of sulphur dioxide in the gas phase from the total weight of the sulphur dioxide injected into the cell.

percent Sulphur Dioxide in the Liquid Phase: The weight of the sulphur dioxide in the liquid phase divided by the total weight of components.

The calculations completed, the data were tabulated, from which curves were constructed. The results and the discussion of the results are included in the section to follow.

RESULTS

RESULTS.

In the investigation of vapour pressures of the three component system magnesium oxide - sulphur dioxide - water, the experimental data for fifteen solutions having different sulphur dioxide concentrations are given. The vapour pressures were measured at appropriate temperatures between 20°C. and 130°C. The fifteen solutions are classified in four groups or "series" corresponding to the different concentrations of magnesium oxide employed. Series A, consisted of three runs, the sulphur dioxide concentrations were 2.19%, 4.30% and 6.24% respectively, while the concentration of the magnesium oxide was approximately 0.6%. Series B, consisted of four runs, the sulphur dioxide concentrations were 3.63%, 4.75%, 5.84 and 6.86% respectively, while the concentration of the magnesium oxide was approximately 1.00%. Series C, consisted of four runs, the sulphur dioxide concentrations were 412%, 5.19%, 6.15%, and 7.11% respectively, while the concentration of magnesium oxide was approximately 1.4%. Series F consisted of four runs, the sulphur dioxide concentrations were 2.68%, 5.40%, 6.11%, 7.07% respectively, while the concentration of magnesium oxide was approximately 1.8%.

In the case of run No. 1F the sulphur dioxide present was not sufficient to dissolve all the magnesium oxide and consequently the system was three phase throughout the run.

However, all the others were two phase over the entire temperature range investigated.

The vapour pressures of the three phase system No. 1F are practically similar to those of pure water, and therefore the results are not of great interest. However, the investigation provided a means of testing the apparatus. When the data obtained from run No. 1F were plotted with total vapour pressure and temperature as ordinates, the values found fell on a curve parallel to the vapour pressure curve of water. The distance between these curves represented a pressure difference of approximately 0.39 cm. It was difficult to investigate the three phase system, since the presence of the solid phase greatly retarded the rate at which the equilibrium was reached, this was more pronounced at the lower temperatures. The conclusions that can be drawn are, that the calibration of the manometer and the determination of the manometer constant are correct and that the manometer is capable of measuring accurately pressures over the entire range investigated.

The percentage of each component is calculated on the basis of the total weight of the sulphur dioxide (in the liquid phase), magnesium oxide and water. The actual concentrations of the magnesium oxide and sulphur dioxide present in each solution examined, will be discussed in another paragraph.

A considerable amount of calculation was involved before the experimental data could be tabulated. The number of observations and the mathematical treatment of each tnat must be made for a particular run was discussed in detail in the previous section. It will be readily realized that it is impossible to include all these data for each run. However, sufficient data has been included to permit the recalculation of any value. The experimental data are summarized in two sets of tables, the series tables and the run tables respectively.

The tables 1 to 4 inclusive are the series tables, they contain values common to every rún in that particular series. Although the column headings are self-explanitory, one or two deserve further explanation. Under the headings "Initial Gas Temperature and Residual Gas Temperature" two temperatures are recorded, the top value is the temperature of the system No.1, the lower value that of the calibrated volumes "F" and "G". The pressures recorded have all been corrected to 0°C.

The figures in the last column represent the average temperature of the gas phase, this temperature did not remain constant throughout a run but varied about five degrees from the figure recorded.

It will be observed that in the case of Series A run No.1, Series B run No.2, Series C, run No.1 and also Series F, run No.2 it was necessary to inject a second amount of sulphur

Series A.

Run	Gms. Water	Gms. MgO	Initial Manom. Press. cms.	Residual Gas Press. cms.	Volume of System No.1 cc.	Volume of "F" + "G"	Initial Gas Temp.	Residual Gas Temp.	Gms. SO_2	Vol. of Gas Phase In Bulb (cc.)	Vol. of Gas Phase In Heated Tube	Temp. of Gas Phase
1	88.822	0.5950	32.55	2.07	103.20	646.22	25.0 25.5	24.9 24.8				
			48.53	1.81	103.20	646.22	26.9 26.9	27.0 27.0	2.0051	13.63	22.53	140°
2	88.822	0.5950	78.67	1.70	103.20	646.22	24.7 24.4	24.8 24.7	4.0367	12.15	22.53	150°
3	88.822	0.5950	76.27	2.49	103.20	646.22	24.0 24.0	23.9 23.9	5.9870	10.74	22.53	175°

TABLE 1

Series B.

Run	Gms. Water	Gms. MgO.	Initial Manom. Press. cms.	Residual Gas Press. cms.	Volume of System No.1 cc.	Volume of "F" + "G"	Initial Gas Temp.	Residual Gas Temp.	Gms. SO_2	Vol. of Gas Phase In Bulb (cc)	Vol. of Gas Phase In Heated Tube	Temp. of Gas Phase
2	74.480	0.8297	36.77	0.91	103.20	646.22	23.1 22.9	23.6 23.5	2.8338	31.35	22.5	185°
3	74.480	0.8297	36.83	1.49	103.20	646.22	25.7 25.6	24.8 24.7	3.7533	30.00	22.5	180°
4	74.480	0.8297	36.82	1.79	103.20	646.22	25.0 24.5	25.2 25.2	4.6682	29.34	22.5	180°
5	74.480	0.8297	36.39	2.41	103.20	646.22	24.8 24.8	24.9 24.6	5.5549	28.69	22.5	185°
1	74.480	0.8297	74.45	2.54	103.20	646.22	24.1 23.9	25.2 24.9	1.8922	-	-	-

TABLE 2

Series G.

Run	Gms. Water	Gms. MgO	Initial Manom. Press. cms.	Residual Gas Press. cms.	Volume of System No.1 cc.	Volume of "F" + "G"	Initial Gas Temp.	Residual Gas Temp.	Gms. SO_2	Vol. of Gas Phase In Bulb (cc)	Vol. of Gas Phase In Heated Tube	Temp. of Gas Phase
1	73.268	1.0486	63.01	0.8	103.19	646.22	25.8 25.9	26.0 25.9				
			61.02	1.04	103.19	646.22	25.8 25.9	25.8 25.8	3.1952	31.36	22.67	125°
2	73.268	1.0486	34.68	1.32	103.19	646.22	24.0 24.0	24.3 24.4	4.0677	30.98	22.67	140°
3	73.268	1.0486	32.54	1.92	103.19	646.22	23.0 22.9	24.5 24.5	4.8708	30.40	22.67	135°
4	73.268	1.0486	33.68	2.41	103.19	646.22	23.9 23.8	24.1 24.1	5.6891	29.82	22.67	140°

TABLE 3

Series F.

Run	Gms. Water	Gms. MgO	Initial Manom. Press. cms.	Residual Gas Press. cms.	Volume of System No.1 cc.	Volume of "F" + "G"	Initial Gas Temp.	Residual Gas Temp.	Gms. SO_2	Vol. of Gas Phase In Bulb (cc)	Vol. of Gas Phase In Heated Tube	Temp. of Gas Phase
1	74.531	1.3489	78.59	0.83	103.19	646.22	24.7 24.7	24.2 24.2	2.0486	31.18	22.67	135°
2	74.531	1.3489	49.51	0.83	103.19	646.22	25.0 25.0	24.0 24.0				
			40.64	1.12	103.19	646.22	25.0 25.0	24.7 24.8	4.3367	29.53	22.67	135°
3	74.531	1.3489	24.91	1.66	103.19	646.22	26.2 26.6	26.0 26.1	4.9378	29.09	22.67	135°
4	74.531	1.3489	34.06	2.11	103.19	646.22	23.5 23.4	23.2 23.2	5.7749	28.49	22.67	130°

TABLE 4

dioxide before the desired concentration was reached. The figures for the first injection of sulphur dioxide for Series B run No.2 are recorded in the last horizontal column of Table 2.

Tables 5 to 19 show the experimental data for each run. From the data curves were plotted on four separate graphs, i.e., one for each series. The reciprocal of the absolute temperature was plotted as abscissa with the logarithm of the total vapour pressure in centimeters as ordinate. The concentration of the sulphur dioxide in the liquid phase was plotted as the other ordinate. The graphs for Series B, Series G and Series F each contained eight curves, while that of Series A contained six, making a total of thirty curves. Figure 4 shows these curves plotted from the experimental data for Series G.

In the final table of results, the values for the total vapour pressure of solutions containing even percentages of sulphur dioxide and magnesium oxide are recorded.

Before it was possible to obtain these values, it was necessary to construct several sets of curves to account for the change in the concentration of the solutions that occurred during the investigation of each Series. Take for example a solution in which the sulphur dioxide concentration was 5% at the start of a run, with increasing temperature, a greater amount of the gas would leave the liquid phase, consequently the concentration of the sulphur dioxide in this phase would decrease. This change in the sulphur dioxide concentration

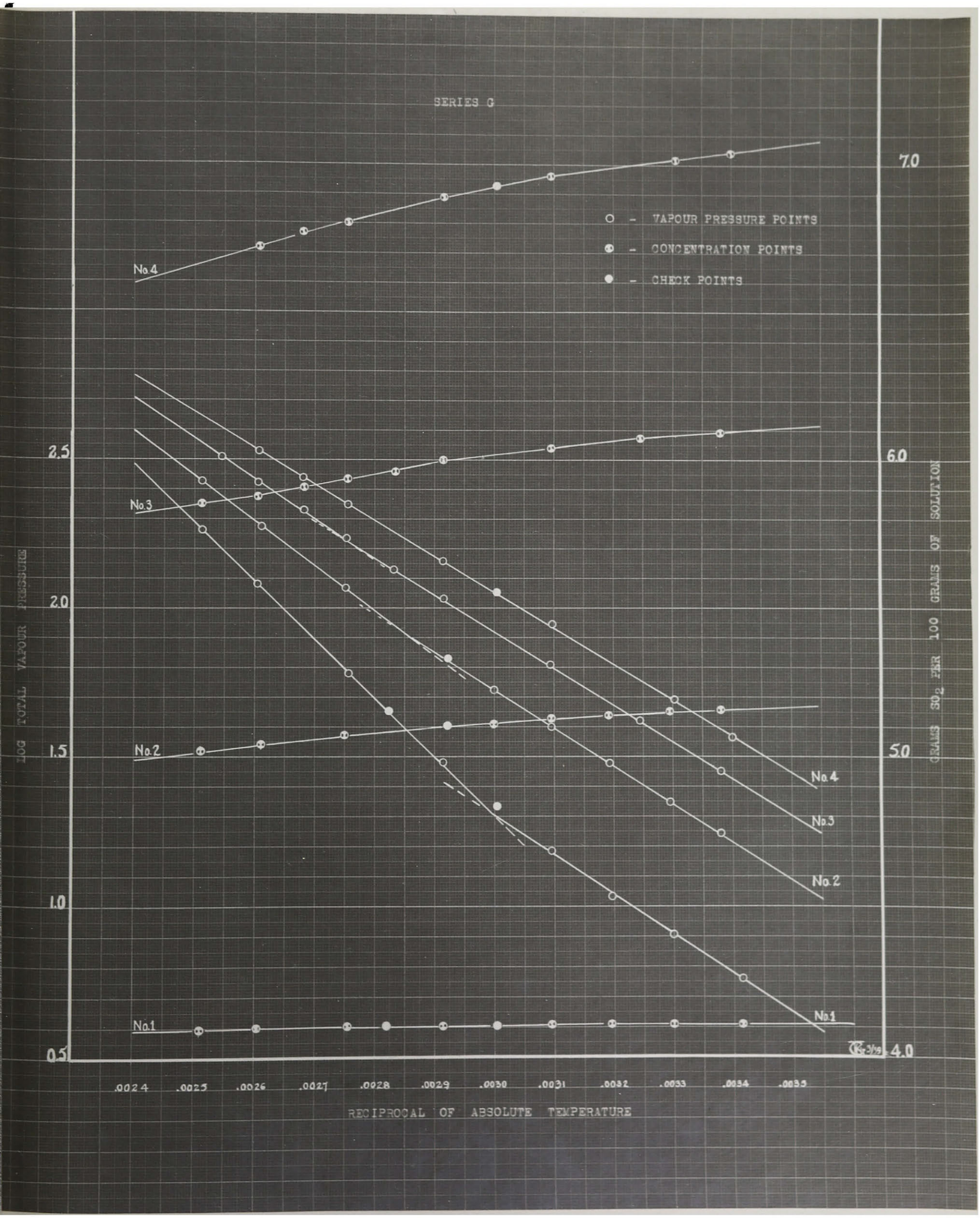

SERIES C
O - VAPOUR PRESSURE POINTS
- CONCENTRATION POINTS
- CHECK POINTS
No.4
No.3
No.2
No.1
LOG TOTAL VAPOUR PRESSURE
2.5
2.0
1.5
1.0
0.5
7.0
6.0
5.0
4.0
GRAMS SO_2 PER 100 GRAMS OF SOLUTION
.0024
.0025
.0026
.0027
.0028
.0029
.0030
.0031
.0032
.0033
.0034
.0035
RECIPROCAL OF ABSOLUTE TEMPERATURE

Figure 4

Series A Run No. 1

88.8215 gms. H_2O ; 0.5950 gms. MgO ; 2.0051 gms. SO_2

Observed Values			Calculated Values			
Bath Temp.	Manom. Scale Reading	Average Manom. Temp.	Percent SO_2 in Solution	Percent MgO in Solution	Bath Temp. Corr.	Vapour Pressure cms.
19.0	358.30	295.4	2.189	0.6508	19.0	5.7
30.9	356.10	296.3	2.187	0.6508	30.9	8.9
40.7	353.13	296.4	2.185	0.6508	40.7	12.8
50.9	348.85	297.1	2.184	0.6508	50.9	18.4
65.8	338.95	297.3	2.181	0.6508	65.8	30.9
73.8	331.42	297.3	2.179	0.6508	73.8	40.6
86.3	315.11	297.4	2.176	0.6508	86.3	61.5
93.8	302.55	297.4	2.175	0.6508	93.8	77.7
99.1	293.05	299.3	2.174	0.6508	99.1	91.3
99.4	291.62	297.8	2.175	0.6508	99.4	92.5
109.6	267.50	298.5	2.173	0.6508	109.6	126.5
120.0	235.85	298.5	2.169	0.6508	120.0	172.9
60.6	343.05	298.1	2.184	0.6508	60.5	25.6

TABLE 5

Series A Run No. 2

88.8215 gms. H_2O ; 0.5950 gms. MgO ; 4.0367 gms. SO_2

Observed Values			Calculated Values			
Bath Temp.	Manom. Scale Reading	Average Manom. Temp.	Percent SO_2 in Solution	Percent MgO in Solution	Bath Temp. Corr.	Vapour Pressure cms.
20.1	344.41	297.4	4.296	0.6367	20.1	23.6
30.3	335.98	297.1	4.287	0.6367	30.3	34.5
40.1	325.52	297.6	4.276	0.6367	40.1	47.8
50.1	312.53	298.0	4.264	0.6367	50.1	64.7
60.2	296.81	297.9	4.251	0.6367	60.2	85.6
70.6	277.16	297.8	4.235	0.6367	70.6	112.6
80.2	256.02	297.9	4.219	0.6367	80.2	142.7
90.3	230.72	298.0	4.201	0.6367	90.2	180.0
100.1	203.15	298.3	4.182	0.6367	100.1	225.7
85.6	243.11	296.8	4.209	0.6367	85.6	161.2
109.9	174.80	296.9	4.162	0.6367	109.9	277.3

TABLE 6

Series A Run No. 3

88.8215 gms. H_2O ; 0.5950 gms. MgO ; 5.9870 gms. SO_2

Observed Values			Calculated Values			
Bath Temp.	Manom. Scale Reading	Average Manom. Temp.	Percent SO_2 in Solution	Percent MgO in Solution	Bath Temp. Corr.	Vapour Pressure cms.
20.2	329.65	295.7	6.238	0.6237	20.2	42.3
30.5	315.55	296.1	6.223	0.6237	30.5	60.2
39.9	299.32	296.5	6.206	0.6237	40.0	81.7
50.1	278.82	295.9	6.185	0.6237	50.1	109.7
70.0	229.10	296.7	6.115	0.6237	70.0	203.0
79.9	200.75	297.0	6.079	0.6237	79.9	257.4
90.2	171.20	297.1	6.044	0.6237	90.1	323.6
100.4	141.90	296.9	6.004	0.6237	100.4	404.3
60.3	254.90	296.4	6.143	0.6237	60.3	158.4
52.3	273.56	297.1	6.182	0.6237	52.3	117.5
60.0	255.50	298.6	6.150	0.6237	59.9	157.4
70.1	228.18	297.6	6.222	0.6237	70.0	204.6

TABLE 7

Series B Run No. 2B

74.479 gms. H_2O ; 0.8297 gms. MgO ; 2.8338 gms. SO_2

Observed Values			Calculated Values			
Bath Temp.	Manom. Scale Reading	Average Manom. Temp.	Percent SO_2 in Solution	Percent MgO in Solution	Bath Temp. Corr.	Vapour Pressure cms.
20.3	357.33	297.2	3.614	1.062	20.3	7.6
30.6	355.19	298.9	3.612	1.062	30.6	10.8
40.3	351.25	298.2	3.608	1.062	40.3	14.9
50.6	345.46	296.8	3.602	1.062	50.7	22.3
60.5	338.63	296.9	3.597	1.062	60.6	31.0
70.7	329.20	296.9	3.591	1.062	70.8	42.9
80.5	317.49	296.8	3.586	1.062	80.5	58.1
90.7	301.94	297.0	3.581	1.062	90.8	78.5
100.6	282.52	297.4	3.576	1.062	100.6	105.1
111.1	256.31	297.6	3.570	1.062	111.1	142.3
123.3	219.79	297.3	3.568	1.062	123.4	197.7
25.7	356.39	297.8	3.613	1.062	25.8	9.0
105.4	271.60	298.7	3.577	1.062	105.4	120.9
29.6	355.40	298.9	3.612	1.062	29.6	10.5

TABLE 8

Series B Run No. 3

74.479 gms. H_2O ; 0.8297 gms. MgO ; 3.7533 gms. SO_2

Observed Values			Calculated Values			
Bath Temp.	Manom. Scale Reading	Average Manom. Temp.	Percent SO_2 in Solution	Percent MgO in Solution	Bath Temp. Corr.	Vapour Pressure cms.
20.5	349.17	297.9	4.716	1.049	20.5	17.9
30.5	343.22	298.6	4.704	1.049	30.5	25.7
50.4	325.41	298.0	4.673	1.049	50.4	48.1
60.6	312.31	297.2	4.656	1.049	60.7	64.8
71.2	296.76	296.5	4.638	1.049	71.3	85.2
80.8	279.50	296.8	4.620	1.049	80.8	109.0
90.9	258.03	298.3	4.600	1.049	90.9	140.1
100.5	233.72	298.1	4.587	1.049	100.5	171.3
111.1	203.90	298.5	4.557	1.049	111.1	224.6
121.0	174.41	298.6	4.538	1.049	120.9	279.2

TABLE 9

Series B Run No. 4

74.479 gms. H_2O ; 0.8297 gms. MgO ; 4.6682 gms. SO_2

Observed Values			Calculated Values			
Bath Temp.	Manom. Scale Reading	Average Manom. Temp.	Percent SO_2 in Solution	Percent MgO in Solution	Bath Temp. Corr.	Vapour Pressure cms.
20.4	340.8	298.1	5.784	1.037	20.4	28.5
29.9	331.69	297.3	5.767	1.037	29.9	39.9
40.5	319.22	297.5	5.744	1.037	40.5	56.0
49.7	305.80	297.8	5.721	1.037	49.8	73.6
60.5	287.50	298.1	5.691	1.037	60.6	98.4
60.3	287.39	295.0	5.691	1.037	60.4	97.5
70.6	267.59	297.6	5.659	1.037	70.7	126.4
80.7	244.83	298.3	5.625	1.037	80.7	159.7
90.5	219.15	297.6	5.592	1.037	90.5	199.2
100.2	192.61	298.0	5.559	1.037	100.2	244.5
110.9	162.42	297.4	5.521	1.037	110.9	303.9
116.8	145.80	297.4	5.501	1.037	116.8	341.5

TABLE 10

Series B Run No. 5

74.479 gms. H_2O ; 0.8297 gms. MgO ; 5.5549 gms. SO_2

Observed Values			Calculated Values			
Bath Temp.	Manom. Scale Reading	Average Manom. Temp.	Percent SO_2 in Solution	Percent MgO in Solution	Bath Temp. Corr.	Vapour Pressure cms.
20.10	333.08	297.9	6.802	1.026	20.10	38.3
30.60	319.88	297.8	6.775	1.026	30.60	55.2
39.80	305.39	297.6	6.746	1.026	39.80	74.1
60.50	264.31	298.4	6.671	1.026	60.60	131.1
70.70	239.29	297.8	6.628	1.026	70.80	167.6
80.40	214.00	298.0	6.584	1.026	80.40	207.6
90.50	186.32	298.4	6.537	1.026	90.50	256.3
107.00	144.90	298.5	6.474	1.026	107.00	344.0

TABLE 11

Series G Run No.1

73.2680 gms. H_2O ; 1.04865 gms. MgO ; 3.1952 gms. SO_2

Observed Values			Calculated Values			
Bath Temp.	Manom. Scale Reading	Average Manom. Temp.	Percent SO_2 in Solution	Percent MgO in Solution	Bath Temp. Corr.	Vapour Pressure cms.
19.9	358.99	297.6	4.123	1.353	20.0	5.8
30.1	357.24	296.7	4.112	1.353	30.1	8.0
39.8	355.06	298.0	4.111	1.353	39.8	10.8
50.1	351.46	298.1	4.110	1.353	50.2	15.3
70.1	339.51	297.9	4.108	1.353	70.2	30.2
59.8	346.19	297.1	4.108	1.353	59.9	21.6
89.9	316.12	297.7	4.106	1.353	90.0	60.2
110.9	272.50	298.6	4.103	1.353	110.9	119.7
125.2	228.55	298.5	4.100	1.353	125.1	184.6
81.3	328.25	298.4	4.107	1.353	81.3	44.8

TABLE 12

Series G Run No. 2

73.2680 gms. H_2O ; 1.04865 gms. MgO ; 4.06775 gms. SO_2

Observed Values			Calculated Values			
Bath Temp.	Manom. Scale Reading	Average Manom. Temp.	Percent SO_2 in Solution	Percent MgO in Solution	Bath Temp. Corr.	Vapour Pressure cms.
22.7	349.20	295.6	5.157	1.338	22.7	17.4
30.6	345.24	295.7	5.150	1.338	30.6	22.4
40.2	339.25	296.0	5.140	1.338	40.2	30.0
49.9	331.59	296.1	5.128	1.338	50.0	39.8
60.2	321.27	296.5	5.115	1.338	60.3	53.1
90.5	273.77	295.9	5.072	1.338	90.5	117.0
109.9	225.45	296.1	5.042	1.338	109.9	188.4
125.2	179.28	296.6	5.019	1.338	125.1	269.0
68.9	310.05	295.6	5.103	1.338	69.0	67.5

TABLE 13

Series G Run No. 3

73.2680 gms. H_2O ; 1.04865 gms. MgO ; 4.8708 gms. SO_2

Observed Values			Calculated Values			
Bath Temp.	Manom Scale Reading	Average Manom. Temp.	Percent SO_2 in Solution	Percent MgO in Solution	Bath Temp. Corr.	Vapour Pressure cms.
22.9	340.19	294.1	6.097	1.324	22.9	28.2
35.3	329.39	294.3	6.075	1.324	35.3	42.0
50.1	312.25	294.9	6.042	1.324	50.2	64.3
70.0	280.64	295.2	5.994	1.324	70.1	107.0
80.0	260.70	295.7	5.965	1.324	80.0	135.5
90.3	236.55	296.0	5.936	1.324	90.3	171.2
99.9	211.10	297.0	5.908	1.324	99.9	212.3
110.7	181.15	297.5	5.880	1.324	110.7	266.1
120.2	153.82	297.9	5.853	1.324	120.1	323.00

TABLE 14

Series G Run No. 4

73.2680 gms. H_2O ; 1.04865 gms. MgO ; 5.6891 gms. SO_2

Observed Values			Calculated Values			
Bath Temp.	Manom. Scale Reading	Average Manom. Temp.	Percent SO_2 in Solution	Percent MgO in Solution	Bath Temp. Corr.	Vapour Pressure cms.
21.3	333.75	295.2	7.045	1.311	21.3	36.7
29.9	324.55	296.6	7.020	1.311	29.9	48.9
49.9	295.31	297.8	6.961	1.311	50.0	87.9
69.9	255.60	300.4	6.889	1.311	70.0	144.9
90.1	204.98	301.1	6.805	1.311	90.1	224.7
100.0	177.91	302.1	6.768	1.311	100.0	275.1
110.6	148.21	301.2	6.722	1.311	110.6	338.4
59.7	278.28	302.7	6.929	1.311	59.8	113.1

TABLE 15

Series F Run No. 1

74.531 gms. H_2O ; 1.3489 gms. MgO ; 2.0486 gms. SO_2

Observed Values			Calculated Values			
Bath Temp.	Manom. Scale Reading	Average Manom. Temp.	Percent SO_2 in Solution	Percent MgO in Solution	Bath Temp. Corr.	Vapour Pressure cms.
35.4	360.23	298.3	2.628	1.731	35.4	4.5
47.6	356.84	294.4	2.628	1.731	47.7	8.4
61.3	350.78	297.9	2.628	1.731	61.4	16.1
70.8	344.05	298.2	2.627	1.731	70.9	24.6
80.1	335.05	297.9	2.627	1.731	80.1	35.9
89.9	322.14	299.0	2.627	1.731	89.9	52.8
100.9	302.44	299.0	2.626	1.731	100.9	78.7
110.0	281.00	299.0	2.625	1.731	110.0	107.9

TABLE 16

Series F Run No. 2

74.531 gms. H_2O ; 1.3489 gms. MgO ; 4.3367 gms. SO_2

Observed Values			Calculated Values			
Bath Temp.	Manom. Scale Reading	Average Manom. Temp.	Percent SO_2 in Solution	Percent MgO in Solution	Bath Temp. Corr.	Vapour Pressure cms.
27.7	356.19	297.9	5.393	1.682	27.7	9.4
35.2	354.37	298.3	5.390	1.682	35.2	11.7
45.1	350.92	298.4	5.389	1.682	45.1	16.1
55.4	346.02	298.9	5.387	1.682	55.5	22.3
65.2	339.03	297.9	5.384	1.682	65.3	30.9
75.1	330.00	298.2	5.381	1.682	75.2	42.5
85.3	317.17	298.8	5.377	1.682	85.3	59.3
105.6	278.10	298.9	5.370	1.682	105.6	112.0
94.3	301.94	298.8	5.374	1.682	94.4	79.3
28.9	355.75	297.6	5.393	1.682	28.9	9.8
68.0	336.48	298.1	5.383	1.682	68.1	34.2

TABLE 17

Series F Run No. 3

74.531 gms. H_2O ; 1.3489 gms. MgO ; 4.9378 gms. SO_2

Observed Values			Calculated Values			
Bath Temp.	Manom. Scale Reading	Average Manom. Temp.	Percent SO_2 in Solution	Percent MgO in Solution	Bath Temp. Corr.	Vapour Pressure cms.
29.9	347.39	297.7	6.077	1.669	29.9	20.3
39.8	341.80	298.4	6.068	1.669	39.8	27.5
50.7	333.78	298.6	6.057	1.669	50.8	37.8
60.7	324.11	298.5	6.046	1.669	60.8	50.1
70.3	312.49	298.0	6.035	1.669	70.4	65.0
80.2	298.29	298.5	6.024	1.669	80.2	84.0
90.4	279.61	298.7	6.010	1.669	90.4	109.8
99.9	258.45	299.0	5.997	1.669	100.0	139.9
109.9	231.31	299.2	5.983	1.669	110.0	180.9
64.9	319.57	299.4	6.042	1.669	65.0	56.3

TABLE 18

Series F Run No. 4

74.531 gms. H_2O ; 1.3489 gms. MgO ; 5.7750 gms. SO_2

Observed Values			Calculated Values			
Bath Temp.	Manom. Scale Reading	Average Manom. Temp.	Percent SO_2 in Solution	Percent MgO in Solution	Bath Temp. Corr.	Vapour Pressure cms.
20.8	342.48	295.9	7.026	1.652	20.8	25.9
29.8	335.50	296.4	7.012	1.652	29.8	34.9
39.6	326.09	296.6	6.995	1.652	39.6	47.0
49.6	314.15	296.7	6.975	1.652	49.7	62.5
60.2	298.95	296.5	6.951	1.652	60.3	82.5
69.8	282.99	296.8	6.928	1.652	69.9	104.4
79.8	263.27	296.7	6.903	1.652	79.8	132.2
90.0	239.79	297.0	6.876	1.652	90.0	166.7

TABLE 19

of the solution, is shown by the slight curvature of the concentration curve in Figure 4. The concentration of the sulphur dioxide in the liquid phase corresponding to any temperature can thus be determined from these curves.

The weight of magnesium oxide remains constant for each series, but the concentration of the magnesium oxide varies for each run because the total weight of the system is increasing with each additional amount of sulphur dioxide injected into the cell. It is evident that the concentration of the magnesium oxide will be appreciably lower at the end of a Series than at the start of the investigation. As mentioned in the previous paragraph, the sulphur dioxide leaves the liquid phase as the temperature of the solution is increased, this causes a slight variation in the concentration of the magnesium oxide, which was found to be negligible.

The graph (Fig. 4) for Series G shows the type of curves obtained when the logarithm of the total vapour pressure is plotted against the reciprocal of the absolute temperature. When there was a relatively large amount of sulphur dioxide in the solution, the resultant curves were nearly straight lines, the curvature being so slight that a straight line could be drawn through all the experimental points; run No.4 (Fig.4) is an example of this type of curve. However, at the lower sulphur dioxide concentrations, it was observed that the curves

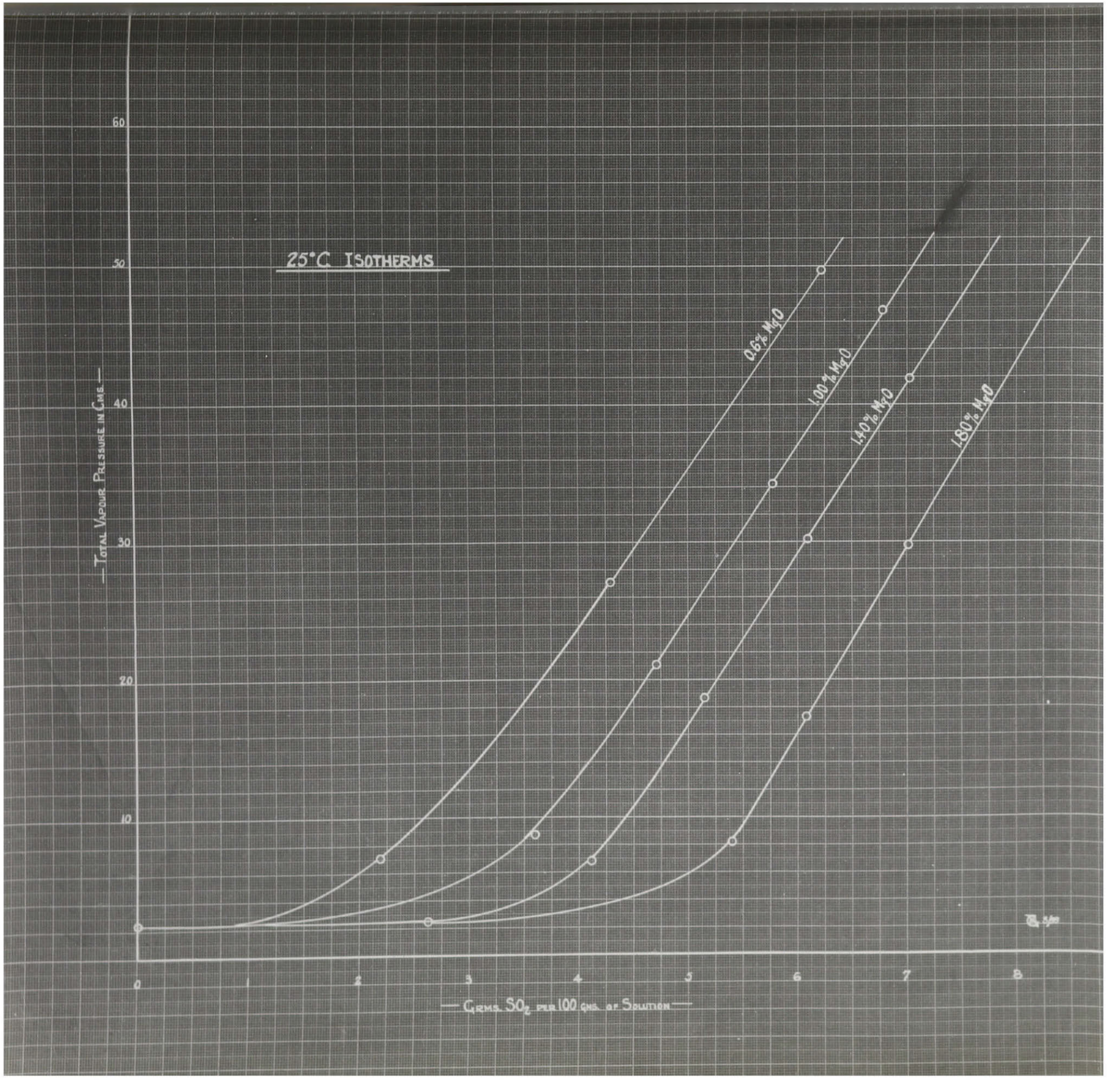

25°C ISOTHERMS
0.63% MgO
1.00% MgO
1.40% MgO
1.80% MgO
60
50
40
30
20
10
0
1
2
3
4
5
6
7
8
— Total Vapour Pressure in Cms. —
— Grms. SO_2 per 100 gms. of Solution —

Figure 5

have a marked curvature, run No.1 (Fig. 4) is typical of these curves. As the sulphur dioxide concentration increases, the curvature becomes less pronounced, this is the case for runs Nos. 2G and 3G. Since Figure 4 was included for illustration purposes only, the points at which the slope of the curves changes are shown on the graph by dotted lines. These observed facts will be discussed in the next section.

A second set of graphs were constructed showing the variation in the total vapour pressure with increased sulphur dioxide concentration at approximately constant magnesium oxide concentrations. These curves were obtained by drawing isotherms through the four sets of curves mentioned above, the isotherms were drawn at 25°C., 50°C., 70°C., 90°C., 110°C. and 130°C. Six graphs with four curves each were obtained, Figure 5 is an example of this type of curve at 25°C.

These curves indicate fairly accurately what is taking place in the solution, but they were not corrected for the variation of the magnesium oxide concentration that occurred during the investigation of a particular series.

To make this correction a third set of six graphs consisting of six curves each were plotted, showing the variations of the total vapour pressure with change in magnesium oxide concentration at constant sulphur dioxide concentrations. These were drawn to show the isotherms at 25°C., 50°C., 70°C., 90°C., 110°C. and 130°C.

To construct these curves, points were located corresponding to the pressures for even percentage concentrations of sulphur dioxide at the nominal concentrations of magnesium oxide used in each series i.e., at 0.6% for Series A, 1.0% for Series B, 1.4% for Series G, and 1.8% for Series F. These points are shown on specimen graph Figure 6 as hollow dots. Then another set of points were located using the same pressures but using the actual calculated magnesium oxide concentrations instaed of the nominal ones. These latter points are shown as solid dots. Through these the curves were drawn. As an example in Figure 6 the hollow point is drawn at exactly 1% magnesium oxide and at a pressure corresponding to the solution containing 6% sulphur dioxide, but from Table 9 the actual concentration of the magnesium oxide was found to be 1.037% when the solution contained approximately 6% sulphur dioxide. The solid point was placed at 1.037% magnesium oxide and level with the hollow point. The curves were drawn through the solid dots, showing the actual change in the total vapour pressure with increasing magnesium oxide concentration when the sulphur dioxide concentration remained constant. The pressures recorded corresponding to zero percent magnesium oxide are those of Campbell (6).

The final set of isotherms corrected for the variation in magnesium oxide concentration were drawn up at 25°C., 50°C., 70°C., 90°C., 110°C. and 130°C. from values taken from the total

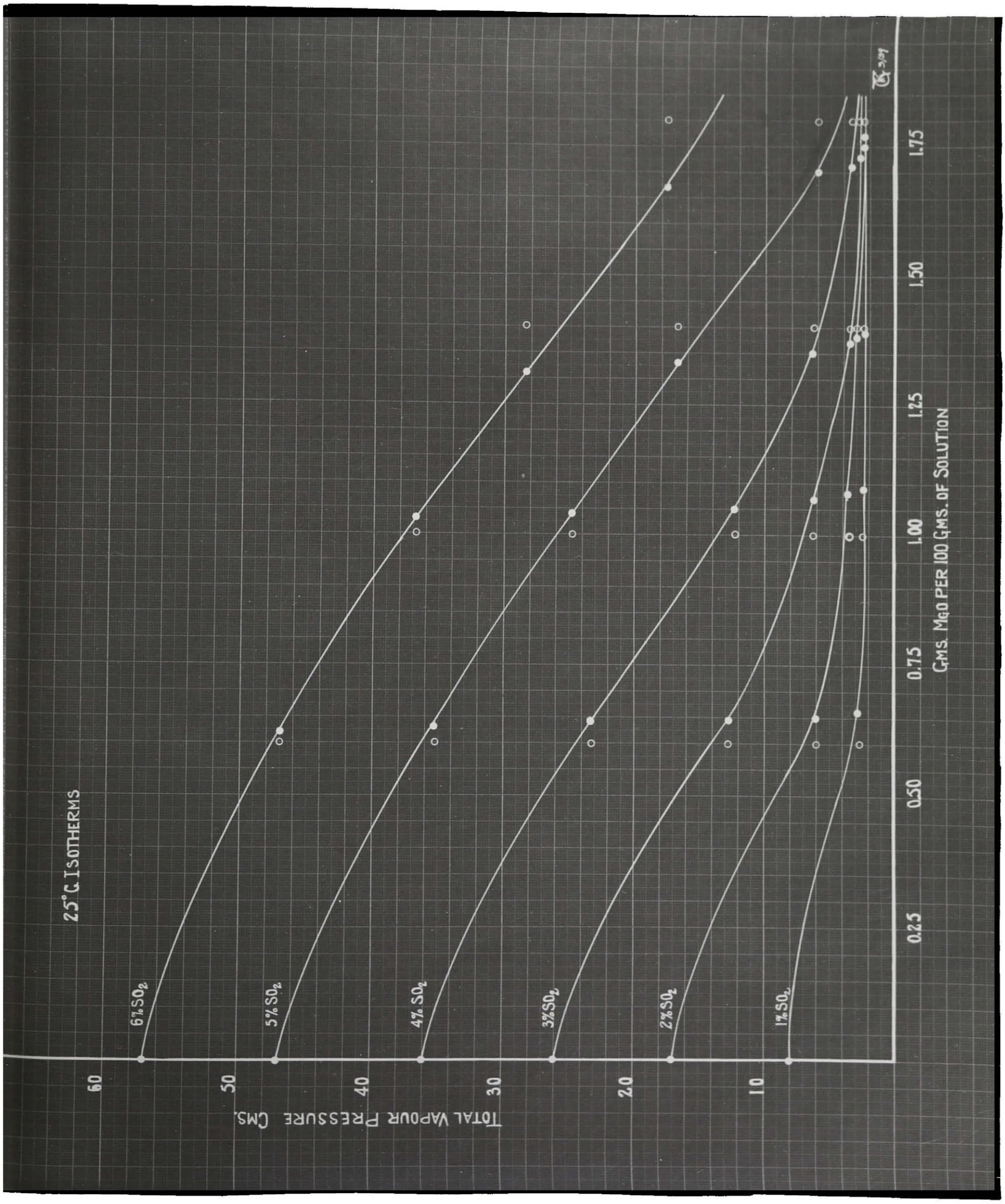

25°C. ISOTHERMS
TOTAL VAPOUR PRESSURE CMS.
60
50
40
30
20
10
6% SO2
5% SO2
4% SO2
3% SO2
2% SO2
1% SO2
0.25
0.50
0.75
1.00
1.25
1.50
1.75
GMS. MgO PER 100 GMS. OF SOLUTION

Figure 6

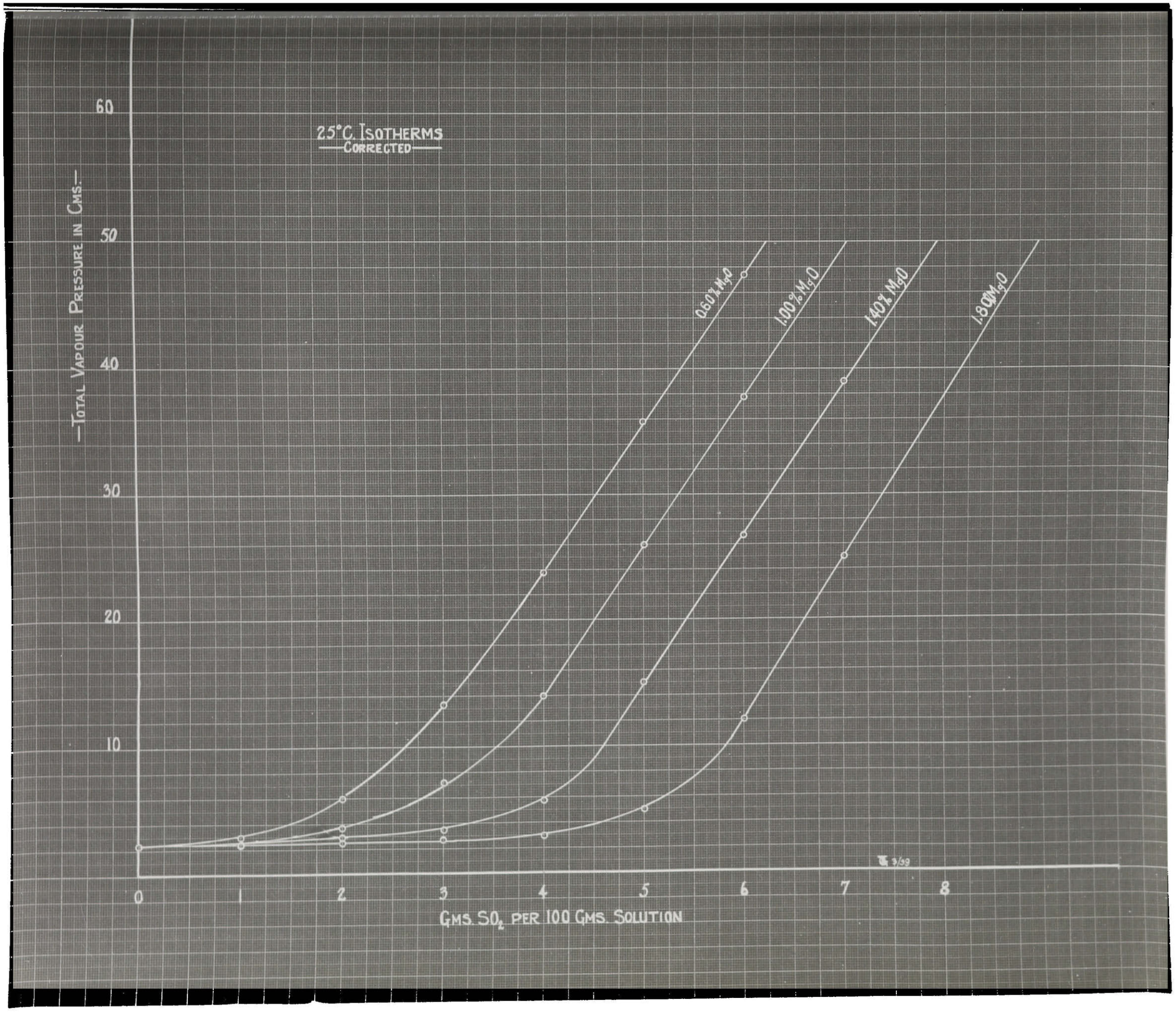

25°C. Isotherms
—Corrected—
—Total Vapour Pressure in Cms.—
60
50
40
30
20
10
0.60% MgO
1.00% MgO
1.40% MgO
1.80% MgO
0
1
2
3
4
5
6
7
8
Gms. SO_2 per 100 Gms. Solution

Figure 7

vapour pressure - percent magnesium oxide curves, by plotting the total vapour pressure against percent sulphur dioxide at constant mangesium oxide concentrations. Figure 7 is an example of this type of curve at 25°C. The data from which these curves were constructed are included in Table 20.

TOTAL VAPOUR PRESSURES OF THE SYSTEM $MgO - SO_2 - H_2O$

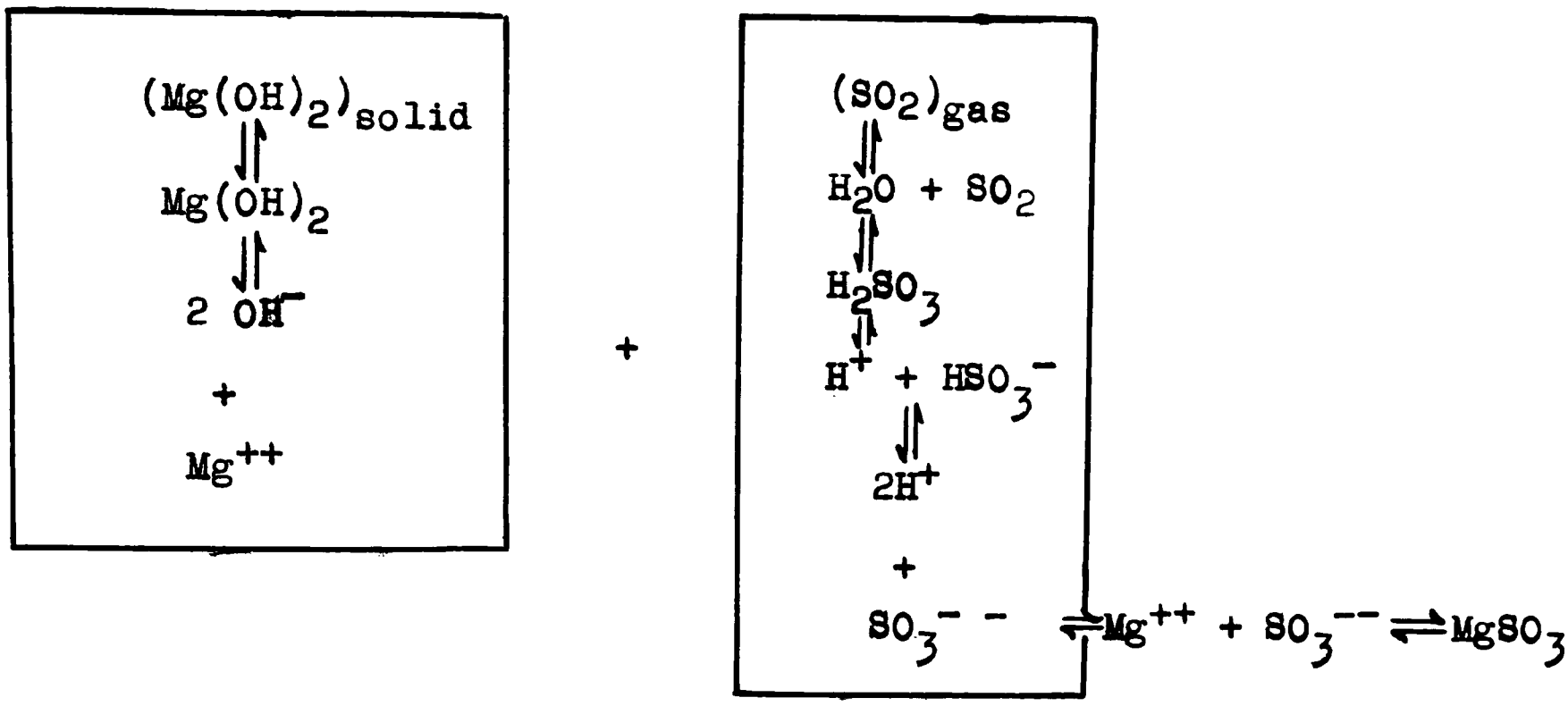
Temperature		25°	50°	70°	90°	110°	130°
SO_2 %	MgO %	V.p. cm	V.p. cm	V.p. cm	V.p. cm	V.p. cm	V.p. cm
1	0.0	9.0	26.0	52.0	97.0	168	275
1	0.6	3.0	11.0	25.0	51.5	110	202
1	1.0	2.5	9.0	23.5	50.0	108	202
1	1.4	2.5	9.0	23.0	50.0	108	202
1	1.8	2.5	9.0	23.0	50.0	108	202
2	0.0	17.0	45.0	83.0	143.0	231	353
2	0.6	6.0	18.5	35.5	69.0	119	216
2	1.0	3.75	10.0	24.5	53.5	108	202
2	1.4	3.0	9.0	23.0	50.0	108	202
2	1.8	2.5	9.0	23.0	50.0	108	202
3	0.0	26.0	64.0	115.0	190.0	290	431
3	0.6	13.4	37.5	62.0	121.0	194	320
3	1.0	7.25	16.0	35.0	66.0	127	222
3	1.4	3.50	10.5	23.0	51.0	108	202
3	1.8	2.75	9.0	23.0	50.0	108	202
4	0.0	36.0	85.0	147.0	237.0	355	518
4	0.6	23.75	59.0	103.0	172.0	270	450
4	1.0	14.0	34.0	64.0	110.0	186	300
4	1.4	5.75	14.5	26.0	56.0	112	207
4	1.8	3.0	10.0	23.0	51.5	108	202
5	0.0	47.0	106.0	183.0	283.0	420	610
5	0.6	35.75	82.5	143.0	235.0	373	575
5	1.0	26.0	58.0	102.4	209.0	267	406
5	1.4	15.0	33.0	57.0	102.0	171	272
5	1.8	5.0	12.0	25.0	55.0	110	202
6	0.0	57.0	128.0	213.0	330.0	484	709
6	0.6	47.4	107.0	184.0	302.0	475.	708
6	1.0	37.75	82.0	141.0	224.5	349	513
6	1.4	26.75	56.0	95.5	161.0	251	378
6	1.8	12.0	29.0	51.0	87.0	172	251
7	0.0	67.5	-	-	-	-	-
7	0.6	58.2	-	-	-	-	-
7	1.0	48.5	-	-	-	-	-
7	1.4	38.0	-	-	-	-	-
7	1.8	26.0	-	-	-	-	-

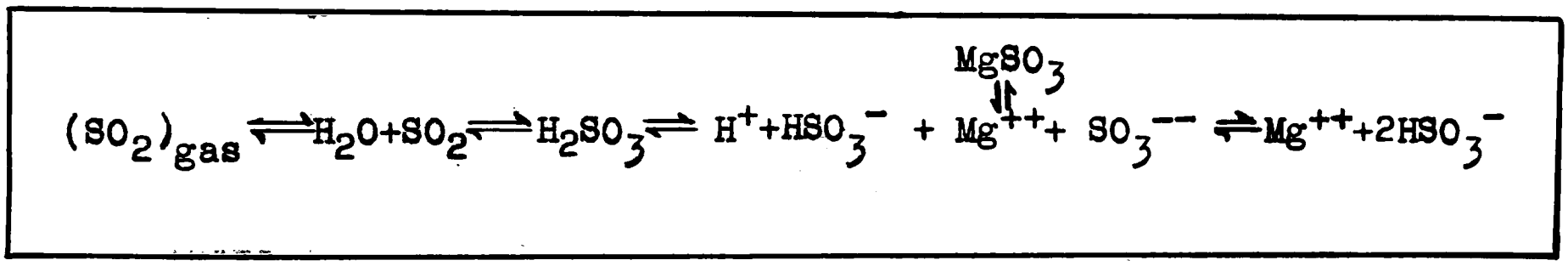
Table 20.

D I S C U S S I O N

DISCUSSION OF RESULTS

In the present section the results obtained from the investigation of the vapour pressures of the three component system magnesium oxide - sulphur dioxide - water will be discussed. It is believed that all the important equilibria that exist in such a system are included in the reaction charts shown below. The various equilibria present can best be represented by three charts; No. I and No. II show the equilibria that exist in the two component systems magnesium oxide - water and sulphur dioxide - water, respectively. Their combination shows the principal equilibria existing in the three component system magnesium oxide - sulphur dioxide - water, when the molar concentrations of the total sulphur dioxide acid is equal to, or less than the molar concentration of the magnesium oxide. Chart No. III shows the principal equilibria that exist in the same system when the molar concentrations of the total sulphur dioxide is in a greater than a one to one ratio.





III

In the above equilibrium diagrams, the substances in the solid or gaseous state have been enclosed in curved brackets, to distinguish them from those in true solution.

As mentioned above Char No. I shows the equilibria that exist in the two component system magnesium oxide - water. On the addition of magnesium oxide to water, the sparingly soluble magnesium hydroxide is formed and that fraction in solution can be considered as almost completely ionized. Consequently an equilibrium is established between the solid magnesium hydroxide and that undissociated in the solution,

which in turn is in equilibrium with the magnesium ion and the hydroxyl ions. According to Kohlrausch and Rose (51) the solubility of magnesium hydroxide in water at 18°C. is 9 mgm. per litre. They found the value of the solubility product of $Mg(OH)_2$ to be 1.22×10^{-11}, at the same temperature. Whipple and Mayer (52) found the solubility to be 12 mgm. per litre at 22°C.

The equilibria existing in the two component system sulphur dioxide - water (Chart No. II) were suggested as a result of the investigations of Maass and Maass (5), Campbell and Maass (6) and Morgan and Maass (7).. It seems advisable to discuss briefly the results and conclusions obtained from the investigation of this system, which may be considered as the three component system, $MgO - SO_2 - H_2O$ when the concentration of the magnesium oxide is zero.

The sulphur dioxide in the gas phase is in equilibrium with the sulphur dioxide molecules in solution, according to the equation

$$(SO_2)_{soln} = h\,(SO_2)_{gas} = hp.$$

where h = Henry's constant

p = partial pressure of SO_2

The sulphur dioxide molecules in solution are partially converted to sulphurous acid molecules, according to the equilibrium:

$$H_2O + SO_2 \rightleftharpoons H_2SO_3$$

In accordance with the mass law, the above equilibrium is governed by the equation,

$$K_1 = \frac{[H_2O]\ [SO_2]}{[H_2SO_3]}$$

K_1 has been evaluated and was found to increase rapidly with rising temperature, thus indicating that the dissolved sulphur dioxide which is present in the solution as sulphurous acid decreased with increasing temperature. Since, at a given temperature, the partial pressure of the sulphur dioxide is proportional to the sulphur dioxide molecules in solution, the partial pressure would be greater at the higher temperatures.

The sulphurous acid in solution ionizes as a monobasic acid and is in equilibrium with its ions,

$$H_2SO_3 \rightleftharpoons H^+ + HSO_3^-$$

the true dissociation constant of sulphurous acid may be expressed as,

$$K_2 = \frac{[H^+]\ [HSO_3^-]}{[H_2SO_3]}$$

this constant does not vary appreciably with temperature.

The sulphurous acid can undergo a second ionization according to the equation:

$$H^+ + HSO_3^- \rightleftharpoons 2H^+ + SO_3^{--}$$

it has been shown that sulphurous acid behaves as a monobasic

acid even at great dilution, nevertheless, this secondary ionization, no matter how small, is a source of the sulphite ions.

A study of the equilibrium diagrams above show that when magnesium oxide is added to the system sulphur dioxide - water, it forms the slightly soluble hydroxide which ionizes to a certain extent. In the presence of a small amount of sulphur dioxide, the magnesium hydroxide combines in a one to one molar ratio with the sulphurous acid to form the soluble magnesium sulphite. Hager (53) found that 100 parts water dissolved 1.2 parts $MgSO_3$ at 20°C., and 0.83 parts at 100°C. In the presence of an excess of sulphur dioxide the magnesium sulphite then combines in a one to one molar ratio with more sulphurous acid to form magnesium bisulphite which only exists in solution.

It is evident that the three component system magnesium oxide - sulphur dioxide - water, under various conditions involves a variety of equilibria. These can now be appropriately discussed in connection with vapour pressure data. For convenience the logarithm of the total vapour pressure vs. the reciprocal of the absolute temperature curves that were plotted from the experimental data (Tables 5 - 19).

For Series F run No. 1 the concentrations of the magnesium oxide and the sulphur dioxide present at the start of the run were 1.73% and 2.63% respectively, consequently

the amount of sulphur dioxide in solution was not sufficient to combine with all the magnesium oxide as magnesium sulphite. As a result the solid phase was present at all times during this particular investigation.

The logarithm total vapour pressure - $\frac{1}{T}$ curve was plotted from the experimental data (Table 16), this curve was slightly convex downward. Where the vapour pressures of pure water were plotted in a similar manner, the resultant curve was below that of run No. 1F but was nearly parallel to it over the entire temperature range investigated; the average distance betweee the two curves represented an average pressure difference of approximately 0.3 centimetres. An illustration of these curves was not included, because when drawn to a reduced scale the distance between them was not apparent. This pressure difference may be due to the presence of free sulphur dioxide in the gas phase, indicating that sulphurous acid is formed to some extent by the partial hydrolysis of magnesium sulphite, which is a salt of a weak base and a moderately strong acid. The sulphurous acid gives rise to free sulphur dioxide as shown in diagram II.

Thus in a solution of magnesium sulphite, the molecules of the salt may hydrolyze in accordance with the equation:

$$MgSO_3 \rightleftharpoons Mg^{++} + SO_3^{--}$$
$$+ \qquad +$$
$$2H_2O \rightleftharpoons 2OH^- + 2H^+$$
$$\downarrow\uparrow \qquad \downarrow\uparrow$$
$$(Mg(OH)_2) \quad H_2SO_3$$
$$\downarrow\uparrow \qquad \downarrow\uparrow$$
$$(Mg(OH)_2)_{solid} \quad (SO_2)_{gas}$$

The magnesium sulphite will not be completely hydrolysed, since it is evident that as the concentration of the hydrogen ions increase, the concentration of the hydroxyl ions must become less and less, until finally, it is too small to unite with the magnesium ions. When this occurs, hydrolysis stops and equilibrium is established.

If, therefore, a solution contains bisulphite ions, it will have a vapour pressure higher than that of water, because of the sulphur dioxide that is formed in such a solution. An explanation is afforded by examining the above equilibria, where it is seen that the bisulphite ions combine with the hydrogen ions present from the dissociation of water, forming sulphurous acid which in turn is in equilibrium with the sulphur dioxide molecules in solution, and finally these molecules are in equilibrium with the sulphur dioxide molecules in the gas phase.

If more sulphur dioxide is added to the solution, so that the amount present is just sufficient to dissolve all the magnesium oxide, and the logarithm total vapour pressure is plotted as ordinate with the reciprocal of the absolute temperature as abscissa, the curves are convex upward. The curve for run 1G (Fig.4) is an example of this type of curve. The slope of this curve changed gradually as the temperature of the solution was increased.

When the data of Campbell (29) for the sulphur

dioxide - water system, were plotted in the same manner, the curves obtained were almost straight lines for solutions of low sulphur dioxide content, but exhibited a definite curvature, convex downward at the higher sulphur dioxide concentrations.

The shape of the curve for run 1G shows that two reactions governing the equilibria are taking place, one predominant at low and the other at high temperatures.

At the low temperature region, the curve deviates from that of the sulphur dioxide - water system, indicating that the solution is saturated with bisulphite ions that result from the dissociation of the magnesium bisulphite. Their presence in the solution represses the dissociation of the sulphurous acid, and as a consequence the equilibrium is established so that there are more sulphur dioxide molecules existing in solution, which will result in an increase in the partial pressure of the sulphur dioxide. Enckell (25) found that sulphur dioxide was less soluble in solutions of calcium bisulphite than in water. Philip (54) showed that inactive gases were less soluble in solutions of electrolytes, than in the pure solvent but he assumes provisionally that the solute is hydrated and the water thus bound is unable to absorb the gas. This explanation does not seem logical for a solution containing magnesium bisulphite which is almost completely ionized.

As the temperature is raised the slope of the curve gradually changes, showing that apparently there are more sulphur dioxide molecules in solution than can be accounted for by the effect of temperature on the equilibrium,

$$SO_2 + H_2O \rightleftharpoons H_2SO_3 \quad ...(1).$$

With an increase in temperature the above equilibrium shifts toward the left and the solution will have a greater concentration of sulphur dioxide molecules at the higher temperatures; this is equivalent to a decrease in the concentration of the sulphurous acid.

In addition to the above equilibrium (with increasing temperature) the following equilibrium

$$Mg^{++} + 2HSO_3^- \rightleftharpoons Mg^{++} + SO_3^{--} + H^+ + HSO_3^-$$
$$\Downarrow$$
$$H_2SO_3 \rightleftharpoons SO_2 + H_2O$$

.... (2).

shifts toward the right, and a molecule of H_2SO_3 is liberated for each molecule of $MgSO_3$ present in the solution. This H_2SO_3 in solution is in equilibrium with the SO_2 molecules in solution, and by virtue of this extra amount of SO_2 molecules in solution the pressure is higher and the curve is steeper. At low temperatures it is evident that the above equilibrium (2) will be toward the left, i.e. the dissolved magnesium salt will be the magnesium bisulphite.

With each additional amount of sulphur dioxide the change in the slope of the curves was less pronounced, this is clearly shown by the curves for runs No. 2G and No. 3G (Fig. 4, page 67). When there is an excess of sulphur dioxide present, the curve is very nearly a straight line because the concentration of the sulphurous acid in the solution is such that is will keep equilibrium (2) far to the left even at high temperatures.

If a solution contains a large excess of sulphur dioxide, as was the case for Series A run No. 3, the curve was approximately the same as when no base was present. This indicates that the influence of the base will be proportionately less as the concentration of the sulphur dioxide is increased.

It was mentioned in the introduction that the object of this investigation was to measure the vapour pressure of the magnesium system, and as far as this data will permit determine the equilibria that exist in such a complex system. In an attempt to obtain a complete understanding of the various equilibria involved, as well as the factors governing the equilibria, the logarithm of the total vapour pressure vs. the reciprocal of the absolute temperature curves were constructed for solutions of constant magnesium oxide and sulphur dioxide concentrations. On the same graph, curves were drawn in a similar manner for aqueous solutions of sulphur dioxide at concentrations corresponding to the difference between the

total and twice the combined as well as the difference of the total and combined. It was observed that in every case, the curves representing the magnesium system were found to lie between those of the total - 2 x combined and the total - combined, and that the relative position of the experimental curve was dependent on the concentration of the sulphur dioxide, that is, with increasing amounts of sulphur dioxide the curve for solutions containing magnesium oxide became proportionately closer to the curve of the total-combined. This would lead one to believe that there exists in this system an equilibrium involving from one to two moles of sulphur dioxide to one of magnesium oxide. Unfortunately it was impossible to determine the exact number of moles of each constituent from the above mentioned curves, since they do not give an exact quantitative representation of the equilibria. However, the partial pressure of the sulphur dioxide is apparently a better measure of the free SO_2 than the value that may be obtained from the difference between the total and combined.

It is evident that if the amount of free sulphur dioxide is known, namely, the SO_2 present in solution that is in no way combined with the MgO, it follows that the number of moles of SO_2 involved in the equilibria can be determined by deducting the value of the free from the total amount of SO_2 present. The amount free SO_2 was obtained by an indirect method based on the following concept:

Solutions containing magnesium oxide and solutions of sulphur dioxide alone produce the same pressure for a given temperature when they contain the same amount of sulphur dioxide and sulphurous acid in solution.

The following sample calculation will serve to illustrate the method as described:

A solution containing 1 percent magnesium oxide and 4 percent sulphur dioxide has a vapour pressure of 14. cm. at a temperature of 25°C. Campbell (4) determined the vapour pressure for solutions of sulphur dioxide in water, this data shows that at the same temperature, a solution containing 1.45 percent SO_2 produces a pressure of 14. cm. There remains 2.3 percent SO_2 to combine with the magnesium oxide. That is, 0.0248 moles of magnesium oxide combined with 0.0359 moles of sulphur dioxide, corresponding to 1.445 to 1 molar ratio of sulphur dioxide to magnesium oxide.

The molar ratio of sulphur dioxide to magnesium oxide were calculated at each of the following temperatures, 25°C., 50°C., 70°C., 90°C. and 110°C., for solutions containing 0.6%, 1.0%, 1.4% and 1.8% magnesium oxide and 3%, 4%, 5% and 6% sulphur dioxide. These values are conveniently presented in Table No. 21. The accuracy of the values obtained by this method will naturally depend on the exactness with which the statement is valid that solutions containing identical amounts

of sulphur dioxide and sulphurous acid present as molecules, have the same pressure at a given temperature.

Three variables can influence the equilibria, namely, magnesium oxide and sulphur dioxide concentration, and temperature. The equilibria can be appropriately discussed by considering the manner in which the molar ratio of SO_2 to MgO (see Table No. 21) varies with one of the variables while the other two are held constant.

Consider the system where the temperature and the sulphur dioxide concentration are kept constant. The molar ratio of SO_2 to MgO approaches but never attains the value of two with increasing amounts of MgO.

However, this does not hold for solutions of low sulphur dioxide content, since it was observed for a 3 percent SO_2 solution the molar ratio decreased when the base was increased. This appears to indicate, that when the solution contains a relatively small amount of magnesium oxide in comparison with the sulphur dioxide, this combines with the SO_2 to form a compound in a molar ratio of one to one, some bisulphite would also be present accounting for the ratio of the molar quantities being greater than one. As more base is added the value of the molar ratio increases, reaching a maximum value, and from this data appear to be always less than two, and then decreases. Consequently more sulphur dioxide combines as magnesium bisulphite, and then again the sulphur dioxide combines in a

one to one molar ratio with any additional magnesium oxide. It may be assumed that at the higher concentrations of the base, the sulphur dioxide is present as magnesium monosulphite.

Now consider the system when the temperature and the magnesium oxide concentration are held constant. In general the value of the molar ratio diminishes as the percentage composition of the sulphur dioxide increased . Since for all systems in a state of equilibrium obey the Mass Action principle, it follows that an increase in the sulphur dioxide would cause a corresponding increase in the value of the molar because more magnesium bisulphite would be present. However this was not found to be the case, indicating that some other magnesium compound may be participating in the equilibrium.

Finally consider the effect of temperature on the equilibria, when the sulphur dioxide and magnesium oxide are constants. The molar ratio of the sulphur dioxide to magnesium oxide increases with temperature. The inferences that can be made are that at the higher temperatures more magnesium is present as the bisulphite. It was mentioned previously that the effect of temperature on the equilibrium favours the formation of the monosulphite. Therefore, the increase in the molar ratio may be attributed to the presence of a compound containing magnesium oxide and sulphur dioxide in a molar ratio of approximately one to one which is stable only at low temperatures. Consequently with use in temperature, this compound

would decompose, liberating magnesium ions in increasing amounts which would be free to combine with the sulphur dioxide as magnesium bisulphite giving rise to a greater molar ratio.

The conclusions that can be drawn are that the values of the molar ratios are sufficient evidence to show that the equilibria that exists in the magnesium system are very complex, and the equation

$$Mg(HSO_3)_2 \rightleftharpoons MgSO_3 + H_2SO_3 \rightleftharpoons H_2O + SO_2 \rightleftharpoons [SO_2]_{gas}$$

does not satisfactorily represent all the constituents participating in the equilibria.

To explain the factors governing this equilibria it may be proposed that there exist in the system a magnesium complex such as a magnesium basic sulphite of constant or variable composition, $x\,MgSO_3.y\,Mg(OH)_2$. The presence of magnesium basic sulphite would account for the molar ratios being small at low temperatures, and also for high sulphur dioxide concentrations. On the other hand, there may be formed by hydrolysis a hydrolysed magnesium sulphite according to the equation:

$$H_2O + Mg(HSO_3)_2 \rightleftharpoons Mg(OH)(HSO_3) + H_2SO_3 \rightleftharpoons H_2O + SO_2 \rightleftharpoons [SO_2]_{gas}$$

The objection to the above hydrolysis taking place, is that the solutions were all acidic, and it is very doubtful whether this would occur to any extent, if at all in an acid media. From the above equilibria, it is observed that an

increase in the sulphur dioxide concentration would result in the formation of more bisulphite, however the molar ratio decreases with increasing sulphur dioxide. Therefore, for solutions at low temperatures, the presence of a basic magnesium sulphite appears to be the most suitable explanation of the observed facts. At the higher temperatures, namely the range used by the industry for the cooking of wood by the sulphite process, it is assumed that there exists in this system only an equilibrium between the magnesium sulphite and bisulphite.

In an attempt to explain the equilibria existing in the calcium system Gishler (3) postulated the existance of a complex containing 1.5 moles of sulphur dioxide per mole of calcium oxide. It is seen from Table No. 21 that there is no justification in assuming that a similar complex is present in the magnesium system because the molar ratios of SO_2 to MgO have not a constant value of 1.5 but vary from 0.995 to 1.85.

Although, magnesium and calcium are members of the same group in the Periodic Table, magnesium has the interesting property of continuing with sulphur dioxide to form the very soluble magnesium sulphite, while on the other hand the corresponding salt of calcium is practically insoluble. In order to determine whether the equilibria existing in the magnesium system differed from that of the calcium system, isothermal curves were constructed for both systems at 25°C., 50°C., 70°C., 90°C., and 110°C., where the Moles of Oxide per 100 grams

MOLAR RATIO OF SULPHUR DIOXIDE TO MAGNESIUM OXIDE

Temperature			25°	50°	70°	90°	110°
SO_2 %	MgO %	Moles MgO	$\frac{SO_2}{MgO}$	$\frac{SO_2}{MgO}$	$\frac{SO_2}{MgO}$	$\frac{SO_2}{MgO}$	$\frac{SO_2}{MgO}$
	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	0.6	0.0149	1.47	1.47	1.54	1.675	1.675
3	1.0	0.0248	1.40	1.60	1.62	1.68	1.695
	1.4	0.0347	1.235	1.29	1.35	1.35	1.35
	1.8	0.0447	1.00	1.05	1.05	1.05	1.05
	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	0.6	0.0149	1.225	1.31	1.355	1.365	1.295
4	1.0	0.0248	1.445	1.60	1.635	1.70	1.735
	1.4	0.0347	1.57	1.70	1.74	1.75	1.765
	1.8	0.0447	1.33	1.38	1.40	1.40	1.40
	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	0.6	0.0149	1.115	1.175	1.15	1.08	-
5	1.0	0.0248	1.260	1.45	1.51	1.56	1.51
	1.4	0.0347	1.44	1.61	1.74	1.75	1.78
	1.8	0.0447	1.57	1.68	1.71	1.72	1.73
	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	0.6	0.0149	0.95	0.995	0.995	-	-
6	1.0	0.0248	1.13	1.38	1.385	1.41	1.385
	1.4	0.0347	1.305	1.53	1.64	1.64	1.63
	1.8	0.0447	1.60	1.67	1.77	1.82	1.85

Table 21.

Solutions were plotted as abscissa with the total vapour pressure in centimeters as ordinate. Figures 8 to 12 inclusive show the curves obtained for solutions containing 3%, 4%, 5%, and 6% sulphur dioxide. The isotherms for both systems were S- curves showing a pronounced curvature at low oxide concentrations.

First consider the curves obtained for the calcium system. The values used were those of Beazley (4) and for convenience are reproduced in Table 22. For low concentrations of calcium oxide the curvature changes gradually, then as the amount of oxide is increased the curvature is steeper, indicating that more sulphur dioxide is taken up as calcium bisulphite, and finally the slope changes and the curve approaches the abscissa asymtotically. An explanation of this observation can be obtained by having access to the data of Beazley (4), since for each concentration of sulphur dioxide, this change in curvature occurs at a vapour pressure corresponding to that at which Beazley found the solubility product of calcium sulphite was just exceeded, and the solid calcium sulphite begins to appear.

Consider the curves of the magnesium system drawn from the values recorded in Table No. 24, these values are taken from Table No.20 (page 90) where percent magnesium oxide has been substituted by Moles MgO per 100 gm. solution. These curves exhibit a very pronounced curvature at both extremities, these are joined by a section that is practically linear. On examination it will be seen that the curves of this system are slightly

above those of the calcium system, a possible explanation is that the magnesium bisulphite is hydrolysed to a greater extent than the corresponding calcium salt, in accordance with the equation:

$$[SO_2]_{gas} \rightleftharpoons H_2O + SO_2 \rightleftharpoons H_2SO_3 \rightleftharpoons H^+ + 2HSO_3^- + [Mg(OH)]^+ \rightleftharpoons 2HSO_3^- + Mg^{++} + H^+ + OH^-$$

this may be applicable to solutions at high temperatures where there is very little SO_2 present as sulphurous acid in solution, but it is very improbable that such a hydrolysis would take place at the lower temperatures since the solutions are definitely acidic in character because of the large amount of sulphurous acid present. There appears to be no obvious explanation for the above mentioned fact. At 25°C. the isotherms for the calcium system are above those of the magnesium system, to account for the reversal of the position of the respective curves, it may be suggested that the experimental values of the vapour pressure of the calcium system are slightly high, since the ratio of sulphur dioxide to calcium oxide was calculated and found to be 0.35 instead of a value in the neighborhood of one for a solution containing 0.50% CaO and 3% SO_2.

Increasing the magnesium oxide concentration, the linear section of the curves indicate that the magnesium oxide combines with the sulphur dioxide that remains in solution as magnesium bisulphite.

In the region of high magnesium oxide concentrations the slope of the curves would suggest that the oxide enters solution as the monosulphite resulting in a smaller decrease of the vapour presence. This is in complete agreement with the deductions made from the values of the molar ratios of sulphur dioxide to magnesium oxide.

This comparison of the isothermal curves shows clearly, that except at low oxide concentrations, the two systems differ in the respect that there is evidently more bisulphite present in a solution containing magnesium oxide for a solution containing calcium oxide.

The limitations of this discussion are governed by the data obtained from the vapour pressure measurements, and until the electrical conductivities of this system are investigated, covering the same concentration range, it will be impossible to determine the exact chemical constitution of the various constituents participating in the equilibria.

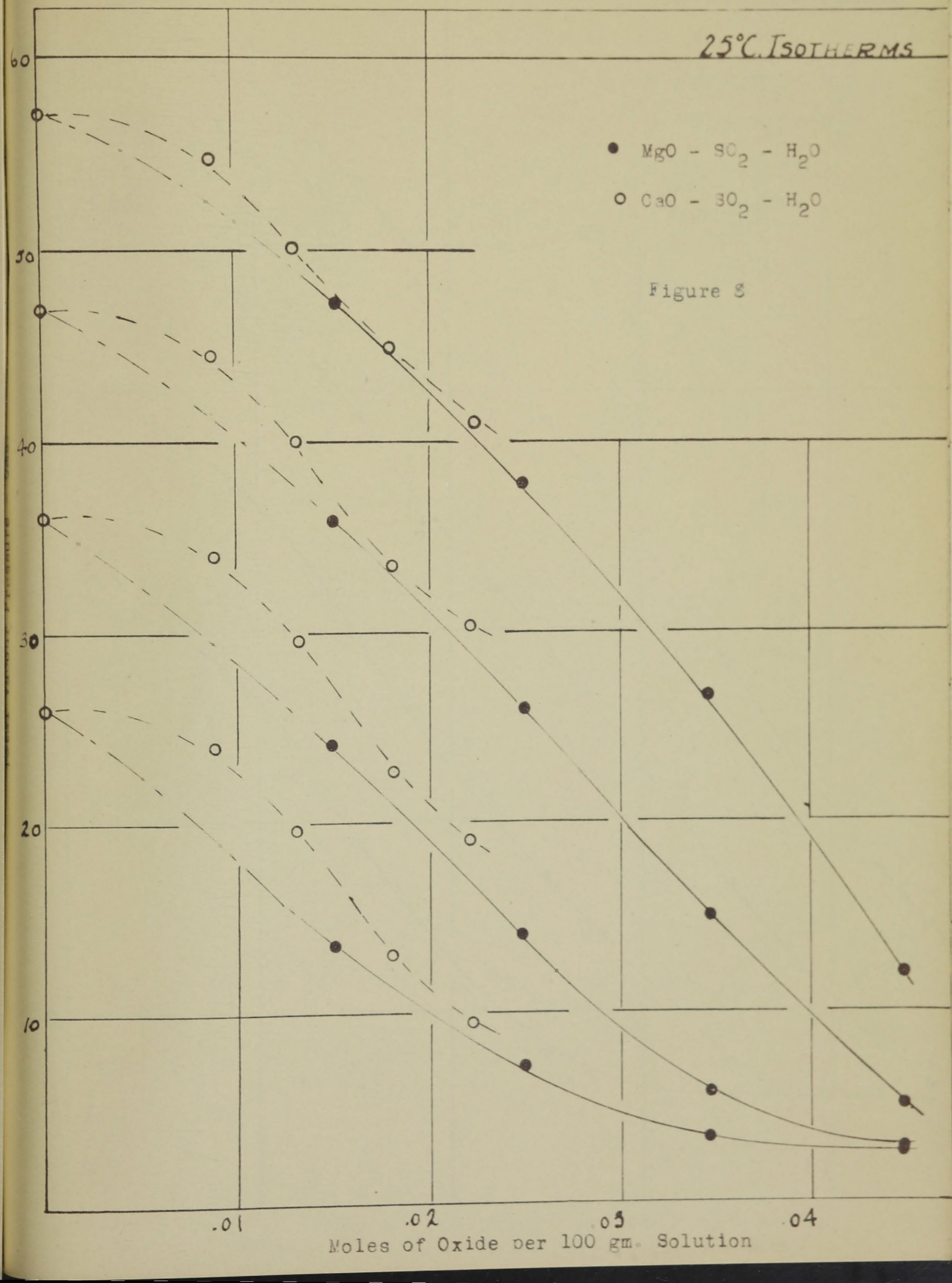

25°C. Isotherms
60
50
40
30
20
10
● MgO - SO2 - H2O
○ CaO - SO2 - H2O
.01
.02
.03
.04
Moles of Oxide per 100 gm. Solution

Figure 8

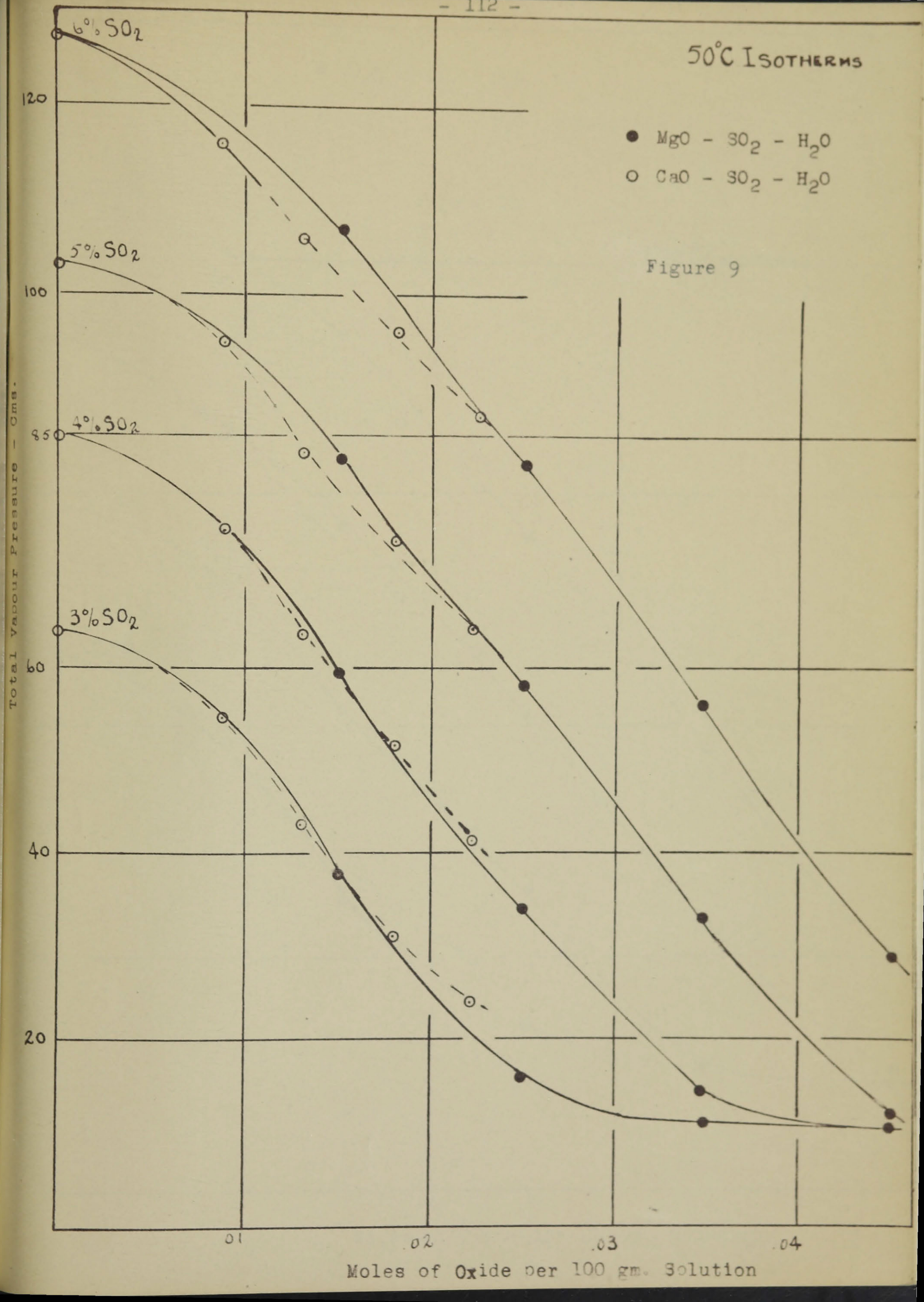

50°C Isotherms
● MgO - SO2 - H2O
○ CaO - SO2 - H2O
6% SO2
5% SO2
4% SO2
3% SO2
120
100
85
60
40
20
Total Vapour Pressure - Cms.
.01
.02
.03
.04
Moles of Oxide per 100 gm. Solution

Figure 9

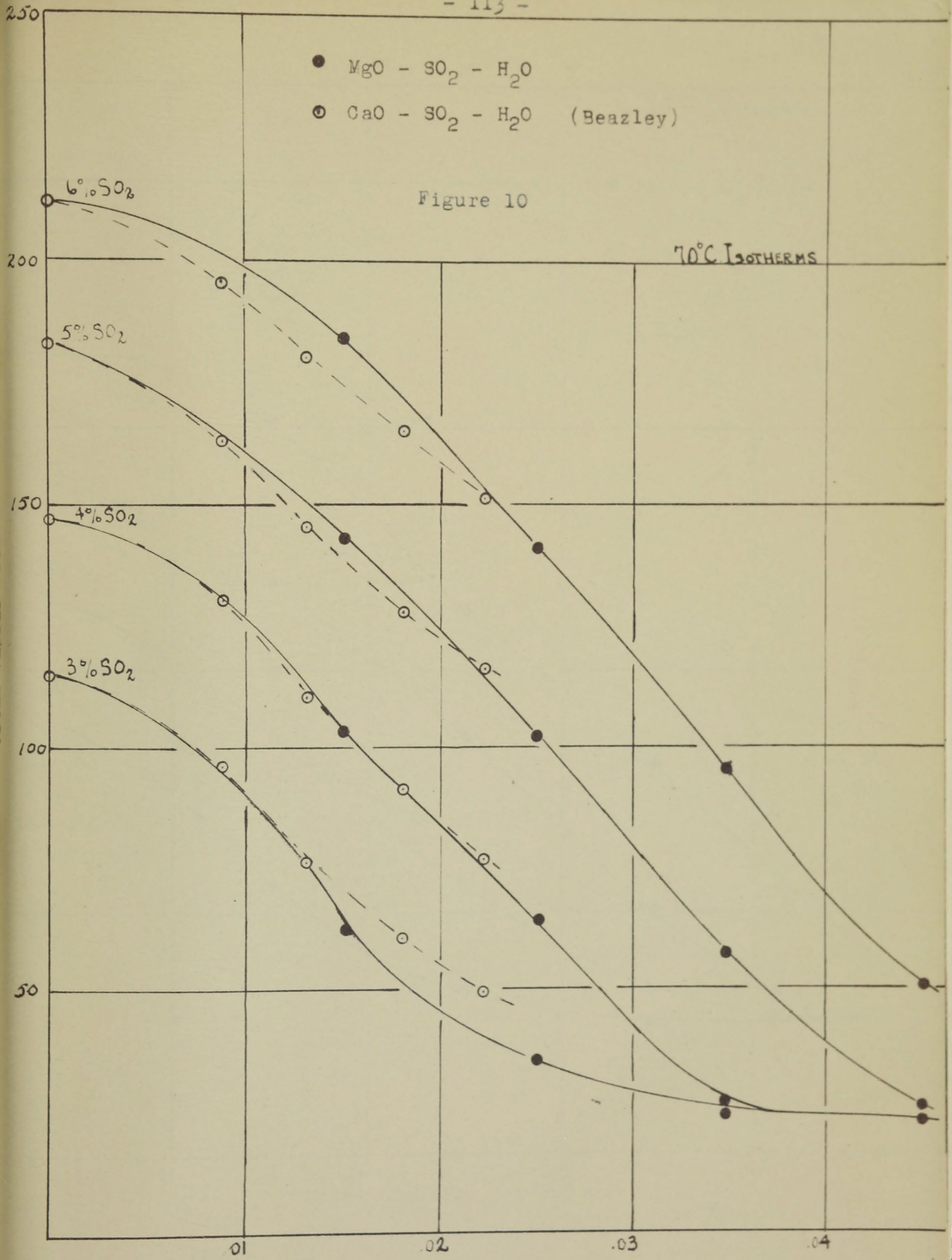

250
200
150
100
50
Total Vapour Pressure - mm.
● MgO - SO2 - H2O
◐ CaO - SO2 - H2O (Beazley)
70°C Isotherms
6% SO2
5% SO2
4% SO2
3% SO2
.01
.02
.03
.04
Moles of Oxide per 100 gm. Solution

Figure 10

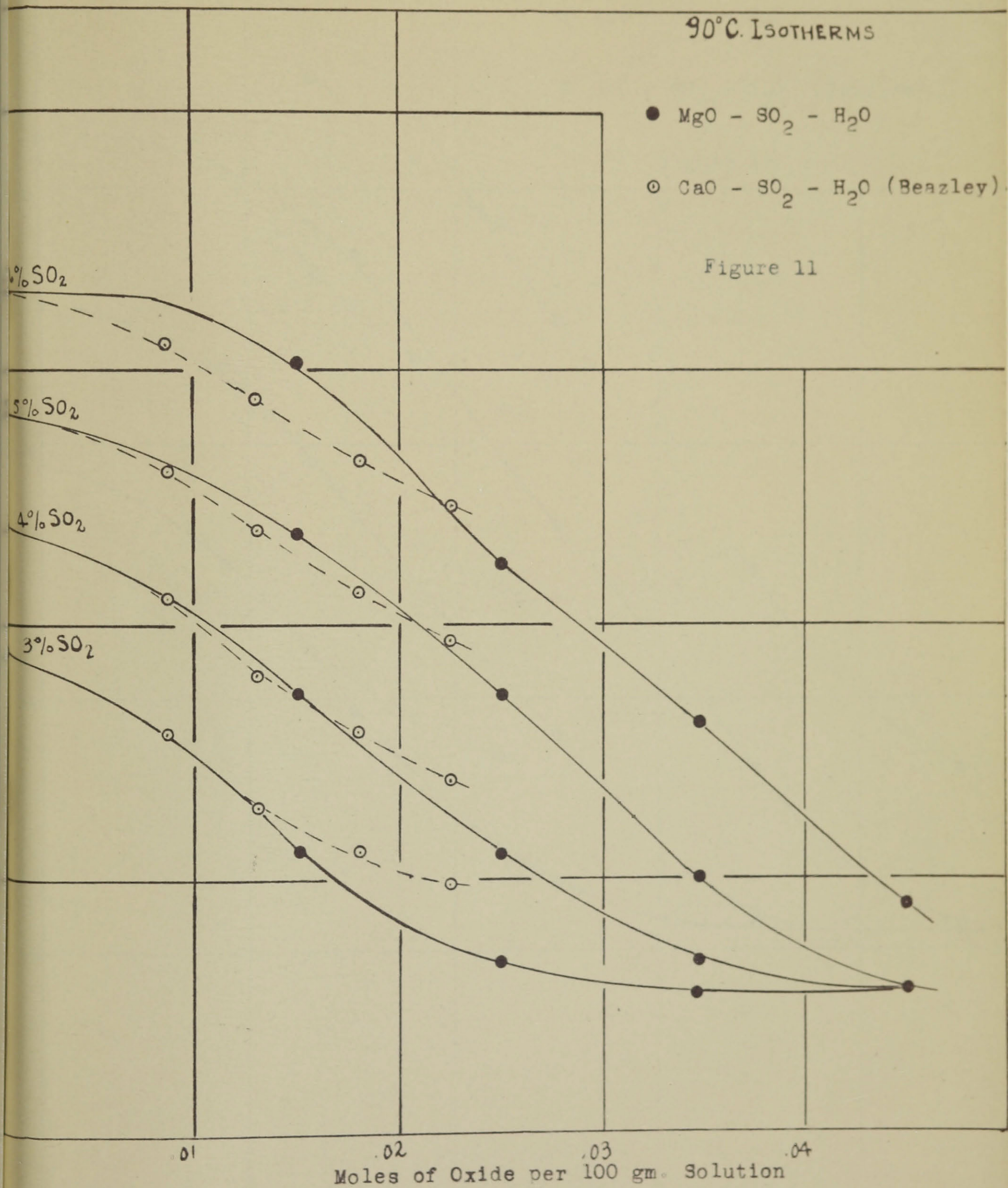

90°C. Isotherms
● MgO - SO2 - H2O
⊙ CaO - SO2 - H2O (Beazley)
6% SO2
5% SO2
4% SO2
3% SO2
.01
.02
.03
.04
Moles of Oxide per 100 gm. Solution

Figure 11

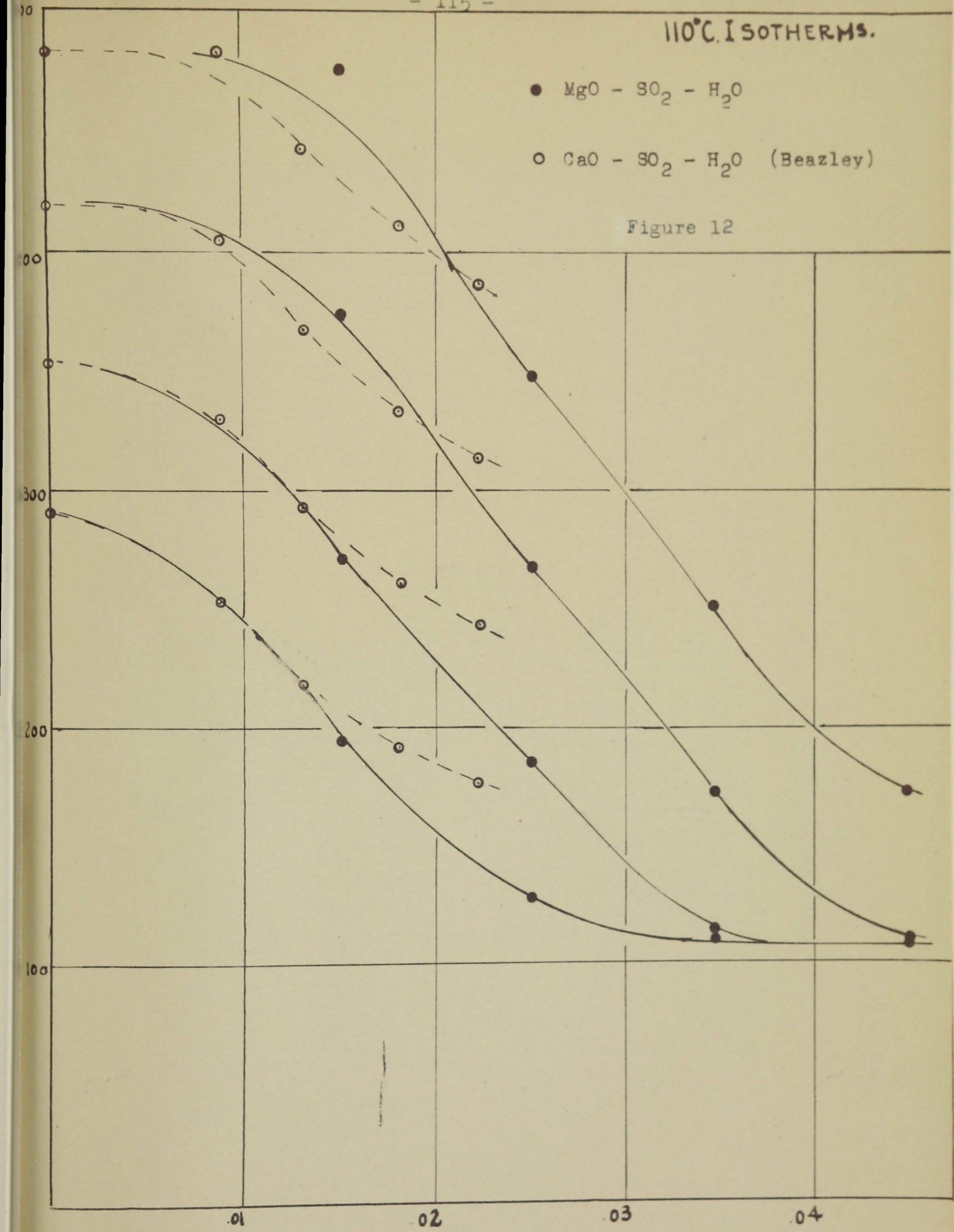

110°C. ISOTHERMS.
● MgO - SO2 - H2O
○ CaO - SO2 - H2O (Beazley)
00
200
300
.01
.02
.03
.04
Moles of Oxide per 100 gm. Solution

Figure 12

SUMMARY

TOTAL VAPOUR PRESSURE OF THE SYSTEM CaO - SO_2 - H_2O.

Temperature		25°	50°	70°	90°	110°
SO_2 %	Moles Oxide per 100 g. soln.	V.p. cm	V.p. cm	V.p. cm	V.p. cm	V.p. cm
3	0.00	26.0	64.0	115	190	290
3	0.00893	24.0	54.5	96.0	157	253
3	0.0134	19.6	43.0	76.0	128	218
3	0.0179	12.8	31.0	60.0	110	191
3	0.0223	9.1	24.0	49.5	97.5	176
4	0.00	36.0	85.0	147	237	355
4	0.00893	34.0	75.0	130	209	329
4	0.0134	29.4	63.5	110	181	292
4	0.0179	22.6	51.5	92.0	158	260
4	0.0223	19.0	41.3	77.0	139	240
5	0.00	47.0	106	183	283	420
5	0.00893	44.5	95.0	163	261	405
5	0.0134	40.0	83.0	145	235	366
5	0.0179	33.4	73.6	128	211	332
5	0.0223	30.2	64.2	116	193	313
6	0.00	57.0	128	223	330	484
6	0.00893	54.8	116	195	311	481
6	0.0134	50.1	106	180	288	443
6	0.0179	44.9	96.1	165	265	410
6	0.0223	41.0	87.0	151	246	385

Table 22.

TOTAL VAPOUR PRESSURES OF THE SYSTEM MgO - SO_2 - H_2O

Temperature		25°	50°	70°	90°	110°
SO_2 %	Moles Oxide per 100 g. soln.	V.p. cm	V.p. cm	V.p. cm	V.p. cm	V.p. cm
3	0.00	26.0	64.0	115.0	190.0	290
3	0.0149	13.4	37.5	62.0	121.0	194
3	0.0248	7.25	16.0	35.0	66.0	127
3	0.0347	3.50	10.5	23.0	51.0	108
3	0.0447	2.75	9.0	23.0	50.0	108
4	0.00	36.0	85.0	147.0	237.0	355
4	0.0149	23.75	59.0	103.0	172.0	270
4	0.0248	14.0	34.0	64.0	110.0	186
4	0.0347	5.75	14.5	26.0	56.0	112
4	0.0447	3.0	10.0	23.0	51.5	108
5	0.00	47.0	106.0	183.0	283.0	420
5	0.0149	35.75	82.5	143.0	235.0	373
5	0.0248	26.0	58.0	102.4	209.0	267
5	0.0347	15.0	33.0	57.0	102.0	171
5	0.0447	5.0	12.0	25.0	55.0	110
6	0.00	57.0	128.0	213.0	330.0	484
6	0.0149	47.4	107.0	184.0	302.0	475
6	0.0248	37.75	82.0	141.0	224.5	349
6	0.0347	26.75	56.0	95.5	161.0	251
6	0.0447	12.0	29.0	51.0	87.0	172

Table 23.

SUMMARY

The investigation of the equilibria existing in the three component system magnesium oxide - sulphur dioxide - water may be considered as a continuation of a general research program of the properties of sulphite liquors.

Previous workers studying the properties of the calcium system obtained results that were of a theoretical as well as practical interest. However, the presence of the insoluble calcium sulphite at the higher temperatures limited the range at which the investigation could be carried out with a two phase system. Because magnesium sulphite is extremely soluble, the inconvenience of the presence of a solid phase during an investigation was overcome by substituting magnesium oxide for calcium oxide. Consequently the solution was two phase throughout the investigation and the establishment of the equilibrium was quite rapid.

The apparatus used, was with several improvements, similar in design to those used by investigators examining the properties of the calcium system.

With this apparatus it was possible to measure accurately the vapour pressure of the magnesium system. The greatest source of error arose not in the actual measurements but originated from the reagents employed. Therefore, extra-

ordinary precautions were taken to remove all possible impurities that may be present in either the magnesium oxide, sulphur dioxide or the water, and in particular the utmost care had to be exercised so that all the occluded gases were removed from the magnesium oxide prior to making a run.

The vapour pressures of the system were measured with magnesium oxide concentrations of 0.6%, 1.0%, 1.40% and 1.80%. For each concentration of magnesium oxide the concentration of the sulphur dioxide was made to range from 1% to 6%. The temperature range covered was between 25°C. and 130°C.

Before it was possible to tabulate the results in a systematic manner, corrections were applied to the experimental data to compensate for the changes that occur in the concentration of both sulphur dioxide and magnesium oxide during a run. Specimen curves as well as type calculations have been included to facilitate the procedure followed.

In an attempt to determine the various equilibria existing in this system, numerous relationships were plotted using the experimental data. From the results obtained, it may be proposed that a magnesium basic sulphite is formed and this complex is only stable at low temperatures, as the temperature is increased it would appear there is an equilibria between magnesium bisulphite and sulphite, and the higher the temperature the larger the proportion of magnesium sulphite present.

Tables and curves are included showing the comparison of the equilibria existing in the magnesium with the calcium system over a range of sulphur dioxide concentrations from 3% to 6%. These curves indicate that the equilibria existing in both these systems differ considerably. It would appear that at the same temperature, there is a larger proportion of bisulphite present in the magnesium system, than in a solution containing calcium of identical concentration.

It was shown that over the range of concentrations in which no precipitation of calcium sulphite occurs, solutions of the magnesium system have higher vapour pressures than equimolecular solutions of the calcium system. Thus magnesium sulphite liquor should be a faster cooking liquor as well as one having the advantage of constituting a medium in which precipitation of solid is much less likely to take place.

CLAIMS OF

ORIGINAL RESEARCH

CLAIMS TO ORIGINAL RESEARCH

1. For the first time vapour pressures of the three component system magnesium oxide - sulphur dioxide - water have been determined within the limits of sulphur dioxide concentrations from 1% to 6% for each of the following magnesium oxide concentrations, 0.6%, 1.0%, 1.40%, 1.80%, and at appropriate temperatures between 25° and 130°C.

2. Prior to starting an investigation, a sample of the purified magnesium oxide was carefully examined for the presence of occluded gases.

3. The amount of magnesium oxide used for any given series was accurately weighed, and since the oxide has the undesirable tendency to take up water during this process, these values were checked by determining the magnesium content of the solutions at the end of each investigation, and the necessary corrections applied.

4. The values of the molar ratio of sulphur dioxide to magnesium oxide appear to indicate that at low temperatures the equilibria involves a compound of magnesium and sulphur dioxide in a one to one ratio; possibly a magnesium basic sulphite. At the higher temperatures it is essentially an equilibrium between magnesium bisulphite and the monosulphite.

5. The equilibria existing in the magnesium system were compared with those of the calcium system at the same temperature and concentration. The result of this comparison would signify that a greater proportion of the sulphur dioxide is present in a solution containing magnesium oxide, as bisulphite.

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