EQUILIBRIA IN
CALCIUM OXIDE-SULPHUR DIOXIDE-WATER
25° - 130° C

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

THESIS

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
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McGill University April 1937.

ACKNOWLEDGMENTS

The writer wishes to express his sincere gratitude:

To Dr. O. Maass, for his valuable advice and encouragement during the course of this research. His genial supervision added a very real pleasure to the investigation.

To Dr. W. Boyd Campbell for his many helpful suggestions and his sustained interest in the problem.

To the Canadian Pulp and Paper Association for a scholarship, the tenure of which made this research possible.

To the Forest Products Laboratories of Canada for laboratory facilities and certain materials supplied.

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INTRODUCTION

INTRODUCTION

When experimental investigations obtain divergent data it becomes of paramount importance to determine which is correct; especially when considerable theory has been built up on the results of the one favoured as being correct. Furthermore, when an industrial process is involved the importance of deciding as to the relative merits of the results previously obtained is enhanced. In the investigation to be described, particular precautions were taken to insure the validity of the experimental data.

This thesis describes an investigation of the equilibrium vapor pressures of the system calcium oxide - sulphur dioxide - water. It thus forms a part of a general investigation into the physical properties of sulphite systems which has been in progress in this laboratory for several years. Two lines of thought were the genesis of these researches; one concerned itself with the purely theoretical phase of the problem, while the other was an expression of the practical and hence commercial aspect, evolving from the fact that certain parts of the system under discussion are identical with the liquors employed in the sulphite cooking of wood.

That this programme of research is of practical utility is evidenced by statements on the part of sulphite pulp manufacturers that the results so far obtained have been of great value. Many express the belief that further work along these lines is not only desirable but imperative if a clear insight into the physico-chemical factors governing the sulphite pulping process is to be gained.

Undoubtedly there has been great progress in the art of cooking wood by the sulphite process, but this progress has been attained chiefly by empirical means; the process is an art and will remain an art rather than a science until sufficient information relative to the physico-chemical mechanisms involved has been attained to put the industry on a scientific foundation.

Aside from the practical aspect of this problem, it holds considerable academic interest in that it represents a typical phase rule study.

Vapor pressure - Composition curves have to be drawn at constant temperature and the conditions of concentration and temperature at which the solid phase makes its appearance must be investigated before a clear insight can be gained into the phase diagram of the system.

In the research to be described in this thesis, the apparatus used consisted essentially of a thermostated glass cell connected to a manometer capable of measuring the pressures produced. Auxiliary parts of the apparatus provided a means of introducing accurately known weights of very pure reagents into the cell. Adequate stirring of the material in the cell was produced by means of a magnetic stirrer.

Vapor pressure measurements were made at lime concentrations of approximately 0.5%, 0.75%, 1.0% and 1.25% and over a range of sulphur dioxide concentrations from 1% to 6%.

As a result of this work a table has been prepared showing the total vapor pressures of this system from 0% to 1.25% CaO in 0.25% steps over a range of SO_2 concentrations from 1% to 6% in 1% steps.

An interesting outcome of this work on the study of vapor pressures of this system, was the development of a new and accurate method for the determination of precipitation temperatures.

Although the fact that precipitate forms in calcium bisulphite sulphur dioxide solutions on heating has long been recognized, very little work has been done on the investigation of this phenomenon.

The so-called "liming up" of digesters and pipe lines in commercial practice is a result of this precipitation. Thus from an industrial point of view it is extremely desirable to obtain figures that show the variation of these precipitation temperatures with changes in calcium oxide and sulphur dioxide concentrations.

The results obtained in this investigation show that all previous determinations are considerably in error in that the precipitation temperature they predict are too high.

A table and a graph have been included showing the variation of these temperatures over a considerable range of calcium oxide and sulphur dioxide concentrations.

HISTORICAL

HISTORICAL

A search of the literature reveals the fact that although sulphur dioxide is a well known compound, there is surprisingly little data as to its physical properties and those of its aqueous solutions.

Realizing the need for such physical data, Dr. O. Maass and his co-workers instituted, in 1923, a primary series of investigations on pure sulphur dioxide. These were followed in later years, by research on its aqueous solutions.

The next logical step in this series of investigations, was to determine what effect the addition of a basic third component would have on the properties of the system. Obviously, from the point of view of the sulphite process, calcium oxide should be the third component.

Although considerable research has already been done on the system calcium oxide - sulphur dioxide - water in this laboratory (41, 42, 43), the data has been obtained by interpolation and extrapolation; furthermore the results of the different investigators do not agree as well as might be expected.

The work to be described in this thesis is, then, a further attempt to arrive at a more exact understanding of the equilibria existing in the system calcium oxide - sulphur dioxide - water.

For convenience in discussion, this three component system may be considered as consisting of three distinct two-component systems, namely, sulphur dioxide - water, calcium oxide - water and calcium oxide - sulphur dioxide. This last named system however will not enter into the discussion because it is concerned only with reactions in the dry state and thus has no direct bearing on a discussion of aqueous solutions.

(a). The System Sulphur dioxide - Water

Although this system has been investigated by several workers, the literature lacks continuity; measurements, for the most part, have been made over rather small ranges of concentration and temperature, and there is surprisingly little agreement between the results of separate investigators working on the same phase of the same system.

Only in the last few years has any semblance of order been established in this system due to the efforts of Maass and his co-workers (21, 22, 23). Following is a summary of the literature on this system:

Sims (1) determined the vapor pressures over aqueous solutions of sulphur dioxide with considerable accuracy over a range of pressures up to 200 cms., and temperature up to 50°C. Schiff (2) and Gerlach (3) give figures for the density of these solutions, as do Giles and Shearer (4), the work of the latter investigators being far superior to that of Schiff and of Gerlach. Ostwald (5) and Barth (6) measured the conductivity of sulphur dioxide - water solutions; McCrae and Wilson (7) worked on the partition proportions of sulphur dioxide between water and chloroform; Walden and Centnerszwer (8) made freezing-point determinations. Drucker (9) combined the results of the last four investigations as a basis for calculating the dissociation constant. Kerp and Bauer (10) made conductivity and freezing-point measurements; Fulda (11) calculating from the heat of dissociation data of Thomsen (12) and Berthelot (13) gave figures for the dissociation constant over the temperature range 7° to 50°C. Wright (14) showed, by a study of adsorption spectra, that a considerable quantity of SO_2, as such, existed in the solution; Baly and Bailey (15) carried this further and proved the presence of the meta-bisulphite ion in bisulphite solutions. Lindner (16) and Smith and Parkhurst (17) measured the vapor pressure of sulphur dioxide - water solutions over a few scattered concentrations and temperatures. Oman (18), Hudson (19) and Enckell (20) determined the solubility of sulphur dioxide in water up to

90°C. Maass and Maass (21) measured the vapor pressures and conductivities of solutions of sulphur dioxide in water over all possible concentrations at temperatures below 27°C. Campbell and Maass (22) investigated the vapor pressures, densities and conductivities of sulphur dioxide - water solutions within the limits of concentration to 8 percent, and at temperatures up to 135°C. Morgan and Maass (23) measured the vapor pressures and conductivities of these solutions from 0° to 25°C., and made extensive calculations involving the equilibria relationships. Johnstone and Leppla (24) investigated the solution of sulphur dioxide in water at low partial pressures and developed a Henry's Law relationship for the unionized portion of sulphurous acid. Terres and Rühl (25) prepared a phase-rule diagram for the system sulphur dioxide - water; Davis (26) published a new nomograph for the solubility of sulphur dioxide in water.

(b). The System Calcium oxide - Water

This second two-component system has been investigated by several workers, but here again a large part of the published data is of little value. This is due largely to the difficulty in avoiding impurities in the system, especially carbon dioxide. According to Bassett (27) particle size of the calcium oxide is also a source of error. The lack of agreement among various workers is an indication of the unreliability of the published results. Ostwald (28) measured the conductivity of calcium hydroxide solutions. He admits that carbon dioxide was probably present, thus casting doubt on his own results. Cavazzi (29) determined the density of calcium hydroxide solutions; Miller and Witt (30) measured the conductivity of a calcium oxide-water solution at 30°C. while making solubility measurements. Whetham (31) gives a conductivity value for this solution at 25°C. Solubility measurements have been made by Maben (32), Lamy (33), Hertzfeld (34), Guthric (35), Moody (36), Haslam, Calingaert and Taylor (37) and Bassett (27). Smolenski and Zero (38) give figures for the solubility of calcium oxide in water, sodium hydroxide solutions, and sucrose solutions; they also studied the pH of these solutions; Rodt (39) worked on the hydrate present in the system calcium oxide - water. Larocque (40) working on conductivity measurements, made probably the best determinations of the solubility of calcium oxide in water up to 30°C. Grieve (41) determined the vapor pressures and conductivities of saturated calcium hydroxide solutions over the temperature range 0°C. to 25°C. Gurd (42) made similar measurements over the range 25°C. to 135°C.

(c). The System Calcium oxide - Sulphur dioxide - Water

Although the literature affords little data on the two two-component systems sulphur dioxide - water and calcium oxide - water, even less data regarding the system calcium oxide - sulphur dioxide - water are available. Most of those who have interested themselves in this system in the past, have done so from a purely practical point of view, and thus have not taken the precautions necessary to obtain results of theoretical interest. The inaccuracy of the results obtained prior to the last five years can probably be traced to one or more of three sources of error; these are, first: uncertainty as to the concentration of sulphur dioxide in the solutions; second: impurity of the reagents used, particularly that of the calcium oxide; third: the great tendency this system has toward supersaturation, and consequently the extremely long time necessary for the attainment of equilibrium.

Smith and Parkhurst, whose work has already been mentioned (17) measured the solubility of sulphur dioxide in water containing varying amounts of bases. Enckell, also previously mentioned (20) determined the solubility of sulphur dioxide in solutions of calcium bisulphite, sulphuric acid, sodium sulphate, and sodium sulphate plus hydrochloric acid. Robart (43), van der Linden (44), and Weisberg (45) measured the solubility of calcium sulphite in water. Schwartz and Müller-Clemm (46) determined the ratio of free to combined SO_2 in sulphite solutions; Farnell (47) worked on the hydrogen ion concentration of sulphite solutions; Bergman (48) determined conductivities of the system calcium oxide - sulphur dioxide - water. Conrad and Beuschlein (49,50) published some pressure-composition curves for this system at 15° and 25°C.

During the past five years a comprehensive study of the system calcium oxide - sulphur dioxide - water has been in progress in this laboratory. Grieve (41) determined conductivities and vapor pressures of the system over the temperature range 0° to 25°C. at calcium oxide concentrations of approximately 1% and 2%, and at sulphur dioxide concentration up to and including more than 5 moles of sulphur dioxide per mole of lime. Gurd (42) investigated the same range of calcium oxide and sulphur dioxide concentrations over the temperature range 25° to 130°C. Gishler (51) includes in his work, vapor pressures and conductivity measurements on this system at lime concentrations of 1.2% and 2.3% and sulphur dioxide concentrations of 0% to 6% over the temperature range 25° to 130°C.

Campbell, Grieve, Gurd and Gishler took every precaution to insure against the possibility of impurities entering the system, and used methods of introducing the reagents into the reaction cell which permitted a high degree of accuracy in the measurement of their concentrations.

The data of Campbell and Maass (22) may be considered as part of this three phase system in which the calcium oxide concentration is zero. Thus it was, that prior to the investigation described in this thesis, data existed relative to the vapor pressures of this three component system at lime concentrations of 0%, 1%, 1.2%, 2%, and 2.3%; and sulphur dioxide concentrations up to and including 6% over the temperature range 25° to 130°C.

There was, however, two reasons why further measurements were necessary: there was a decided lack of agreement between the results obtained by these former workers. Gurd and Gishler, independently of one another, obtained vapor pressure measurements which checked, but which were not in agreement with those of Grieve at low temperatures. The conductivity data of all three were in good agreement. Because of the experimental agreement between Gurd and Gishler, their data were used in the theory developed, but only applied to higher temperatures, i.e., at 50°C and above. Grieve's data left question as to the validity of the values at 25°C and lower.

Furthermore, no experimental data was available on systems with lime concentrations between 0 and 1 percent. It was considered that the lime concentrations chosen for the investigation under discussion, i.e. 0.5%, 0.75%, 1.0% and 1.25%, would serve to fill in the existing gaps and also act as a check on those results of previous investigators which had been obtained.

(d) Precipitation Temperatures

In 1931 the first investigation into precipitation temperatures of the system calcium oxide - sulphur dioxide - water was carried out in this laboratory by Russell (56). Prior to this date Saunderson (57) had shown that the precipitate consisted of sodium sulphite (Na_2SO_3), but had made no determinations of precipitation temperatures. Russell admits his measurements were rough, and his method far from perfect. The figures he obtained showed that precipitation took place at a lower temperature than was formerly believed by the industry. Gurd (42) includes two measurements on precipitation temperatures in his thesis which also fall low. Gishler (56) gives precipitation temperature over a considerable range of CaO and SO_2 concentrations which are lower than the values of Russell and Gurd.

The results obtained in the investigation under discussion show that precipitation begins at a temperature even lower than those predicted by the three aforementioned investigators.

Tables and graphs including the figures of previous investigators will be found in the section on results. A discussion of the results will follow later.

In the experimental work, extreme precautions were taken to ensure the purity of the reagents used, and the technique of preparing the solutions allowed very accurate measurement of their concentrations.

The calculations involved in this problem were very lengthy, but not difficult. Many correction factors had to be taken into consideration; some of these corrections could be computed mathematically, while others were arrived at by graphical methods.

The section immediately following this introduction will consist of a detailed description of the apparatus; this in turn will be followed by an exhaustive description of the technique involved in the manipulation of the apparatus and the preparation of solutions; following this the nature of the calculations involved will be discussed. The latter parts of the thesis will be devoted to the tabulation of results, their interpretation, and a discussion of their significance.

EXPERIMENTAL

EXPERIMENTAL SECTION

This section is most conveniently discussed under the following headings and their sub-headings:

A. Purpose and Description of Apparatus.
    1. General Description.
    2. Gas Purification Section.
    3. Gas Measuring Section.
    4. Gas Introduction Section.
    5. The Cell - Manometer Section.
    6. The Oil Bath, Heaters, etc.

B. Experimental Technique.
    1. Preparation and Purification of Materials.
    2. Preparation of Solutions.
    3. Making a "Run".

C. Factors to be Considered in the Calculation of the Results.
    1. Calculations on Apparatus.
    2. Calculations on the Introduction of the Reagents.
    3. Corrections Applied to Readings.
    4. Calculations Necessary to Get Readings in a Form in Which They can be Plotted.

A. Purpose and Description of Apparatus

1. General.
2. Gas Purification System.
3. Gas Measuring System.
4. Gas Introduction System.
5. The Cell - Manometer System.
6. The Oil Bath, Heaters, etc.

1. General:

The purpose of this apparatus, of necessity, was to provide a means of bringing together known weights of water, calcium oxide, and sulphur dioxide in the absence of all impurities which could possibly affect the results. The presence of air, and in particular carbon dioxide had to be avoided. To meet these requirements, the apparatus was designed so that known weights of air-free water, lime free from carbonate, and pure sulphur dioxide were brought together in the cell itself.

Gas from a supply cylinder was purified by three fractional distillations and stored in a bulb. The gas measuring system provided a means of accurately weighing portions of this gas, which were subsequently brought into the cell (which already contains the water and the lime) through the medium of the gas introduction system.

The cell was connected to a closed-end manometer capable of measuring the pressures developed,by glass tubing heated to a temperature higher than that of the oil bath to ensure the absence of any liquid phase in any portion of the apparatus except in the cell itself.

A thermostated oil bathequipped with the necessary heaters, cooling coils, stirrers, etc. surrounded the cell and provided accurate temperature control.

The reagents in the cell were continually stirred by means of an all-glass magnetic stirrer to ensure complete mixing and true equilibrium.

2. Gas Purification System:

The following sections and their sub-sections will be devoted to a detailed description of the various integral parts of the apparatus. No attempt will be made to explain the function of any part, as this sort of description falls more naturally into the section on Experimental Technique.

A diagram of the apparatus will be found in Figure I. The gas purification system occupies the right hand side of the figure. It was constructed entirely of soft glass, and a seal made to the sulphur dioxide cylinder by means of DeKhotinsky cement. A drying tube containing phosphorus pentoxide served to dry the gas taken from the cylinder. An exhaust, "O" connected through a mercury valve to the fume cupboard allowed the rejection of unwanted sulphur dioxide gas.

This section of the apparatus also included the evacuation system, so arranged that a water vacuum pump, a Cenco Hyvac pump, or a Langmuir mercury diffusion pump backed by the Hyvac could be used to evacuate the entire apparatus or any portion thereof. Another drying tube containing P_2O_5 protected the pumps from moisture.

A McLeod Gauge "E" served to test the efficiency of the pumping system, and also provided a means of testing for slow leaks in the apparatus. A simple manometer "D" was used for rough pressure measurements, and also acted as a safety valve when gas was introduced from the supply cylinder. Four bulbs

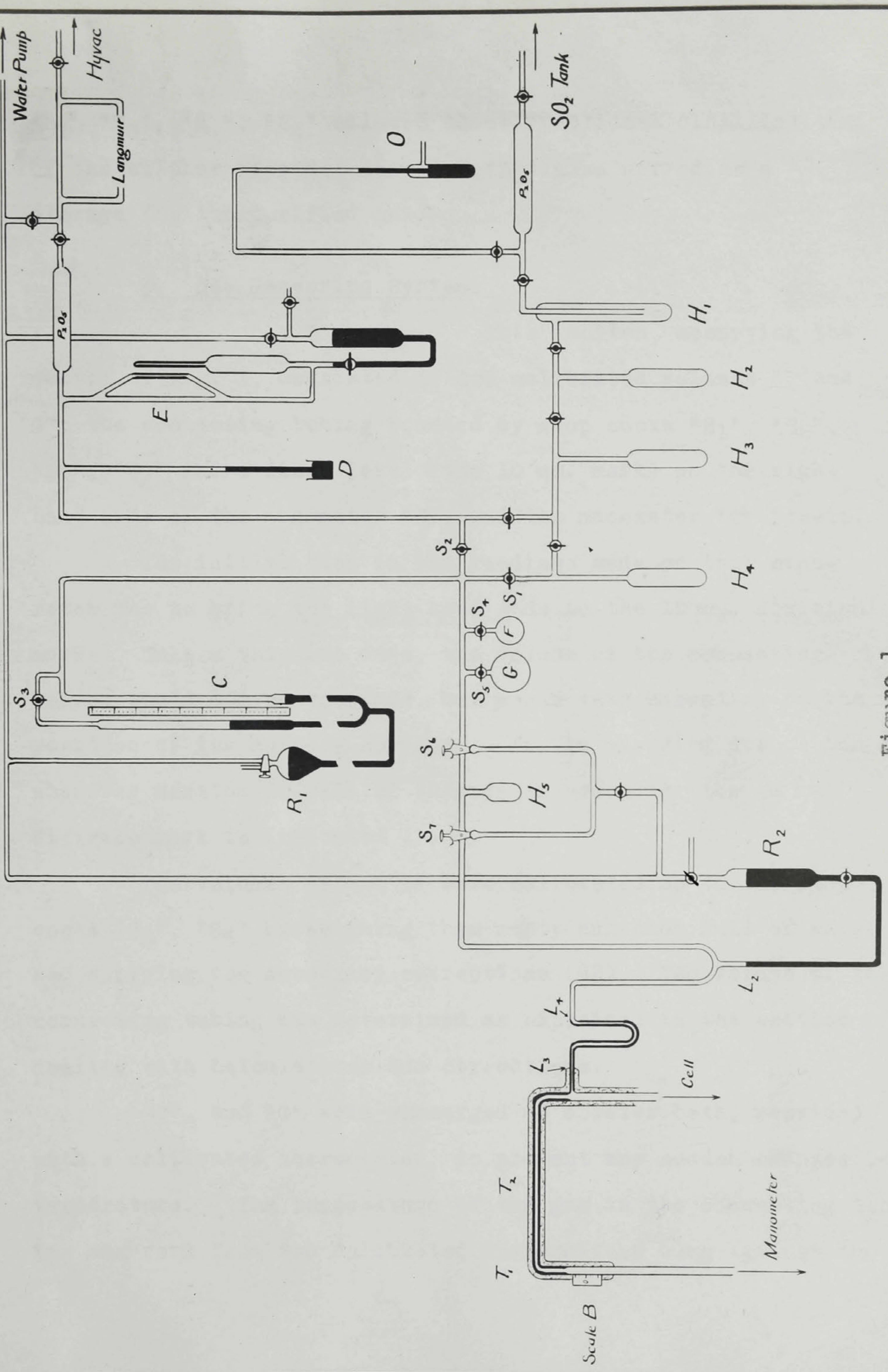
Water Pump
Hyvac
Langmuir
P_2O_5
O
SO_2 Tank
P_2O_5
H_1
H_2
H_3
H_4
E
D
S_2
S_1
S_4
F
S_5
G
S_3
C
R_1
S_6
S_7
H_5
R_2
L_2
L_4
L_3
Cell
T_2
T_1
Manometer
Scale B
WB 1/10/27

Figure 1

"H_1", "H_2", "H_3", "H_4" allowed three fractional distillations of the sulphur dioxide; the last,"H_4" also served as a storage for the purified gas.

3. Gas Measuring System:

This section, occupying the center of Fig. I, consisted of two calibrated volumes "F" and "G"; the connecting tubing bounded by stop cocks "S_1", "S_2", "S_3", "S_6" and a fixed level (the 10 mm. mark) on the right hand side of the manometer "C"; and the manometer "C" itself.

The initial step in all readings made on this manometer was to bring the right hand side to the 10 mm. division mark. Unless this was done, the volume of the connecting tubing would not be constant, but would vary depending on the position of the mercury surface. In the ensueing discussion whenever mention is made of this reference mark, the 10 mm. division mark is indicated .

The volumes "F" and "G" were calibrated up to the stopcocks "S_4", "S_5" by weighing them empty and then full of water and applying the necessary corrections (42). The volume of the connecting tubing was determined as explained in the section dealing with calculations and corrections.

"F", and "G" were submerged in a water bath, provided with a calibrated thermometer, to prevent any sudden changes in temperature. The temperature of the gas in the connecting tubing was read from two calibrated thermometers hung against the glass tubing.

The left hand side of the manometer "C" was evacuated through the stop cock "S_3" by means of the Langmuir pump backed by the Hyvac. The mercury in the right hand arm could always be adjusted to the 10 mm. mark by applying vacuum or air pressure to the mercury reservoir "R_1". The difference in level between the mercury in the two arms, after a glass scale correction had been applied (as explained in the section on corrections), was a measure of the pressure in this gas measuring system.

4. Gas Introduction System:

This system connects with the previously described system through the stop cock "S_6". It consists of the two vacuum stop cocks "S_6" and "S_7", the bulb "H_5" and the connecting tubing bounded by the stop cock "S_7" and fixed marks "L_2" and "L_3".

The plugs of the stop cocks "S_6", "S_7" were held in the seats by air pressure. This was necessary to prevent the plugs from popping out due to the pressure exerted by the sulphur dioxide as it warmed up in bulb "H_5" just prior to its introduction into the cell. Bulb "H_5" served as a temporary storage for the gas. (See section on Preparation of Solutions). The "U" tube just above the point "L_2" served as a mercury cut-off while preparing the solutions. The second "U" tube (below "L_3"), was of Pyrex capillary tubing and comprised the "frozen mercury seal" as described later.

Just above the first mentioned "U" tube there was a graded, Pyrex-to-soft-glass seal by means of which it was possible to join the Pyrex part of the apparatus to the soft glass part. By applying air pressure to the mercury reservoir "R_2" connected to this "U" tube, mercury could be raised into the "frozen mercury seal"; the mercury was lowered when necessary by applying vacuum to the same reservoir.

This so called "frozen mercury seal" deserves special description. While a run was in progress it was essential that the cell-manometer system be cut off or isolated from the remaining parts of the apparatus. It was also desirable at the end of a run, to be able to add more sulphur dioxide to the solution already in the cell so that a series of runs could be made on solutions having the same water and calcium content, but with increasing percentages of sulphur dioxide. An ordinary stop cock of course was useless, because the pressures developed in the cell during a run would blow the plug out of its seat. The frozen mercury in the U-shaped capillary tube solved this problem very nicely: it could be opened or closed when desired, and once frozen would stand more pressure than the glass walls themselves.

5. The Cell - Manometer System:

This section of the apparatus was constructed entirely of Pyrex glass; in the following description when the diameter of glass tubing is referred to, the figure given represents the outside diameter.

In Fig. II is shown a detailed drawing of the cell proper; dimensions are as shown. The volume of the cell was approximately 80 cc. The side arm "V" was used for the introduction of calcium oxide; the side arm "W" was blown on to an auxiliary bulb into which the known weights of water were transferred from the weight pipette. A more detailed account of this auxiliary bulb will be found in the section on Experimental Technique.

To ensure complete mixing and true equilibrium pressures, the reagents in the cell had to be vigorously stirred at all times. This was accomplished by means of the all-glass electromagnetic stirrer shown in Fig. II. The bottom part of this stirrer was provided with a number of protuberances which served to break the surface of the liquid at each stroke. A three inch soft iron nail (with the head ground off) sealed into the top end of the stirrer allowed the stirrer to be moved up and down by means of an electro magnet to be described later. The top end of the stirrer reached well up into the shaft which connected the cell proper to the remainder of the apparatus. This shaft, or neck, was made of sufficient diameter to allow the stirrer to move freely up and down. The diameter, however, was kept as small as possible so as to keep the gas space above the liquid in the cell at a minimum. All tubing connecting the cell to the manometer was kept small for the same reason.

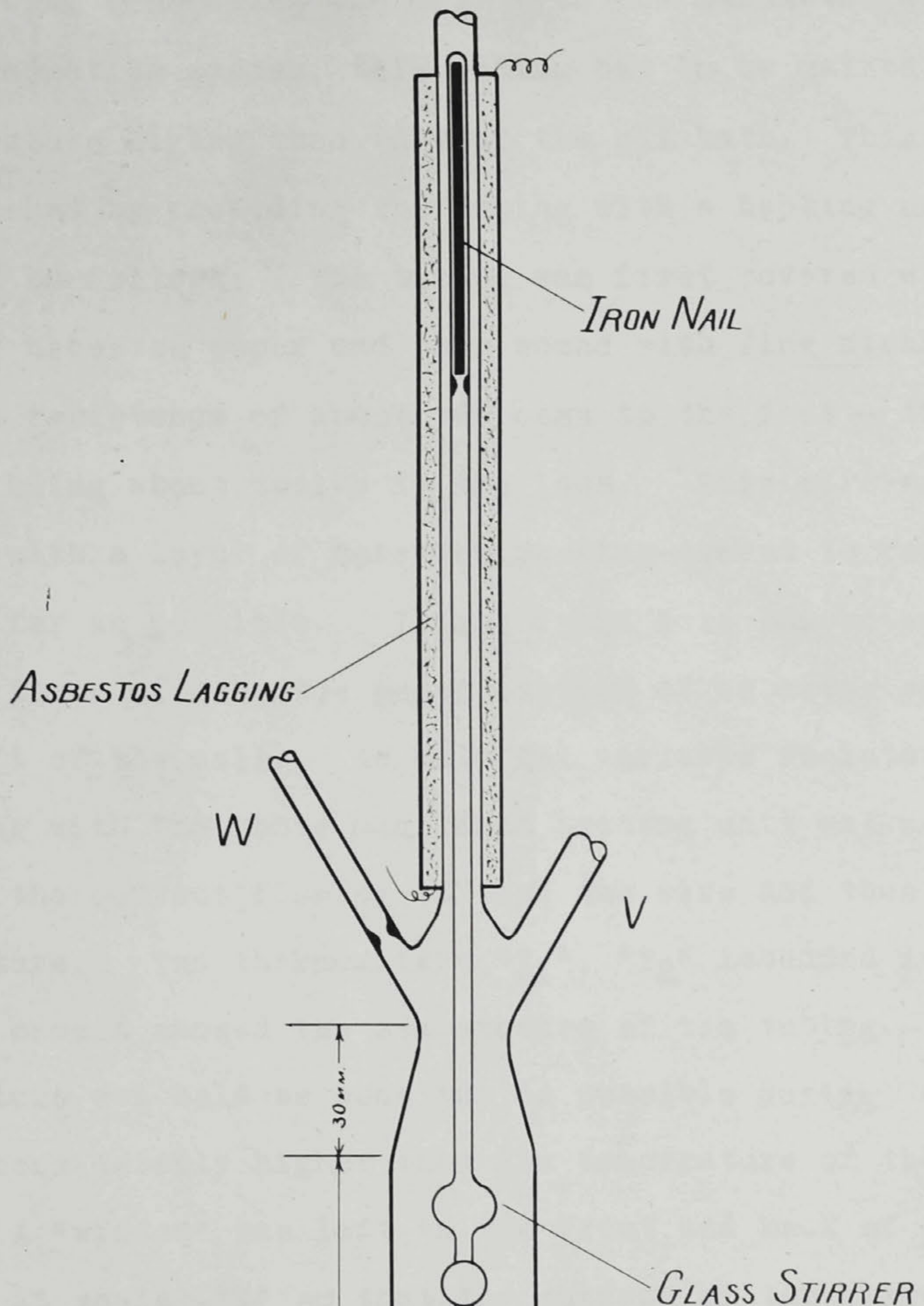

Figure 2

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In order to prevent condensation of water in the glass tubing connecting the cell with the manometer and the gas-introduction system, this tubing had to be maintained at a temperature higher than that of the oil bath. This was accomplished by providing the tubing with a heating unit constructed as follows: The tubing was first covered with a layer of asbestos paper and then wound with fine nichrome wire having a resistance of about two ohms to the foot — the turn spacing being about twelve to the inch. This wire was then covered with a layer of asbestos packing-cement to reduce heat loss as far as possible. It was found more convenient to use several turns of asbestos paper instead of asbestos cement on the shaft of the cell. An external variable resistance wired in series with the above mentioned heating unit was used to control the current flowing through the wire and thus its temperature. Two thermometers "T_1", "T_2" imbedded in the lagging cement showed the temperature of the tubing. This temperature was held as constant as possible during a run and always considerably higher than the temperature of the oil bath.

A "window" was left in the front and back of the asbestos packing at scale "B" so that the surface of the mercury could be observed; a twenty-five watt lamp was mounted behind these "windows". The zero mark on scale "B" was five cms. above the bottom of the lagging, and since the mercury surface in scale "B" was maintained at zero during a "run" this caused the five cms.

of mercury in this tube to be heated to the same temperature as the lagging. This was essential in order to prevent condensation of water on the mercury surface; however it necessitated a correction in the manometer reading due to the change in density of the heated mercury. This correction is fully explained in the section on corrections.

It should be also noted that the lagging continues well over on the "frozen mercury seal" tube to prevent the liquid phase from appearing on this mercury surface.

Figure III shows a detailed drawing of the manometer. In order to measure pressures of six or seven atmospheres in a room about four meters high, it was necessary to use a manometer of the "closed-end" type. The manometer used in this work was that constructed and calibrated by Gurd; a detailed description will be found in his thesis (42).

Essentially, the manometer consisted of a Pyrex tube, one cm. in diameter and about 380 cms. long mounted on a suitable wooden support and provided with a scale composed of four wooden metre sticks placed end to end. The Pyrex tube was surrounded over its whole length by a soft glass tube about 2.5 cm. in diameter. This outer tube served to protect the inner tube from any sudden changes in temperature. Three thermometers, one at the top, another at the center, and the third at the bottom, hanging in this dead air space made it possible to read the temperature of the air trapped over the mercury in the manometer.

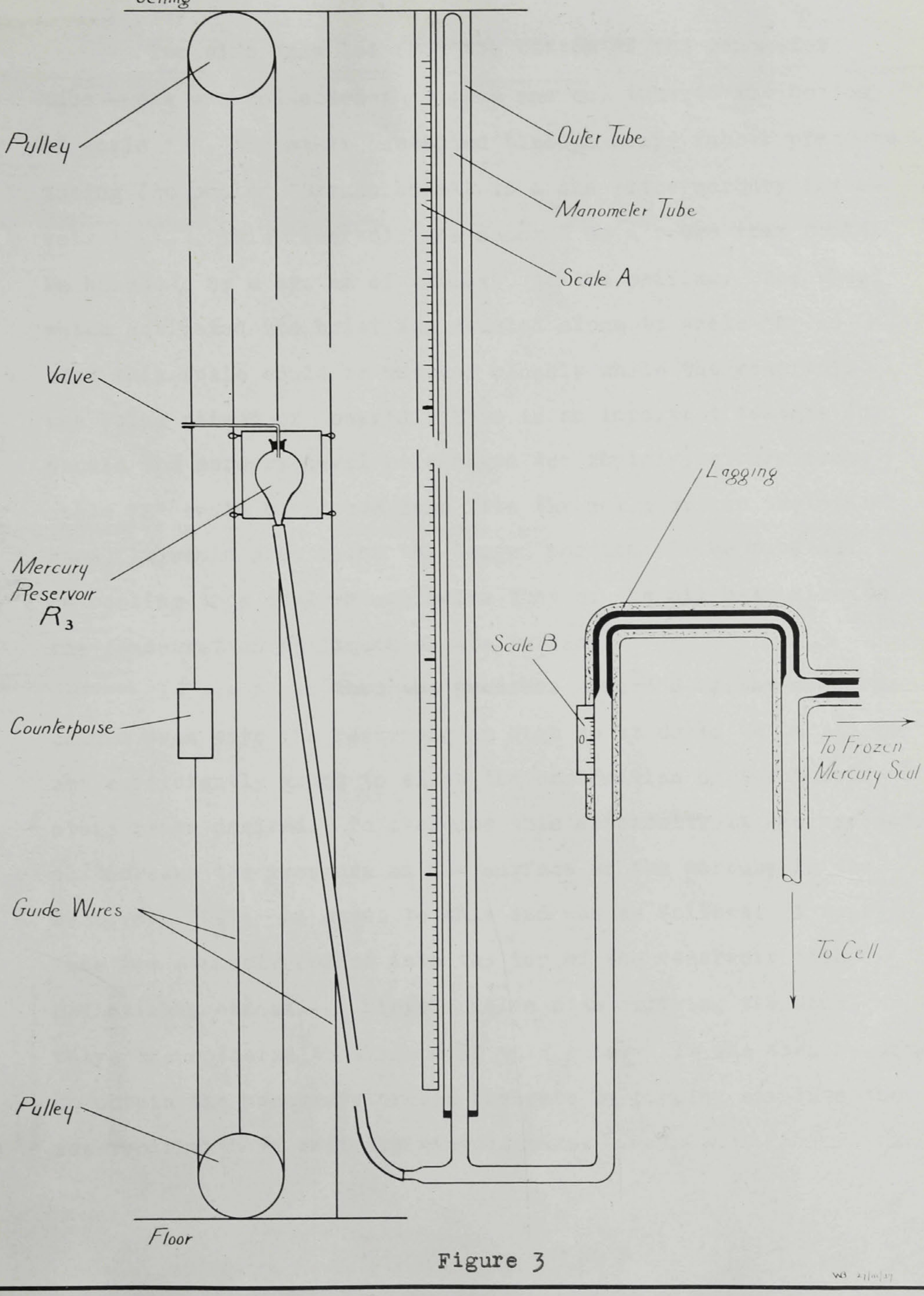

Ceiling
Pulley
Outer Tube
Manometer Tube
Scale A
Valve
Lagging
Mercury
Reservoir
R_3
Scale B
0
Counterpoise
To Frozen
Mercury Seal
Guide Wires
To Cell
Pulley
Floor

Figure 3

WB 27/10/27

Two side arms led from the bottom of the manometer tube — one was connected through a one cm. tube to the bottom of scale "B", the other connected through heavy rubber pressure tubing (so called "Oxygen hose") to a one litre mercury reservoir "R_3". This reservoir was mounted on a board that could be hoisted, by a system of pulleys, to the ceiling. The wheel which activated the hoist was mounted close to scale "B" so that this scale could be watched closely while the reservoir was being raised or lowered. This is an important feature for should the mercury level be changed too rapidly,mercury from scale "B" would be forced over into the cell; or, on the other hand, it would drop below the lagged portion of the tube and on cooling to a temperature below that of the oil bath,allow the condensation of liquid on its surface.

It was found that the pressure afforded by the mercury column even with the reservoir as high as it could be lifted was not sufficiently great to allow the exploration of the temperature range desired. To overcome this difficulty it was necessary to increase the pressure on the surface of the mercury in the reservoir "R_3". A means to this end was as follows: A copper tube was securely sealed into the top of the reservoir with DeKhotinsky cement — a bicycle valve stem carrying the usual valve was soldered to the end of this tube. It was then possible to obtain the necessary excess pressure by pumping air into the reservoir with an ordinary bicycle pump.

The following calibration of the manometer is from the thesis of Gurd (42).

Corrected volume	Scale reading
3.0303 cc.	3.90
6.1244	7.85
27.884	36.15
49.734	65.05
67.493	87.85
69.467	90.30
71.275	92.38
93.210	120.30
115.21	148.50
138.02	178.00
139.96	180.50
140.95	181.68
142.21	183.25
164.11	211.50
186.26	240.45
209.52	271.15
210.38	272.15
211.83	273.82
233.91	301.25
255.63	328.63
281.58	360.90
282.96	362.51
283.92	363.43
284.91	364.61
289.35	370.49

The solenoid which activated the magnetic stirrer deserves special attention. Since vigorous stirring was of prime importance to ensure true equilibrium conditions, the stirrer had to be designed and operated to meet these conditions. The stirrer was of necessity rather heavy and thus the ampere-turns factor of the magnet had to be fairly large. A small magnet with few turns of wire would have to be supplied with a current so great that the heat developed would char the insulation. On the other hand a large magnet drawing a relative small current was awkward to install beacuse of the space it requires. Several designs and hook-ups were tried; the system finally adopted was constructed as follows:

A piece of Pyrex tubing 15 cms. long and of diameter just large enough to accommodate the lagged shaft of the cell was wound with a copper cooling coil. After two layers of asbestos paper were wound over this copper tubing, three pounds of double-cotton-covered annunciator wire were wound on. The whole was then sheathed in a galvanized iron shell which helped to concentrate the magnetic field as well as protect the insulation of the wire.

Two banks of 32 C.P. carbon-filament lamps controlled the current through the solenoid - one bank of six sockets supplied a steady current, the second bank of four sockets supplied an additional, intermittent current. The first bank was wired directly in series with the solenoid and the direct current main.

Enough lamps were put in this bank to supply a current large enough to suspend the stirrer about a centimeter from the bottom of the cell. The second lamp back was wired in series with an interrupter in such a way that when the circuit was made, a current proportional to the number of lamps in the bank was added to the aforementioned steady current. The number of lamps in this second bank controlled the length of the stirrer stroke.

The combined effect of the current passing through the solenoid and the heat radiated by the tube heating unit inside it caused the solenoid to heat up considerably. To offset this cold water was circulated through the copper coil around which the wire was wound. The flow of water was regulated so that the water leaving the cooling coil was just about at room temperature. Too much cooling may cause the cell shaft to be cooled to such an extent that liquid would condense there. This happened on one occasion, but the fact immediately made itself evident by causing the magnetic stirrer to stick in the shaft.

The circuit interrupter consisted of a Cenco Mercury Switch (No. F-3565-B) fastened to an arm activated by an eccentric which in turn was belted to an electric motor through a reducing gear. Thus the speed with which the stirrer moved up and down could be controlled by changing the speed of the motor. These three factors, i.e., the two lamp banks and the speed of the motor, gave a very flexible control over the motion of the stirrer, and satisfactory stirring could be produced at all times.

6. The Oil Bath, Heaters, Thermoregulator, etc:

The cell was immersed in an oil bath consisting of a Pyrex jar 18 inches deep and 8 1/2 inches in diameter full of diethylene glycol. The oil was deep enough so that the two side arms "V" and "W", and the end of the lagging on the cell shaft were under its surface.

The oil bath was equipped with three bare nichrome wire heating units -- the first of these, of about 700 watts capacity, was connected in series with a system of external variable resistances and short-circuiting switches, and the relay which in turn was controlled by the thermoregulator. The current through this heater could thus be varied over a wide range of values. The second heating unit of about 400 watts capacity was wired in series with an external variable resistance by means of which its current could be varied over a small range. The third heater, of about 800 watts capacity, was wired directly to the 110 volt A.C. line. It was used in conjunction with the two other heaters to bring the oil quickly to any desired temperature.

The relay used was one supplied by the American Instrument Co., Catalogue No. 1001-01. This proved to be a very satisfactory instrument in the respect that the activation coils passed a very small current thus eliminating sparking in the thermoregulator, and also in the respect that it could break a comparatively high current on the power side without the usual troublesome sticking of the points.

The current supplying the relay was furnished by an American Instrument Co. rectifying transformer, Catalogue No. 1050-05.

The thermoregulator was of the all-mercury expansion type. After several designs were tried and rejected one was finally designed which had a very high surface/volume ratio achieved by winding ten feet of 7 cm. Pyrex tubing into two tight spirals one inside the other. This high surface/volume ratio allowed rapid heat interchange between the oil and the mercury thus eliminating any temperature lag. This instrument maintained the bath temperature within ± 0.05° Centigrade.

A cooling coil consisting of twelve feet of copper tubing served to cool the bath rapidly when necessary. When operating the bath at low temperatures it was found expedient to allow a small amount of cold water to circulate through this cooling coil.

Calibrated thermometers graduated in tenths of a degree centigrade were used to read the temperature of the oil bath.

A motor driven stirrer with four, three-inch paddles produces adequate stirring at all times. A constant level device prevented the oil from over flowing as it expanded with rising temperature.

Because of the relatively high pressures developed in the cell and since no pressure tubing was used in its construction, there was considerable danger of explosion at high temperatures. For this reason a box-like structure of wood was built around the oil bath and the tubing connecting the cell to the manometer. This shield was equipped with heavy, shatter-proof glass windows so placed that the thermometers and scale "B" could be read.

B. Experimental Technique.

1. Preparation and Purification of Materials.
2. Preparation of Solutions.
3. Making a "Run".

Experimental Technique

The preceeding pages contain a detailed specification of the apparatus; it is the purpose of the following sub-sections to explain exactly how each part of the apparatus was used. The description may seem too detailed in parts, but it was considered advisable to sacrifice brevity for explicitness.

1. Preparation and Purification of Materials:

Water, calcium oxide and sulphur dioxide were the components of the system under investigation in this project. The preparation and purification of each will be discussed.

A considerable quantity of clean dry mercury was used in the apparatus and was cleaned in the usual way: first bubbling air through it for several hours,then letting a fine spray fall through a 15% solution of nitric acid in the usual mercury cleaning tower. This was followed by three or four washings with distilled water in the same apparatus.

All bulbs and tubing that were to contain mercury were scrupulously cleaned with hot chromic acid, followed by several rinsings with distilled water.

The only purifications the water underwent was distillation and out-gassing. This out-gassing process will be fully explained under the section on Preparation of Solutions.

The sulphur dioxide gas underwent four fractional distillations with the rejection of the first and last portions each time. It was judged that such purification would certainly remove any traces of sulphur trioxide that may have been present in the gas as supplied by the cylinder. The actual technique involved in this distillation of the gas will be fully described later.

The calcium oxide used in this research had to be of the highest possible purity. The presence of carbonate in particular had to be avoided because carbon dioxide would be formed on the addition of sulphur dioxide to the lime-water mixture. This carbon dioxide escaping into the gas phase would cause every vapor pressure measurement made to be in error.

Most samples of so called "chemically pure" calcium oxide contain large enough quantities of carbonate to render them useless for this work. This necessitated the development of a method of preparing this substance in an extremely pure state. Once prepared it had to be handled in such a way that it had no opportunity of picking up carbon dioxide and moisture from the air.

Clear, natural crystals of Iceland Spar, which is calcium carbonate in a very pure form, were obtained from the Eimer and Amend Co. A select crystal was pulverized in a mortar and heated in an electrically heated muffle furnace in a platinum boat. A current of dry, carbon-dioxide-free air, obtained by passing air through two bottles containing a strong solution of potassium hydroxide, a soda lime tower, and finally a calcium chloride tower, was passed through the furnace during the heating. The furnace was held at bright-red heat for a week at the end of which time the boat containing the oxide was quickly transferred to a vacuum dessicator containing phosphorus pentoxide to remove any water vapor, and pellets of sodium hydroxide to remove any carbon dioxide. The dessicator was evacuated and the oxide allowed to cool.

When it became necessary to open the dessicator to remove a sample of lime for the preparation of a run, air was very slowly admitted through a tower containing soda lime and calcium chloride. While weighing out the sample the oxide was kept for the least possible time in contact with the air. During this procedure no appreciable amount of moisture or carbon dioxide was picked up by the lime.

Samples of the oxide prepared as described above were tested for absolute purity by two methods capable of detecting the least trace of carbonate. In the first method (52) some oxide was placed on a microscope slide and immediately covered by a warm solution of gelatin in water. The slide was quickly chilled which caused the gelatin to set. The solid particles were then brought into focus under a microscope set for a magnification of about 100 diameters, and a drop of hydrochloric acid touched to the gelatin. The acid diffused through the gelatin and immediately generated bubbles of carbon dioxide if any carbonate were present. A similar test was run on some lime taken from the laboratory shelf which was known to contain carbonate. The bubbles of carbon dioxide formed in this case were caught in the gelatin and could very easily be observed.

In the second method of testing, some of the prepared oxide together with some carbon-dioxide-free water and a few cc. of chloroform were placed in a small distilling flask connected by a delivery tube to a small bubbling tube containing a solution of barium hydroxide in water. The apparatus was air tight and so arranged that a gentle stream of CO_2-free air could be drawn through the whole set up. Hydrochloric acid was then added from a burette protruding into the distilling flask. Any carbonate present was immediately decomposed yielding carbon dioxide which would be carried over into the barium hydroxide solution by the current of air and also by the chloroform vapor produced by gently warming the flask. The absence of any cloudiness in the barium hydroxide solution proved the absence of any carbonate in the original sample of lime.

Samples of the calcium oxide prepared according to the aforementioned method gave negative tests for carbonate with both of the testing procedures described.

2. Preparation of Solutions:

Under this heading will be described the exact procedure followed in introducing known weights of calcium oxide, water and sulphur dioxide into the cell. Parts of this discussion have appeared before in the preceeding pages, but every step will be fully described here for clarity.

The cell was thoroughly cleaned and dried. After the solenoid had been slipped over the shaft, both were clamped in position and the cell sealed to the remainder of the apparatus. The join was covered with asbestos paper, the nichrome wire wound in place and connected up, and the outer lagging put on. The solenoid was wired up to the lamp banks and the magnetic stirrer tested.

The side arm "V" was sealed shut and an auxiliary bulb blown on to side arm "W". This bulb was constructed from a piece of thrity-five mm. Pyrex tubing and had a volume of about 125 cc. It was provided with a side arm which was bent in such a way that when this arm was blown on to "W", the auxiliary bulb was outside the oil bath. This side arm had a constriction close to the cell to facilitate its later sealing off under vacuum. A top tube provided an inlet for water into the auxiliary bulb. When the bulb was in position this top tube was sealed off and the apparatus completely evacuated. Before this evacuation was started the mercury reservoir "R_3" of the large manometer was lowered to the floor to insure that no mercury would be drawn over into the cell. The diffusion pump, backed by the Hyvac, was run for several hours to insure the removal of all moisture and then the apparatus left for a few hours to test for leaks.

Next, dry carbon dioxide-free air was slowly let into the apparatus through a soda lime tower and a phosphorus pentoxide tube. The side arm "V" and the top tube of the auxiliary tube were blown open ready to receive the lime and the water. The calcium oxide was quickly weighed and introduced into the cell through the side arm "V" through medium of black glazed paper and a specially prepared glass funnel — a camel's hair brush being used to sweep the fine dust into the cell. Side arm "V" was then sealed shut.

The water was weighed in a large weight pipette and carefully transferred to the auxiliary bulb in such away that no water adhered to the inlet tube. The inlet tube was sealed shut, and the water rapidly but carefully frozen by surrounding the bulb with a Dewar flask containing a saturated solution of carbon dioxide in acetone. Care was taken to freeze the water from the bottom up because of the danger of breaking the tube if the surface froze over before the body of the liquid was frozen. The pumps were started and the apparatus exhausted. Because of the low vapor pressure at the temperature of the freezing solution (-78°C.) no appreciable amount of water vapor was lost during the evacuation.

This was the first step in the out-gassing process previously referred to. To continue — mercury was raised into the U-tube from reservoir "R_2" and the ice allowed to thaw. The mercury prevented any water vapor from escaping into the remainder of the apparatus. As the ice thawed the air that had been dissolved in the water escaped into the empty cell. When the ice had completely thawed, it was frozen again as described before. Because of the low air pressure over the water only a very small amount of air dissolved in the water. A period of fifteen minutes was allowed for all water vapor to condense and freeze, the mercury was withdrawn from the U-tube, and the apparatus completely exhausted once more. This routine was repeated four or five times or until no more bubbles were seen as the ice melted. After the last evacuation stop cock "S_7" was closed. This completed the out-gassing process.

After the ice had thawed after the final freezing, the water was slowly warmed up to room temperature and finally distilled into the cell. This was a long-drawn-out process, but was hastened somewhat by cooling the oil bath to a low temperature with either tap water (in the winter) or brine (in the summer) and surrounding the auxiliary tube with a Dewar flask full of warm water.

When all the water had distilled over into the cell the auxiliary bulb was flamed with a hand torch to drive the last traces of water vapor over into the cell, and finally sealed off close to the cell at the aforementioned constriction in the side arm.

This completed the formation of the water — calcium oxide mixture and everything was now ready for the introduction of the desired amount of sulphur dioxide.

Bulb "H_1" was surrounded by a carbon dioxide - acetone freezing mixture and sulphur dioxide distilled in from the supply cylinder after passing thru the P_2O_5 tube. The rate at which the gas left the cylinder and condensed could be estimated by watching the mercury level in the tube leading to the gas exhaust valve. About 25 cc. of liquid SO_2 was distilled over and the valve on the cylinder closed. The freezing mixture was removed from bulb "H_1" and about 5 cc. of liquid allowed to escape through the mercury valve to the fume cupboard. After this low boiling fraction had escaped, about 15 cc. of liquid were distilled over into bulb "H_2" and the last 5 cc. in "H_1" rejected through the valve. This routine was continued until finally bulb "H_4" contained about 5 cc. of extremely pure liquid sulphur dioxide. These three distillations with the rejection of the first and last portions in each case, assured the purity of the gas finally used to make the solution in the cell.

Stop cocks "S_1", "S_6", "S_7" were now opened and the standard volumes and tubing flushed out several times with pure sulphur dioxide from bulb "H_4". Stop cock "S_1" was then closed, the apparatus evacuated until the McLeod Gauge showed the pressure to be at least as low as 10^{-3} mm., and stop cocks "S_2" and "S_7" closed.

Stop cock "S_1" was then opened and the freezing mixture removed from bulb "H_4" — as the liquid SO_2 evaporated, the pressure in the system could be followed on the small manometer "C". When the desired pressure was reached, "S_1" was closed and the unwanted liquid SO_2 in "H_4" allowed to evaporate through the mercury valve to the fan. The right hand side of manometer "C" was brought to the reference mark (10 mm. division), by applying air pressure or vacuum, as the case may be, to the mercury reservoir "R_1", and the following readings taken and recorded:

(a) The difference in level of the mercury in the arms of the manometer "C".

(b) The temperature of the mercury in the manometer.

(c) The temperature of the water surrounding the standard volumes "F" and "G".

(d) The temperature of the connecting tubing.

Bulb "H_5" was then surrounded with a freezing mixture which caused the gas in the standard volumes and the connecting tubing to condense in it. While waiting for equilibrium between the liquid and the gas, the magnetic stirrer was started and the lamp banks adjusted so that there was violent stirring of the water-calcium oxide mixture in the cell. This stirring together with the fact that the oil bath was cooled to as low a temperature as possible greatly facilitated the solution of the sulphur dioxide.

When there was no further condensation of liquid in bulb "H_5", stop cock "S_6" was closed, the mercury withdrawn from the U tube into reservoir "R_2" by the application of vacuum, and the carbon dioxide - acetone freezing mixture removed from around bulb "H_5". A few minutes were allowed for the liquid SO_2 to warm up and stop cock "S_7" opened. The pressure which had developed in "H_5" during the warming up caused the gas to rush down the connecting tube, through the capillary and into the cell where it at once began to dissolve in the water. By watching the level of the mercury in the tube just below scale "B" the rate at which the gas dissolved could be estimated. If too much pressure developed, that is, if the liquid sulphur dioxide evaporated at a greater rate than that at which the resulting gas could dissolve in the water, bulb "H_5" was surrounded momentarily by the freezing solution.

When all the liquid had evaporated from bulb "H_5" and the sulphur dioxide in the tubing was in equilibrium with the calcium oxide - sulphur dioxide - water system in the cell, the mercury was lifted into the U tube and the mercury-seal capillary to the point marked "L_3", and the capillary U-tube surrounded by a Dewar flask containing a carbon dioxide-acetone freezing solution.

The gas remaining in the tubing between stop cock "S_6" and the level of the mercury in the U-tube was condensed back into bulb "H_5" by replacing the freezing mixture; stop cock "S_7" was then closed and "S_6" opened. The freezing mixture was removed from around bulb "H_5", and the liquid allowed to evaporate into the standard volumes and the connecting tubing. After equilibrium had been reached, the pressure and temperature of the gas was measured as described before by first bringing the right hand side of manometer to the reference mark.

The method of calculating the exact weight of sulphur dioxide actually introduced into the cell from a knowledge of these temperatures and pressures will be fully discussed under the sections dealing with calculations.

Everything was now in readiness to start a run. The discussion of the procedure followed while making a run will follow shortly.

After a run had been completed on a solution prepared as described in the foregoing paragraphs, another solution having the same amount of calcium oxide and water but containing a higher percentage of sulphur dioxide could be prepared as follows:

The bath was cooled to room temperature, the mercury seal allowed to thaw by removing the freezing mixture and the mercury drawn down into the reservoir "R_2". Warming the cell slightly forced any remaining mercury out of the capillary. The amount of sulphur dioxide which was desired to be added for the second r was "weighed", condensed into bulb "H_5" and introduced into the cell as described before; the mercury was lifted into the capillary again, the seal frozen and the next run started.

After the desired range of sulphur dioxide concentrations had been covered for a given percentage of calcium oxide, the cell was cut out, cleaned and dried, and the complete procedure of preparing the solutions as described above repeated.

3. Making a Run:

After the mercury seal had been frozen, all electrical connections to the heaters, etc. were carefully inspected; the tube heating unit was connected and the tubing brought to the proper temperature (about 200°C). The thermo-regulator - relay - heater circuit was wired up and the heaters started. As the temperature increased, the mercury reservoir "R_3" of the large manometer was adjusted so as to keep the level of the mercury in scale "B" between the zero mark and the bottom of the lagging.

When the temperature was reached at which the first vapor pressure determination was to be made, the thermoregulator was set and time allowed for the system to come to equilibrium. The system was considered to be in equilibrium when the mercury level in scale "B" remained constant over the period of an hour. While equilibrium conditions were being approached the mercury reservoir "R_3" was frequently adjusted so as to keep the mercury surface in scale "B" at the zero mark.

Early experiments showed that the system under investigation exhibited a great tendency toward supersaturation. This is in agreement with the experience of former workers (41),(42), (51). This effect was so pronounced that on many occasions it took as long as ten or twelve hours for the system to come to equilibrium. When only two phases (gas and solution) were present, equilibrium was attained much more rapidly - usually two hours proved to be sufficient.

Preliminary tests were made with ascending and descending temperature in order to ascertain if the direction from which the equilibrium point was approached had any influence on its value. It is reasonable to suppose that with ascending temperature the value of the vapor pressure would be too low because of the fact that the gas is slow in leaving the solution. With descending temperature the converse is true because of the slowness with which the gas again dissolves in the solution. The tests showed however, that direction of approach had no effect on the value of the vapor pressure if sufficient time was allowed for the system to come to equilibrium. This interval proved to be about two hours in the case of a two phase system and upwards of six hours for a three phase system. More will be said about this later in the section dealing with the discussion of results.

Two or three check points were taken with descending temperature on most of the runs, and these points fell on the curves within experimental error.

While operating the oil bath at the higher temperatures it was found more convenient to employ two heaters. One of these was on constantly and all but kept the bath at the desired temperature; the other was wired up with the thermoregulator and supplied the small increment necessary to maintain the bath at the temperature desired.

When equilibrium was finally attained as indicated by the constancy of the mercury level in scale "B" over the period of an hour, the followings were taken and recorded:

1. The temperature of the oil bath.
2. Information necessary to make stem connection (if any) for the thermometer in the oil bath, i.e. temperature and length of the emergent stem.
3. Height of the mercury in large manometer.
4. Top, middle and bottom temperatures of large manometer.
5. Temprature of the heated tube connecting to cell to the manometer.

When these readings had been taken, the temperature of the oil bath was increased and the next reading taken; and so on until either a temperature of 140°C was reached or until the pressure had increased to about five atmospheres. Above five atmospheres the chances of an explosion were rather great. Furthermore, calculations on the first runs showed that if the log of the vapor pressures were plotted against the reciprocal of the absolute temperature a straight line resulted which made extrapolation reasonably accurate.

As the higher pressures were developed in the cell, it was necessary to pump air into the mercury reservoir "R_3" with the bicycle pump as previously described in order to keep the mercury in scale "B" at the zero mark.

The check points were obtained by cooling the oil bath by means of the copper cooling coil. During this cooling, great care had to be exercised to prevent mercury from being 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. Corrections Applied to Readings.
4. Calculations Necessary to get Readings in a Form in which they can be plotted.

1. Calculations on the Apparatus:

The calculations involved in this problem were exceedingly lengthy but not difficult. Most of the work was done on a Fuller Calculator which afforded five figure accuracy throughout. In the following sections all the calculations made will be explained, and where necessary, sample or type calculations included.

In order to calculate the weight of the sulphur dioxide gas introduced into the cell, the volume of all the connecting tubing had to be accurately known as well as the volumes "F" and "G" (See Fig. I) into which the gas was expanded. These so called "standard volumes", "F" and "G", were calibrated to the stop cocks by weighing the amount of water they hold and applying the necessary corrections for buoyancy, etc.

So as to avoid confusion in the ensuing discussion, the apparatus will be arbitrarily divided into the following "units".

Unit No. I:

The connecting tubing bounded by the stop cocks "S_1", "S_2", "S_3", "S_4", "S_5", "S_7" and a reference mark (the 10 mm. division) on the small manometer "C".

Unit No. II:

The tubing bounded by stop cock "S_7", the mercury level "L_2" and the reference point "L_4".

Unit No. III:

The tubing included between the points "L_4" and "L_3".

Unit No. IV :

Bounded by the point "L_3", and the zero point on scale "B". This unit includes the cell itself.

The volume of unit No. I was determined by expanding into it dry air at a known temperature and pressure from the standard volumes "F" and "G", reading the resultant pressure on the small manometer "C", and applying the gas laws. The standard volumes were totally submerged in water to protect them from any sudden fluctuation in temperature. Hot or cold water, as necessary, was added to bring these volumes to exactly room temperature just before a determination was made; this eliminated the necessity of a temperature correction.

The small manometer was equipped with a glass scale which necessitated the usual glass scale temperature correction. These corrections were read from tables (53).

In the following formula:

$$P_1V_1 = P_2V_2,$$

P_1 = Air pressure in standard volumes (usually atmospheric).

V_1 = Standard volume.

P_2 = Resultant pressure after expansion.

V_2 = Total volume after expansion.

Transposing, we have:

$$V_2 = \frac{P_1V_1}{P_2}$$

Now V_2, the total volume after expansion is equal to the standard volume plus the unknown volume, or:

$$V_2 = V_1 + x$$

where x = the unknown volume.

Substituting this value for V_2 into the above equation, the result is:

$$V_1 + x = \frac{P_1V_1}{P_2}$$

or

$$x = \frac{P_1V_1}{P_2} - V_1$$

To evaluate the volume of unit No. II, the tubing at the point "L_4" was sealed shut, the mercury in "R_2" brought to the reference work "L_2", and air expanded into this evacuated space as in the case of unit No. I. In this latter case, three determinations were possible at each evacuation - the air from unit No. I was first expanded, the resultant pressure read, and then a similar procedure followed for "F" and "G" in turn.

Unit No. III consisted entirely of capillary tubing. 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 mercury gave the volume.

The total volume represented by Units II, III and IV was determined by blowing the apparatus together again at the point "L_4", bringing the mercury in scale "B" to the zero mark and expanding air from the known volumes (Unit No. I, "F", and "G") into it.

To make corrections for the amount of sulphur dioxide that existed in the gas phase during a run the volume of Unit No. IV as an individual unit had to be known. This was found by subtracting the sum of the volumes of Units No. II and III from the figure representing the total volume of Units II, III and IV.

The Manometer Constant:

Since the large manometer was of the closed-end type, a manometer constant had to be determined in order that scale readings could be expressed in terms of pressure in centimeters of mercury. This constant was evaluated as follows:

Using a large cathetometer as a level, a point was found on the large manometer scale "A" which was exactly level with the zero point on scale "B". Scale "A" starts with zero at the top and reads down to about 400 cms. at the bottom. The point on scale "A" which was level with zero on scale "B" was found to be the 280.60 cm. division. With the cell open to the air the mercury reservoir "R_3" was raised until the mercury stood at zero on scale "B", and a reading of scale "A" taken. In the one particular determination under discussion, this reading was 290.30 cms. The wall barometer was read and after the necessary correction to zero (54) was made, the atmospheric pressure was found to be 76.42 cms.

Subtracting 280.60 from this reading of scale "A" gives us the difference in level between the mercury in scale "A" and that in scale "B":

$$\begin{array}{r} 290.30 \\ \underline{280.60} \\ 9.70 \text{ cms.} \end{array}$$

A correction had to be made to bring this figure to the corresponding figure at 0°C. by multiplying by the density of mercury at the temperature of the manometer and dividing by the density of mercury at 0°C.

$$\frac{9.70 \times 13.541}{13.596} = 9.65 \text{ cms.}$$

From the figures of Gurd (42) for the calibration of the manometer, the volume of the air trapped above the mercury surface in the manometer above the 290.30 division was found by interpolation to be 225.11 cc.

Now the pressure exerted by this enclosed air is equal to atmosphere pressure plus the corrected difference between the mercury levels, i.e.

$$\begin{array}{r} 76.42 \\ \underline{9.65} \\ 86.07 \text{ cms.} \end{array}$$

From the gas laws we have:

$$PV = KT$$

or,

$$K = \frac{PV}{T}$$

where:

K = A constant.

P = Pressure of the trapped air.

V = Volume of the trapped air.

T = Absolute temperature of the trapped air.

The temperature of the trapped air was averaged from the readings of the three thermometers hung against the manometer tube.

Substituting values into the above equation, the value of the manometer constant was found to be:

$$\frac{86.07 \times 225.11}{295.8} = 65.50 \text{ (cm. and cc.)}$$

Several determinations of this constant were made at different atmospheric pressures all of which checked to within one part in six thousand.

2. Calculations on the Introduction of Reagents:

No correction or calculations were necessary relative to the introduction of calcium oxide or of water. The buoyancy correction involved in weighing the water was negligably small. The bulb from which the water was distilled into the cell proper, was flamed with a hand-torch just prior to sealing off, and since its volume was only of the order of 125 cc., it contained only a negligable weight of water vapor.

The weight of sulphur dioxide introduced into the cell was calculating from a knowledge of the pressure exerted by the gas in a known volume, at a known temperature. All small manometer readings had to be corrected to 0° C. as explained before. The weight of SO_2 was calculated from the formula of Maass and Maass (21)

$$m = \left[68.06 + (M - 64.06)\ P\right] \times \frac{PV}{RT}$$

where:

m = mass of gas in grams.

P = Pressure in atmospheres.

T = Temperature absolute.

V = Volume in litres.

R = 0.08207.

M, the molecular weight of the gas, is given from a curve constructed from the following data:

t° C.	M
38.05	65.20
22.9	65.27
10.35	65.42
1.4	65.60
0.8	65.61
-6.55	65.76

After the water in the cell was in equilibrium with the gas in the tubing and the mercury seal had been raised and frozen, the residual gas in the connecting tubing was condensed back into the known volume, and its temperature and pressure read. To arrive at the true weight of gas in the cell, the weight of this residual gas had to be subtracted from the weight of the SO_2 in the known volumes before introduction.

A small amount of sulphur dioxide was trapped in the tube between the top of the mercury in the "U" tube and stop cock "S_7". The volume of this much tubing was calculated from a knowledge of the length and the internal diameter; the temperature was that of the freezing mixture (-78° C.) and the pressure, the vapor pressure of SO_2 at that temperature. Knowing these figures the weight of the gas could be calculated from the gas laws, and was found to be 0.0006 gm.

So that this point will be absolutely clear, the data for an actual case will be given and the complete calculation shown.

In this particular case under discussion the following data were recorded:

1 . Total volume of the standard volumes("F" plus "G") = 714.62 cc.

2 . Volume of connecting tubing (so called Unit No. I) = 102.13 cc.

3 . Pressure of the SO_2 in these volumes before injection into the cell as read from the small manometer = (798.7 - 10.0) = 787.8 mm.

4 . True pressure after the glass scale correction had been made = 784.5 mm.

5 . Temperature of volumes "F" and "G" = 25.4° C.

6.. Average temperature of connecting tubing = 24.7° C.

7 . Molecular weight of SO_2 at the average temperature = 65.25.

8 . Pressure of the SO_2 in the volumes and tubing after injection had taken place = (30.5 - 10.0) = 20.5 mm. The glass scale correction was negligably small in this case.

9 . Temperature of the volumes "F" and "G" = 25.2° C.

10 . Average temperature of connecting tubing = 24.9° C.

11 . Molecular weight of SO_2 at the average temperature = 65.25 .

Substituting these figures into the formula previously given -

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

we have:

$$+ \left[64.06 + 1.19 \times \frac{784.5}{760} \times \frac{784.5 \times 102.13}{760 \times 1000 \times .08207 \times 297.8}\right]$$

$$+ \left[64.06 + 1.19 \times \frac{784.5}{760} \times \frac{784.5 \times 714.62}{760 \times 1000 \times .08207 \times 298.5}\right]$$

$$- \left[64.06 + 1.19 \times \frac{20.5}{760} \times \frac{20.5 \times 102.13}{760 \times 1000 \times .08207 \times 298.0}\right]$$

$$- \left[64.06 + 1.19 \times \frac{20.5}{760} \times \frac{20.5 \times 714.62}{760 \times 1000 \times .08207 \times 298.3}\right]$$

Of these four parts the first plus bracket represents the weight of sulphur dioxide in the connecting tubing before injection into the cell. The second plus bracket represents the weight of the gas in the volumes "F" and "G" before injection. The first negative bracket represents the weight of the gas in the connecting tubing after injection, and the second negative bracket represents the weight of the gas in the volumes "F" and "G" after injection. The algebraic sum of these four brackets minus 0.0006 gm. which is the weight of the gas trapped between the mercury in the "U" tube and stop cock "S_7", represents the weight of sulphur dioxide introduced into the cell.

3. Corrections applied to the Readings:

For each point on the Log vapor pressure – $\frac{1}{T}$ curve the following readings were taken:

1. Time.
2. Temperature of the oil bath.
3. Temperature and length of the emergent mercury thread (if any) of the bath thermometer.
4. Height of mercury on scale "A". (Large Manometer).
5. Temperature of the large manometer at top, middle and bottom.
6. Average temperature of the heated tubing connecting the cell with the manometer.

The reading of the temperature of the oil bath was subject to two corrections: first, the error inherent in the thermometer itself, and second, the stem correction; if any.

The first of these corrections was read from the calibration tables for the thermometers; the second was calculated from the usual formula:

$$S = 0.00016\, n\, (t' - t)$$

where:

n = Length of exposed mercury column in terms of scale degrees.

t' = Temperature of the bath.

t = Average temperature of the stem.

Further along in the calculations a correction had to be added to the pressures because of the six cms. of mercury in scale "B" which was heated above the temperature of the bath. An explanation may help:- The mercury in tube "B" is heated — it expands and its density decreases — hence it takes up a position above the zero on scale "B". To bring it back to zero the leveling bulb "R_3" of the manometer must be lowered; this also lowers the mercury level in the large manometer tube. Thus the pressures as read on the manometer are too low.

As stated before, the usual glass scale correction had to be applied to all readings taken on the small manometer "C". Corrections that had to be applied to readings taken on the large manometer will be discussed at length in the following paragraphs.

Time	Temperature	Correct Temperature	$\frac{1}{T}$	Scale (cms.)	Mercury Pressure	Correct Mercury Pressure	Volume (cc.)	t_1	t_2	t_3	Ave. Man. Temperature	Air Pressure	Total Pressure (cms.)	Log Pressure	P.p. Water	Times Mole Fraction	P.p. SO_2	Temp. of Gas Phase	Weight SO_2 in Gas Phase	Weight SO_2 in Liquid Phase	Percent SO_2 in Liquid Phase	Stem Correction
3	15.2	15.2	.003468	322.30	-41.70	-41.52	250.61	24.0	25.1	26.1	298.2	77.94	36.6	1.564	1.3	1.3	35.3	206	0.0385	4.8437	6.860	. . . . No Emergent Stem . . . .
6	27.3	27.3	.003329	306.50	-25.90	-25.78	238.08	23.1	24.9	25.6	297.6	81.88	56.3	1.751	2.7	2.7	53.6	211	0.0568	4.8254	6.834	
9	40.2	40.2	.003192	285.05	-4.45	-4.43	220.85	24.3	25.2	26.2	298.8	88.62	84.4	1.926	5.5	5.5	78.9	211	0.0815	4.8007	6.798	
12	52.5	52.5	.003072	259.20	21.40	21.30	200.47	24.2	25.1	26.0	298.7	97.60	119.4	2.076	10.5	10.2	108.9	209	0.1101	4.7721	6.758	
15	65.3	65.3	.002955	228.25	52.35	52.12	176.92	23.8	24.9	25.4	298.3	110.45	162.8	2.212	19.0	18.5	144.3	203	0.1436	4.7368	6.710	
18	76.8	76.8	.002858	194.10	86.50	86.13	150.59	23.3	24.6	25.0	297.9	129.57	215.9	2.334	31.1	30.3	185.6	206	0.1807	4.7015	6.658	
21	90.4	90.4	.002754	158.30	122.30	121.76	122.80	23.6	24.6	25.1	298.0	158.95	280.9	2.449	53.4	52.1	228.8	210	0.2175	4.6647	6.606	
24	105.7	104.8	.002646	119.30	161.30	160.59	92.43	23.4	24.4	25.0	298.1	211.22	372.0	2.571	92.8	90.5	281.5	209	0.2615	4.6207	6.544	
28	60.7	60.7	.002996	239.60	41.00	40.89	185.60	23.2	24.1	24.9	297.6	105.03	146.1	2.165	15.4	15.0	131.1	204	0.1313	4.7509	6.728	
31	35.6	35.6	.003240	293.30	-12.70	-12.65	227.53	21.4	22.2	22.9	295.7	85.12	72.7	1.862	4.4	4.3	68.4	206	0.0715	4.8107	6.813	
34	14.0	14.0	.003483	323.45	-42.85	-42.68	251.51	21.3	23.1	23.6	295.8	77.03	34.6	1.539	1.2	1.2	33.4	208	0.0364	4.8458	6.862	

Table 1

4. Calculations Necessary to get Readings in a Form in Which They can be Plotted:

In order to make these calculations clear and comprehensive, the data for one particular run - Series D No. 3 - will be tabulated and exhaustively discussed.

Table 1 shows a copy of a typical page of data, and represents the figures associated with the run under discussion. The column headings will be explained one by one starting from the left hand side:

Time:	Absolute time having no influence on this work, only relative times are used. Zero corresponds to the time at which the thermoregulator was set prior to the first vapor pressure reading.
Temp:	The temperature of the thermostated oil bath as read from the thermometer.
Correct Temp:	The true temperature of the oil bath i.e., after corrections for thermometer and emergent stem had been made.
$\frac{1}{T}$:	The reciprocal of the absolute temperature of the oil bath.
Scale:	The reading as taken from scale "A".

Mercury Pressure: The figures in this column were obtained by subtracting 280.60 from the reading of scale "A" if said reading was numerically greater than 280.60. In such a case the "mercury pressure" is negative. If, on the other hand, the reading of scale "A" was numerically less than 280.60, then 280.60 is subtracted from said reading. In this latter case the "mercury pressure" is positive. It must be remembered that the figure 280.60 represents the point on scale "A" that is level with the zero point on scale "B". The figures in this column, then, represent the difference in level between the mercury surfaces in scales "A" and "B": negative if "A" is below "B" and positive if "A" is above "B".

Correct: Mercury Pressure The figures in this column are the result of correcting the figures in the previous column to 0°C.

Volume: These figures represent the volume of the closed manometer tube above the point recorded in column marked "Scale".

t_1, t_2, t_3 : The temperature of the manometer tubing at the bottom, the middle, and the top respectively.

Ave. Man. Temp. : The average temperature of the manometer in degrees Absolute.

Air Pressure : From a knowledge of the manometer constant, the average absolute temperature of the manometer and the volume of the air trapped above the mercury surface, the pressure exerted by this air can be calculated. The figures in this column represent these pressures.

Total Pressure : The algebraic sum of "Correct Mercury Pressure" and "Air Pressure" plus a small correction that arises because of the six centimeters of hot mercury in scale "B".

Log Pressure : The logarithm of "Total Pressure".

P.P. Water. : The partial pressure of water vapor at the temperature recorded in column headed"Correct Temp."

Times Mole Fraction : The figures in the previous column multiplied by the mole fraction of water present in this particular run, i.e.,

$$\left[\frac{\frac{\text{Weight of } H_2O}{18}}{\frac{\text{Weight } CaO}{56} + \frac{\text{Weight } SO_2}{64} + \frac{\text{Weight } H_2O}{18}} \right]$$

P.P. SO_2 : These figures represent the partial pressure of sulphur dioxide at the temperature recorded in column headed "Correct Temp.". They were obtained by subtracting the figures in "Times Mole Fraction" from the figures in "Total Pressure".

Temp. of Gas Phase. : The average temperature as recorded by the two thermometers imbedded in the lagging of the heated tube connecting the cell with the manometer.

Wt. SO_2 in Gas Phase : To arrive at these figures, the gas volume was divided into two parts; that in the cell immediately over the solution; which was at the same temperature as the solution; and that which was in the heated tubing at a higher temperature. Knowing these volumes, the temperatures, and the partial pressure of sulphur dioxide, the weight of the gas in each part could be calculated directly from the gas laws. The sum gave the total weight of SO_2 in the gas phase.

It should be noted here that the weight of water vapor present in the gas phase was negligably small compared to the total weight of the system.

Wt. SO_2 in Liquid Phase:	The total weight of sulphur dioxide introduced into the cell minus the weight of this gas in the gas phase gave these figures.
Percent SO_2 in Liquid Phase :	The weight of SO_2 in the liquid phase divided by the total weight of the system.
Stem Correction :	Data for correcting the oil bath thermometer for emergent stem (if any).

When all these calculations had been completed, the material was ready to be plotted. The tabulation of results and their subsequent graphical representation belongs in the sections dealing with results and for this reason will not be included here.

RESULTS

RESULTS

The experimental data consists of fifteen complete "runs", that is, vapor pressure determinations at appropriate temperatures between 25° and 130°C. on each of fifteen separate and distinct solutions. The data falls naturally into four groups or "series" corresponding to the different percentages of lime investigated. Series A, consists of four runs made on solutions containing approximately 0.50% calcium oxide and with sulphur dioxide concentrations of 1.11%, 2.07%, 3.86% and 6.71% respectively. More will be said later about the actual concentrations of lime and sulphur dioxide present in the different runs. Series B consists of four runs made on solutions containing approximately 0.75% calcium oxide and with sulphur dioxide concentrations of 1.53%, 2.96%, 3.01% and 5.77% respectively. In Series C the calcium oxide concentration was approximately 1.00%, and the sulphur dioxide concentrations were 2.21%, 3.41%, 4.47% and 6.60%. Series D consisted of three runs made on solutions containing approximately 1.25% calcium oxide and with sulphur dioxide concentrations of 2.52%, 3.91% and 6.86%.

Whenever percentage composition is mentioned, the figures given were obtained by dividing the weight of the component in question by the total weight of the system i.e., the weight of water plus the weight of calcium oxide plus the weight of sulphur dioxide.

Before any attempt was made to obtain any experimental data relative to the system calcium oxide - sulphur dioxide - water, the apparatus was ridigly tested three times. As a preliminary test of the manometer, the vapor pressure of pure water was determined over the range 40° to 140°C. The points obtained fell on the curve drawn from information taken from the International Critical Tables (56) well within the experimental error. The next step was to test the gas-measuring section of the apparatus, and also, incidentally, to test the validity of the correction necessitated by the fact that some sulphur dioxide leaves the liquid phase during a run. This was accomplished by introducing a calculated amount of sulphur dioxide into the cell which already contained the pure water employed in the aforementioned test, and measuring the vapor pressure of this sulphur dioxide - water system over the appropriate temperature range. After the necessary corrections were made, including the correction due to some sulphur dioxide being present in the gas phase, the results were plotted, and found to fall on a curve constructed from the data of

Campbell (22) for a solution having the same sulphur dioxide concentration.

As a final test a three component system was made up containing 1.12% calcium oxide and approximately 1.01% sulphur dioxide. This system was of course three-phase throughout the entire run since the sulphur dioxide added was insufficient to convert all the calcium oxide present into the soluble calcium bisulphite. The fact that this was a three-phase system is significant due to the fact that three phase systems are the most difficult to investigate because of the slowness with which equilibrium is reached. With ascending temperature runs, the pressures will have a tendency to be too low if insufficient time is allowed for the attainment of equilibrium, because the sulphur dioxide is relatively slow in leaving the liquid phase. The data obtained from this last test were plotted with vapor-pressure and temperature as ordinates. The points fell on a smooth curve exactly parallel with the curve representing the vapor pressure of water. The distance between these curves was constant throughout the entire range and represented a pressure difference of one centimetre.

Although the data obtained in this test run are in perfect agreement with the remainder of the experimental results the actual figures will not be given because of a slight uncertainty about the exact weight of sulphur dioxide that was present in the system.

These three tests definitely show that: (i), the apparatus is functioning properly, (ii), the calibration of the manometer and the determination of the manometer constant are correct and (iii), the manometer is capable of measuring low pressures accurately.

A great deal of calculation was involved in the co-relation and tabulation of the experimental data, and a vast number of curves had to be drawn. Table 1 shows the number of experimental observations necessary, and the mathematical treatment of each reading for one particular run (Series D, Run No. 3). It is obviously impracticable and unnecessary to include all this data for each run. It was considered expedient however, to include sufficient data to permit of check calculations is so desired. As a means to this end, two sets of tables are included containing the necessary information in a condensed form. These will be referred to as the "series" tables and the "run" tables.

Tables 2 - 5 are the "series" tables; each contains information common to all the runs in its particular series. The headings are for the most part self explanatory, but some deserve explanation. "P_1", represents the corrected

Series A

Run No.	Gms. Water Present	Gms. Lime Present	Sulphur Dioxide Added						Gms. SO_2 Present	Volume of Gas Phase		Temp. Of Gas Phase
			P_1 cms.	P_2 cms.	V_1 cc.	V_2 cc.	t_1	t_2		In Bulb. (cc.)	In Heated Tube	
1	65.114	0.3403	32.46	1.54	100.80	587.82	24.1 24.2	24.0 24.4	0.7406	21.3	20.0	200°
2	65.114	0.3403	29.11	1.36	100.80	587.82	25.6 25.5	26.0 25.9	1.3999	20.9	20.0	205°
3	65.114	0.3403	46.44	2.58	100.80	714.62	25.7 25.9	25.8 25.8	2.6577	20.0	20.0	205°
4	65.114	0.3403	77.18	3.08	100.80	714.62	26.3 27.3	25.7 25.8	4.7630	18.4	20.0	205°

Table 2

Series B

Run No.	Gms. Water Present	Gms. Lime Present	Sulphur Dioxide Added						Gms. SO_2 Present	Volume of Gas Phase		Temp. Of Gas Phase
			P_1 cms.	P_2 cms.	V_1 cc.	V_2 cc.	t_1	t_2		In Bulb. (cc.)	In Heated Tube	
1	74.958	0.5974	43.47	1.56	101.59	714.62	27.6 28.1	26.8 26.8	1.1785	20.0	18.5	160°
2	74.956	0.5965	82.91	2.32	101.59	714.62	24.4 24.4	24.5 24.9	2.3181	19.0	18.6	160°
3	74.837	0.6001	84.22	1.97	101.59	714.62	25.1 25.5	25.0 25.5	2.3595	20.0	29.5	165°
4	74.898	0.5948	83.32	2.09	101.59	714.62	23.4 23.5	23.9 23.9				
			83.34	2.69	101.59	714.62	24.0 24.0	24.5 24.7	4.6743	18.0	31.5	155°

Table 3

Series C

Run No.	Gms. Water Present	Gms. Lime Present	Sulphur Dioxide Added						Gms. SO_2 Present	Volume of Gas Phase		Temp. Of Gas Phase
			P_1 cms.	P_2 cms.	V_1 cc.	V_2 cc.	t_1	t_2		In Bulb. (cc.)	In Heated Tube	
1	77.422	0.7977	34.05	2.66	101.57	714.62	26.0 26.1	24.9 25.0	1.7711	11.0	20.6	145°
2	77.457	0.7975	34.06	1.61	101.57	714.62	24.3 23.8	25.5 25.4	2.7792	16.0	18.8	155°
3	77.457	0.7975	34.22	3.66	101.57	714.62	24.9 24.8	24.0 24.1	3.6821	16.0	18.1	155
4	77.457	0.7975	68.21	2.70	101.57	714.62	23.2 23.0	23.1 23.0	5.5691	14.0	18.8	155°

Table 4

Series D

Run No.	Gms. Water Present	Gms. Lime Present	Sulphur Dioxide Added						Gms. SO_2 Present	Volume of Gas Phase		Temp. Of Gas Phase
			P_1 cms.	P_2 cms.	V_1 cc.	V_2 cc.	t_1	t_2		In Bulb. (cc.)	In Heated Tube	
1	74.988	1.0018	70.10	1.35	102.13	714.62	27.3 27.5	26.6 27.0	1.9736	20.0	29.5	165°
2	64.866	0.8650	49.38	1.16	102.13	714.62	25.6 26.3	25.4 25.8				
			52.62	2.01	102.13	714.62	25.6 25.8	25.4 25.6	2.6929	20.2	20.0	210°
3	64.866	0.8650	78.45	2.05	102.13	714.62	24.7 25.4	24.9 25.2	4.8822	18.6	20.0	210°

Table 5

pressure of sulphur dioxide in the gas measuring system before injection into the cell, "P_2" represents the corrected pressure after injection. "V_1" is the volume of the connecting tubing (Unit No. 1) of the gas measuring system, "V_2" is the volume of the bubls "F" and "G" (See Fig. 1) either singly or two together. Under "t_1" are listed temperatures in groups of two; the first of these represents the temperature of the connecting tubing, the second that of the bulbs "F" and "G" before injection of the gas. Under "t_2" are listed the corresponding temperatures after the injection of the gas into the cell.

The figures in the last column represent the average temperature of the gas phase; the temperature did not remain absolutely constant during a run, but the variation was not more than two or three degrees from the average.

Notice that in Series B, run No. 4, and also in Series D, run No. 2, two injections of sulphur dioxide gas were necessary to bring the solution in the cell up to the desired concentration.

Notice also that in Series C, run No. 1, there was 0.8844 gms. of sulphur dioxide in the system before this injection. An accident occurred just after run C-1 and the cell had to be cut out, cleaned and a fresh start made. The run immediately after this accident was discarded and run C-2 started. This accounts for the presence of 1.8551 gms. of sulphur dioxide in the system prior to injection C-2.

Tables 6 - 20 show all necessary data for each run; the column headings are self explanatory. For convenience the composition of each run is shown just above the table.

The data from the fifteen runs were plotted on four graphs drawn to a large scale, one graph for each series of runs. The reciprocals of the absolute temperatures were plotted as abscissae, the log of the total vapor pressure in centimetres as the left ordinate, and the concentration of sulphur dioxide in the solution as the right hand ordinate. Thus each graph contained eight curves, (with the exception of Series D, which contained six) making in all thirty curves. Figure 4 shows these curves for Series C drawn to a small scale. It should be noted here that Figures 4, 5, 6 and 7 are included solely for the purpose of illustration as in most cases the scales are too small to be practical; all the data for the reconstruction of curves is given in tables.

In ofder that the results from this investigation be comprehensive and of some value to future workers, it was deemed imperative that the final tables contain figures representing the total vapor pressures of solutions containing even percentages of sulphur dioxide and calcium oxide,

Series A Run No. 1

65.114 gms. H_2O ; 0.3403 gms. CaO ; 0.7406 gms. SO_2

Observations			Calculated Values			
Bath Temp.	Manom. Scale Reading	Average Manom. Temp.	Percent SO_2 in Solution	Percent CaO in Solution	Temp. of Soln.	Vapor Pressure cms.
20.7	347.20	296.7	1.114	0.514	20.7	4.4
40.2	342.75	297.0	1.109	0.514	40.5	11.2
60.3	333.10	296.9	1.106	0.514	60.3	22.9
80.9	310.70	298.0	1.099	0.514	80.8	51.2
100.6	277.60	298.9	1.089	0.514	99.6	94.2
121.1	216.60	299.4	1.081	0.514	120.9	180.6
141.0	141.85	299.1	1.058	0.514	140.5	316.4
85.9	304.75	298.4	1.097	0.514	85.8	58.7

Table 6

Series A Run No. 2

65.114 gms. H_2O ; 0.3403 gms. CaO ; 1.3999 gms. SO_2

Observations			Calculated Values			
Bath Temp.	Manom. Scale Reading	Average Manom. Temp.	Percent SO_2 in Solution	Percent CaO in Solution	Temp. of Soln.	Vapor Pressure cms.
20.1	341.35	298.7	2.073	0.509	20.1	13.3
40.4	330.65	297.9	2.059	0.509	40.4	26.2
60.5	313.75	298.2	2.042	0.509	60.5	47.3
80.6	286.50	298.3	2.021	0.509	80.6	82.3
100.7	244.90	297.2	1.998	0.509	99.7	138.4
120.9	183.70	297.8	1.973	0.509	120.7	233.5
140.9	114.10	298.1	1.934	0.509	140.4	387.0
84.2	279.90	297.3	2.018	0.509	84.2	90.8

Table 7

Series A Run No. 3

65.114 gms. H_2O ; 0.3403 gms. CaO ; 2.6577 gms. SO_2

Observations			Calculated Values			
Bath Temp.	Manom. Scale Reading	Average Manom. Temp.	Percent SO_2 in Solution	Percent CaO in Solution	Temp. of Soln.	Vapor Pressure cms.
20.2	329.75	298.0	3.860	0.500	20.2	27.4
35.0	315.20	297.8	3.836	0.500	35.0	45.4
50.3	294.95	299.2	3.805	0.500	50.3	71.5
65.3	267.70	298.4	3.767	0.500	65.3	107.5
80.3	233.90	299.2	3.725	0.500	80.3	154.8
95.5	193.10	298.7	3.689	0.500	95.5	212.0
110.8	150.50	299.5	3.631	0.500	110.2	297.7
120.4	122.30	299.7	3.599	0.500	120.2	364.9
75.7	244.95	299.9	3.738	0.500	75.7	139.3

Table 8

Series A Run No. 4

65.114 gms. H_2O ; 0.3403 gms. CaO ; 4.7630 gms. SO_2

Observations			Calculated Values			
Bath Temp.	Manom. Scale Reading	Average Manom. Temp.	Percent SO_2 in Solution	Percent CaO in Solution	Temp. of Soln.	Vapor Pressure cms.
20.4	310.40	298.6	6.709	0.485	20.4	51.4
32.7	289.25	298.5	6.672	0.485	32.7	78.8
45.3	261.30	299.2	6.625	0.485	45.3	116.4
57.3	230.30	298.8	6.575	0.485	57.3	159.9
70.4	192.20	298.7	6.510	0.485	70.4	219.4
82.8	155.30	298.3	6.442	0.485	82.8	287.1
96.3	118.20	299.0	6.362	0.485	96.3	375.8
60.4	221.70	298.4	6.558	0.485	60.4	172.9
25.6	302.30	299.0	6.693	0.485	25.6	61.7

Table 9

Series B Run No. 1

74.958 gms. H_2O ; 0.5974 gms. CaO ; 1.1785 gms. SO_2

Observations			Calculated Values			
Bath Temp.	Manom. Scale Reading	Average Manom. Temp.	Percent SO_2 in Solution	Percent CaO in Solution	Temp. of Soln.	Vapor Pressure cms.
20.1	348.30	298.8	1.531	0.779	20.1	4.8
40.2	343.55	298.0	1.529	0.779	40.2	10.4
60.4	333.60	298.7	1.525	0.779	60.4	22.7
81.1	312.00	299.0	1.519	0.779	81.1	49.6
100.0	276.50	294.5	1.512	0.779	100.1	94.3
119.5	210.50	300.0	1.479	0.779	119.4	190.2

Table 10

Series B Run No. 2

74.956 gms. H_2O ; 0.5965 gms. CaO ; 2.3181 gms. SO_2

Observations			Calculated Values			
Bath Temp.	Manom. Scale Reading	Average Manom. Temp.	Percent SO_2 in Solution	Percent CaO in Solution	Temp. of Soln.	Vapor Pressure cms.
20.2	338.35	298.0	2.956	0.766	20.2	16.7
40.4	325.80	298.0	2.940	0.766	40.4	32.1
60.6	305.45	297.2	2.922	0.766	60.6	57.3
80..9	274.75	299.4	2.898	0.766	80.9	98.2
100.5	228.55	298.3	2.871	0.766	100.8	162.2
120.6	161.20	297.7	2.826	0.766	120.5	294.9
134.1	115.40	299.4	2.787	0.766	133.8	384.8

Table 11

Series B Run No. 3

74.837 gms. H_2O ; 0.6001 gms. CaO ; 2.3595 gms. SO_2

Observations			Calculated Values			
Bath Temp.	Manom. Scale Reading	Average Manom. Temp.	Percent SO_2 in Solution	Percent CaO in Solution	Temp. Of Soln.	Vapor Pressure cms.
20.7	339.75	297.3	3.010	0.771	20.7	14.8
39.9	327.85	297.3	2.992	0.771	39.9	29.5
60.7	306.85	296.3	2.965	0.771	60.7	55.4
80.3	277.10	300.0	2.933	0.771	80.3	95.2
99.4	233.60	298.8	2.903	0.771	99.5	155.0
116.5	178.85	297.3	2.870	0.771	116.1	241.9
135.4	114.30	297.2	2.806	0.771	135.1	385.8
80.4	274.60	293.4	2.932	0.771	80.4	96.6

Table 12

Series B Run No. 4

74.898 gms. H_2O ; 0.5948 gms. CaO ; 4.6743 gms. SO_2

Observations			Calculated Values			
Bath Temp.	Manom. Scale Reading	Average Manom. Temp.	Percent SO_2 in Solution	Percent CaO in Solution	Temp. of Soln.	Vapor Pressure cms.
19.4	321.70	297.8	5.769	0.742	19.4	37.4
35.8	299.20	298.1	5.727	0.742	35.8	65.9
51.1	270.50	298.5	5.674	0.742	51.1	103.7
65.3	237.30	298.8	5.618	0.742	65.3	149.7
81.5	193.60	299.9	5.543	0.742	81.5	217.5
95.2	154.20	299.5	5.473	0.742	95.3	290.0
108.5	120.90	300.4	5.411	0.742	107.9	369.1
62.1	243.65	300.0	5.602	0.742	65.1	141.0

Table 13

Series C No. 1.

77.422 gms. H_2O ; 0.7977gms. CaO ; 1.7711 gms. SO_2

Observations			Calculated Values			
Bath Temp.	Manom. Scale Reading	Average Manom. Temp.	Percent SO_2 in Solution	Percent CaO in Solution	Temp. of Soln.	Vapor Pressure cms.
24.7	345.40	297.4	2.208	0.997	24.7	7.9
30.2	344.50	298.8	2.207	0.997	30.2	9.4
35.1	342.95	298.6	2.206	0.997	35.1	11.3
49.8	336.05	296.7	2.203	0.997	49.8	19.2
65.5	323.85	296.9	2.197	0.997	65.5	34.9
80.2	304.65	296.9	2.190	0.997	80.2	58.3
94.7	277.15	298.4	2.180	0.997	94.7	94.7
110.2	236.45	298.4	2.168	0.997	109.6	150.8
125.5	180.75	298.0	2.149	0.997	125.3	238.8
140.4	126 45	298.1	2.137	0.997	140.0	253.0

Table 14

Series C Run No. 2

77.457 gms. H_2O ; 0.7975 gms. CaO ; 2.7792 gms. SO_2

Observations			Calculated Values			
Bath Temp.	Manom. Scale Reading	Average Manom. Temp.	Percent SO_2 in Solution	Percent CaO in Solution	Temp. of Soln.	Vapor Pressure cms.
19.8	340.70	299.4	3.414	0.984	19.8	14.2
30.0	335.20	298.1	3.408	0.984	30.0	20.6
40.0	328.40	298.0	3.401	0.984	40.0	29.0
50.0	319.90	298.5	3.394	0.984	50.0	39.6
65.0	302.95	299.3	3.381	0.984	65.0	61.2
81.2	275.95	299.2	3.362	0.984	81.1	96.5
95.3	242.65	298.7	3.342	0.984	95.3	142.0
114.4	188.50	297.7	3.329	0.984	114.1	225.1
122.4	150.00	298.9	3.281	0.984	122.3	298.1
126.6	135.45	299.3	3.270	0.984	126.5	331.1
89.6	254.30	298.2	3.346	0.984	89.6	125.8
40.5	327.50	296.2	3.401	0.984	40.5	29.4
25.2	337.55	296.9	3.411	0.984	25.2	17.2

Table 15

Series C Run No. 3

77.457 gms. H_2O ; 0.7975 gms. CaO ; 3.6821 gms. SO_2

Observations			Calculated Values			
Bath Temp.	Manom. Scale Reading	Average Manom. Temp.	Percent SO_2 in Solution	Percent CaO in Solution	Temp. of Soln.	Vapor Pressure cms.
19.9	332.60	297.1	4.467	0.973	19.9	23.5
30.7	323.50	295.8	4.462	0.973	30.7	34.4
41.1	312.45	296.8	4.443	0.973	41.1	48.5
56.0	292.05	297.3	4.419	0.973	56.0	77.9
71.3	263.90	296.6	4.396	0.973	71.4	111.9
84.8	233.20	297.4	4.370	0.973	84.8	155.1
99.6	193.65	298.2	4.340	0.973	99.7	216.7
118.6	135.20	297.4	4.292	0.973	118.5	330.7
90.7	217.30	298.1	4.357	0.973	90.8	179.0
60.8	283.95	298.6	4.414	0.973	60.8	85.7
32.1	322.20	297.8	4.451	0.973	32.1	39.1

Table 16

Series C Run No. 4

77.457 gms. H_2O ; 0.7975 gms. CaO ; 5.5691 gms. SO_2

Observations			Calculated Values			
Bath Temp.	Manom. Scale Reading	Average Manom. Temp.	Percent SO_2 in Solution	Percent CaO in Solution	Temp. of Soln.	Vapor Pressure cms.
21.2	315.30	297.3	6.596	0.951	21.2	44.8
30.7	301.40	297.4	6.578	0.951	30.7	62.6
45.3	273.85	297.9	6.545	0.951	45.3	98.9
71.1	208.80	297.8	6.469	0.951	71.2	192.0
86.4	164.60	297.6	6.413	0.951	86.4	268.3
100.3	125.70	297.9	6.361	0.951	100.4	354.3
55.7	249.35	296.4	6.516	0.951	55.7	131.8

Table 17

Series D Run No. 1

74.988 gms. H_2O ; 1.0018 gms. CaO ; 1.9736 gms. SO_2

Observations			Calculated Values			
Bath Temp.	Manom. Scale Reading	Average Manom. Temp.	Percent SO_2 in Solution	Percent CaO in Solution	Temp. of Soln.	Vapor Pressure cms.
19.6	348.50	298.4	2.522	1.285	19.6	4.4
40.7	342.55	299.6	2.518	1.285	40.7	12.0
61.1	329.05	299.3	2.509	1.285	61.1	28.5
80.3	306.20	299.2	2.495	1.285	80.2	57.1
100.7	264.05	294.5	2.474	1.285	100.7	111.2
120.8	202.30	299.1	2.445	1.285	120.6	203.0
140.2	131.30	299.4	2.398	1.285	138.7	341.6
75.0	312.70	298.3	2.497	1.285	75.0	48.8

Table 18

Series D Run No. 2

64.866 gms. H_2O ; 0.8650 gms. CaO ; 2.6929 gms. SO_2

Observations			Calculated Values			
Bath Temp.	Manom. Scale Reading	Average Manom. Temp.	Percent SO_2 in Solution	Percent CaO in Solution	Temp. of Soln.	Vapor Pressure cms.
20.1	338.75	298.2	3.911	1.264	20.1	16.4
35.3	330.15	298.7	3.899	1.264	35.3	27.0
50.2	317.40	298.4	3.883	1.264	50.2	42.8
65.3	300.00	298.9	3.865	1.264	65.3	64.9
80.2	270.50	299.2	3.833	1.264	80.2	104.0
95.4	228.40	299.3	3.799	1.264	95.4	162.9
112.4	174.75	299.0	3.745	1.264	111.8	250.1
129.6	117.55	299.3	3.683	1.264	129.4	377.8
90.3	242.50	299.0	3.805	1.264	90.3	142.2
35.1	329.70	297.1	3.899	1.264	35.1	27.2

Table 19

Series D Run No. 3

64.866 gms. H_2O ; 0.8650 gms. CaO ; 4.8822 gms. SO_2

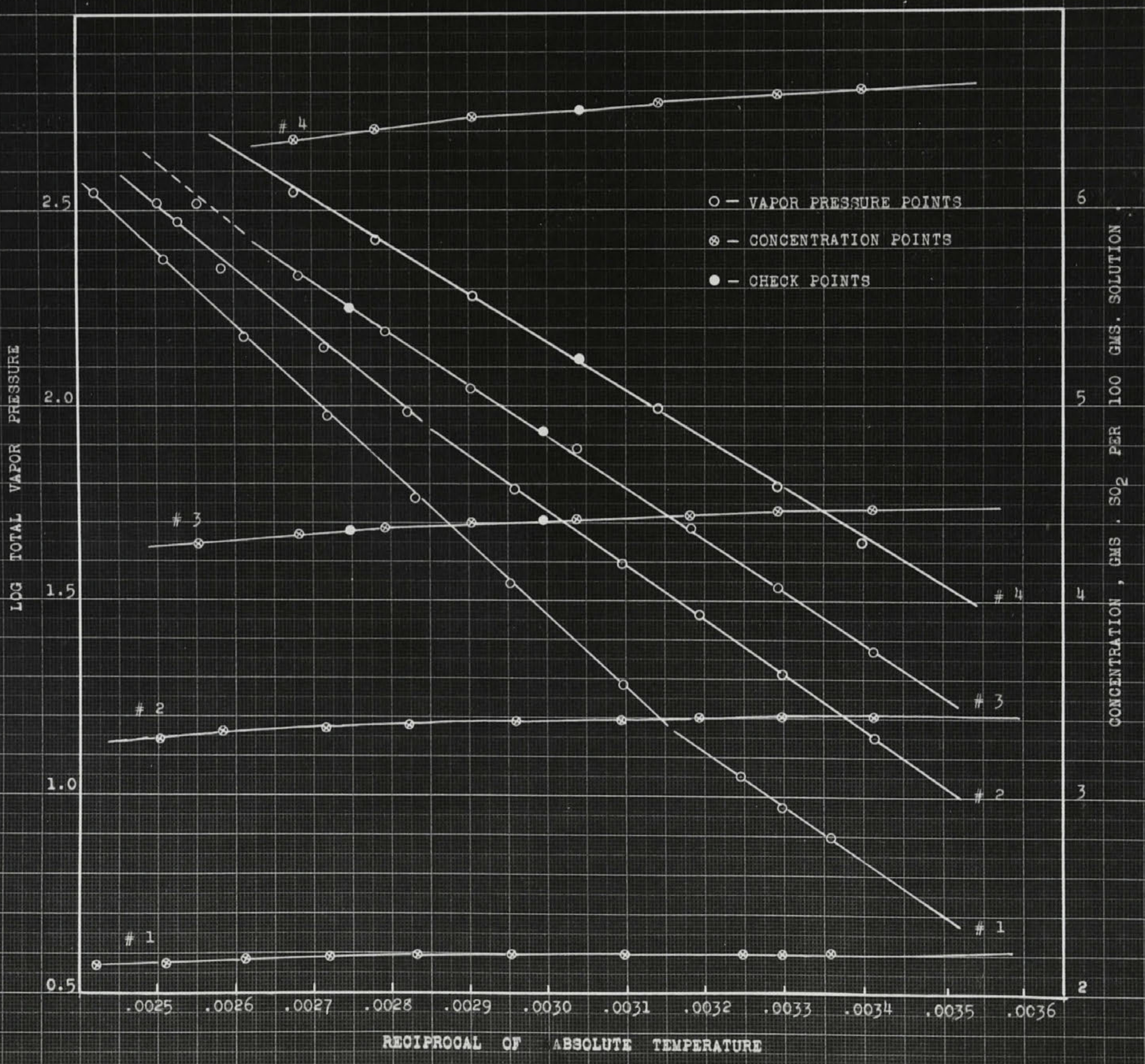
Observations			Calculated Values			
Bath Temp.	Manom. Scale Reading	Average Manom. Temp.	Percent SO_2 in Solution	Percent CaO in Solution	Temp. of Soln.	Vapor Pressure cms.
15.2	322.30	298.2	6.860	1.225	15.2	36.6
27.3	306.50	297.6	6.834	1.225	27.3	56.3
40.2	285.05	298.8	6.798	1.225	40.2	84.4
52.5	259.20	298.7	6.758	1.225	52.5	119.1
65.3	228.25	298.3	6.710	1.225	65.3	162.8
76.8	194.10	297.9	6.658	1.225	76.8	215.9
90.4	158.30	298.0	6.606	1.225	90.4	280.9
105.7	119.30	298.1	6.544	1.225	104.8	372.0
60.7	239.60	297.6	6.728	1.225	60.7	146.1
35.6	293.30	295.7	6.813	1.225	35.6	72.7
14.0	323.45	295.8	6.862	1.225	14.0	34.6

Table 20

that is, figures at 1% SO_2, 2% SO_2, 3% SO_2, etc., and 0.25% CaO, 0.50% CaO, 0.75% CaO, etc.

To arrive at these figures many corrections had to be made and a great many curves drawn. All this arises from the fact that although a given solution may contain 2.00% SO_2 at the start of a run, as the temperature increases, more and more gas leaves the liquid phase; thus the percentage of SO_2 present diminishes with increase in temperature. This change in concentration is shown by the slightly curved lines in Figure 4. Thus, by drawing the "vapor pressure" curves on the same graphs as the "change in composition" curves, one is able to read the exact sulphur dioxide concentration of any curve at any given temperature.

Now consider the case of a series of runs. The weight of calcium oxide is constant through the series (except where it was necessary to make a fresh start after an accident). But the total weight of the system is increasing as one goes from run to run due to the addition of sulphur dioxide. Thus although one starts a series of runs with 0.50% CaO present in the cell, this percentage is appreciably lower than this value by the time the series has been completed. Even the fact that the liquid phase is losing sulphur dioxide to the gas phase during a run causes a slight change in the percentage of calcium oxide from point to point, but this change is



WB 13/iv/37

Figure 4

negligably small and will not be included in the following discussion.

Series C was chosen as an example for a particular purpose: when the log vapor pressure $- \frac{1}{T}$ curves were plotted it was found that although some of the curves were perfectly straight lines, other exhibited sharp bends or "kinks". These "kinks" have a very definite significance — they represent the exact precipitation temperature of the solutions. More will be said about these precipitation temperatures later on in the discussion of the results. Series C shows three of these "kinks" in curves #1, #2 and #3. Precipitation occurred in #3 just before the last reading was taken; for this reason, the top part of this curve is shown as a dotted line. Because these "kinks" show up poorly when the curves are plotted on a small scale, a small break has been left in these curves where the "kinks" occur.

Isotherms at 25°, 50°, 70°, 90°, 110° and $130^{\circ}C$. were drawn through the four sets of curves mentioned above, and a second set of six graphs each containing four curves (twenty-four curves in all) showing the variation of total vapor pressure with change in sulphur dioxide concentrations for approximately constant calcium oxide concentrations. Figure 5 shows a sample of this type of curves for $25^{\circ}C$.

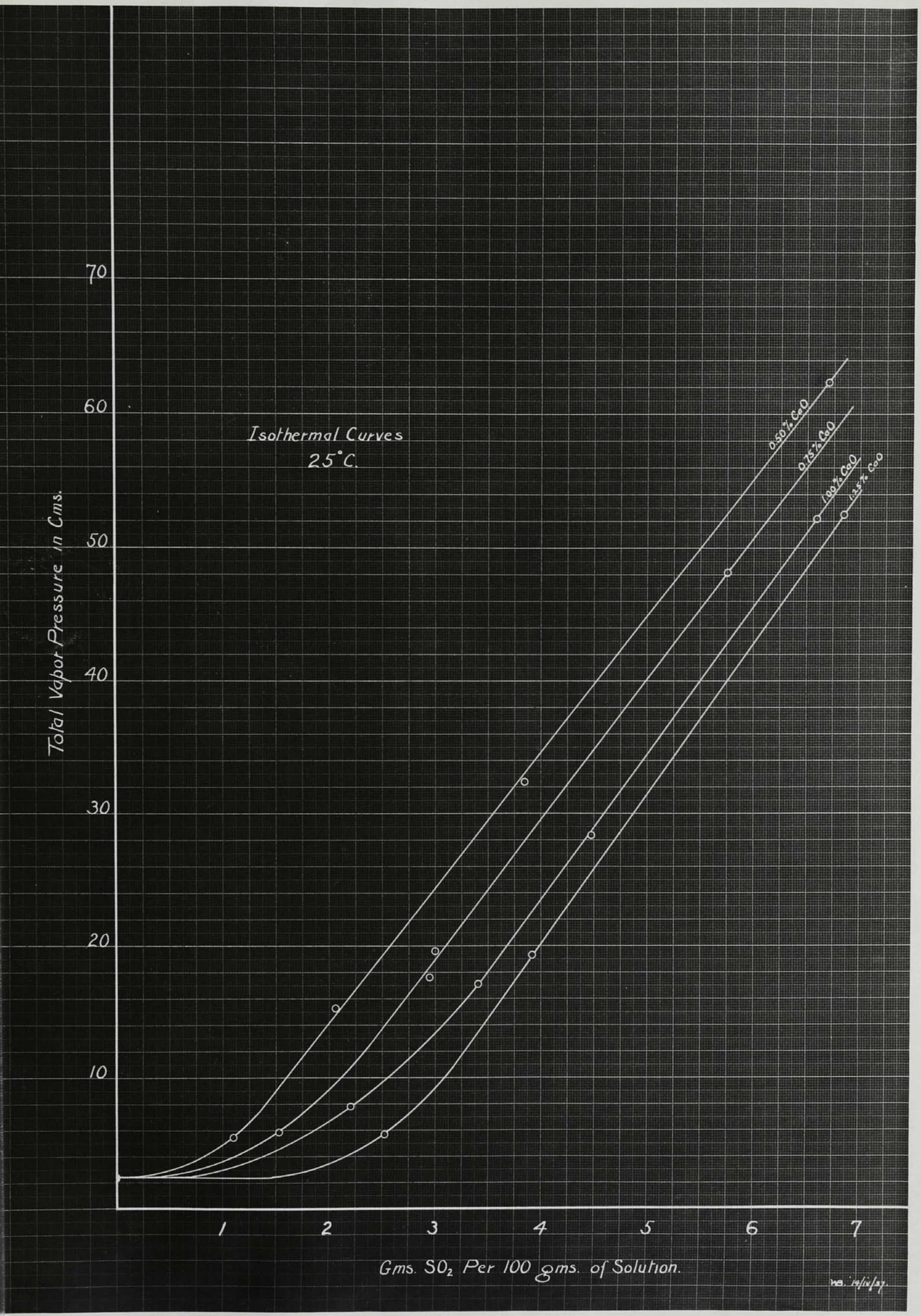

Isothermal Curves
25°C.
Total Vapor Pressure in Cms.
70
60
50
40
30
20
10
0.50% CaO
0.75% CaO
1.00% CaO
1.25% CaO
1
2
3
4
5
6
7
Gms. SO2 Per 100 gms. of Solution.
HB. 14/iv/37.

Figure 5

Although these curves give a fairly accurate picture of just what is happening in this system, they do not entirely fulfill the requirements because of the fact that the concentration of calcium oxide does not remain constant through the series.

To make correction for this variation in the percentage of lime a third set of six graphs, each consisting of twelve curves (seventy-two curves in all) were drawn as follows:

Total vapor pressure was plotted against "even" percent of calcium oxide. "Even" percentages of calcium oxide means that 0.50% was taken as representing Series A, 0.75% as representing Series B, 100% for Series C and 1.25% for Series D. The values for zero percent lime are those of Campbell (22). Figure 6 shows a sample of this type of graph for 25°C. in which the dotted curves and the hollow points represent the data plotted for the so called "even" percentages of lime. Now on the same graphs, the actual percentages of lime were plotted as solid points. For example: in the 6% SO_2 curve in Figure 6 a hollow point appears at exactly 1.00% lime; Table 17 (page 90) shows that for approximately 6% SO_2 the lime percentage was 0.95% instead of 1.00%, thus a solid point is placed on the 0.95% co-ordinate level with the 1.00% point. This procedure

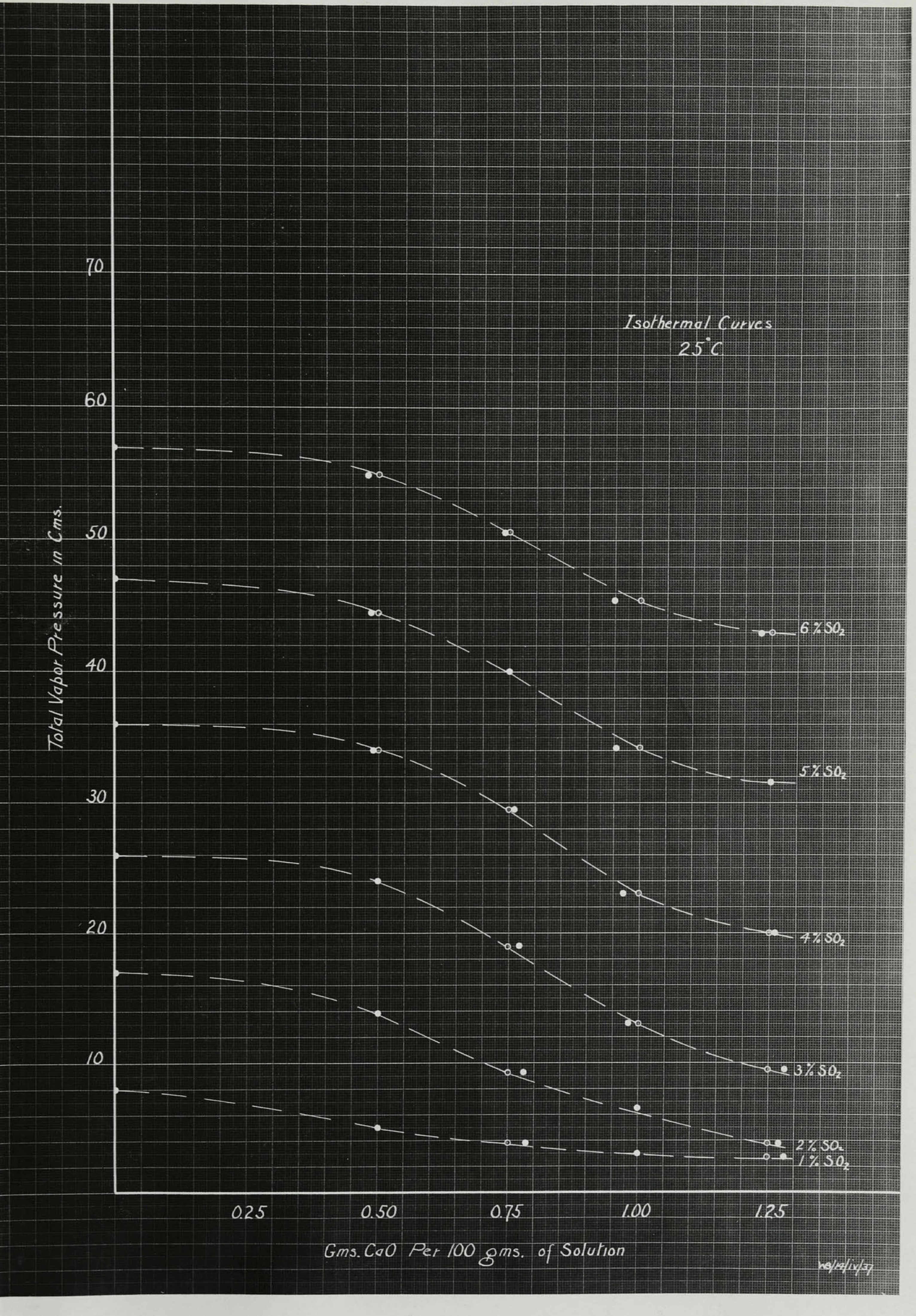

Isothermal Curves
25°C
Total Vapor Pressure in Cms.
70
60
50
40
30
20
10
0.25
0.50
0.75
1.00
1.25
Gms. CaO Per 100 gms. of Solution
6% SO₂
5% SO₂
4% SO₂
3% SO₂
2% SO₂
1% SO₂
WS/14/IV/37

Figure 6

was followed with all the curves and a second set of curves drawn through the solid points. For the sake of clearness these last curves were omitted from Figure 6. These curves represent the actual variation of vapor pressure with calcium oxide concentration for a constant concentration of sulphur dioxide.

To complete the task a fourth and final set of six graphs each containing four curves (twenty-four curves in all) were drawn from values taken from the vapor pressure - percent calcium oxide curves, by plotting vapor pressure against percent sulphur dioxide for constant percentage of calcium oxide. Figure 7 shows a sample of this type of curves for 25°C., and Table 21 contains all the figures necessary for the reconstruction of the final aggregation of curves at 25°, 50°, 70°, 90°, 110° and 130°C.

For purposes of comparison, Table 22 shows a photostat of a page from the thesis of Gishler (51).

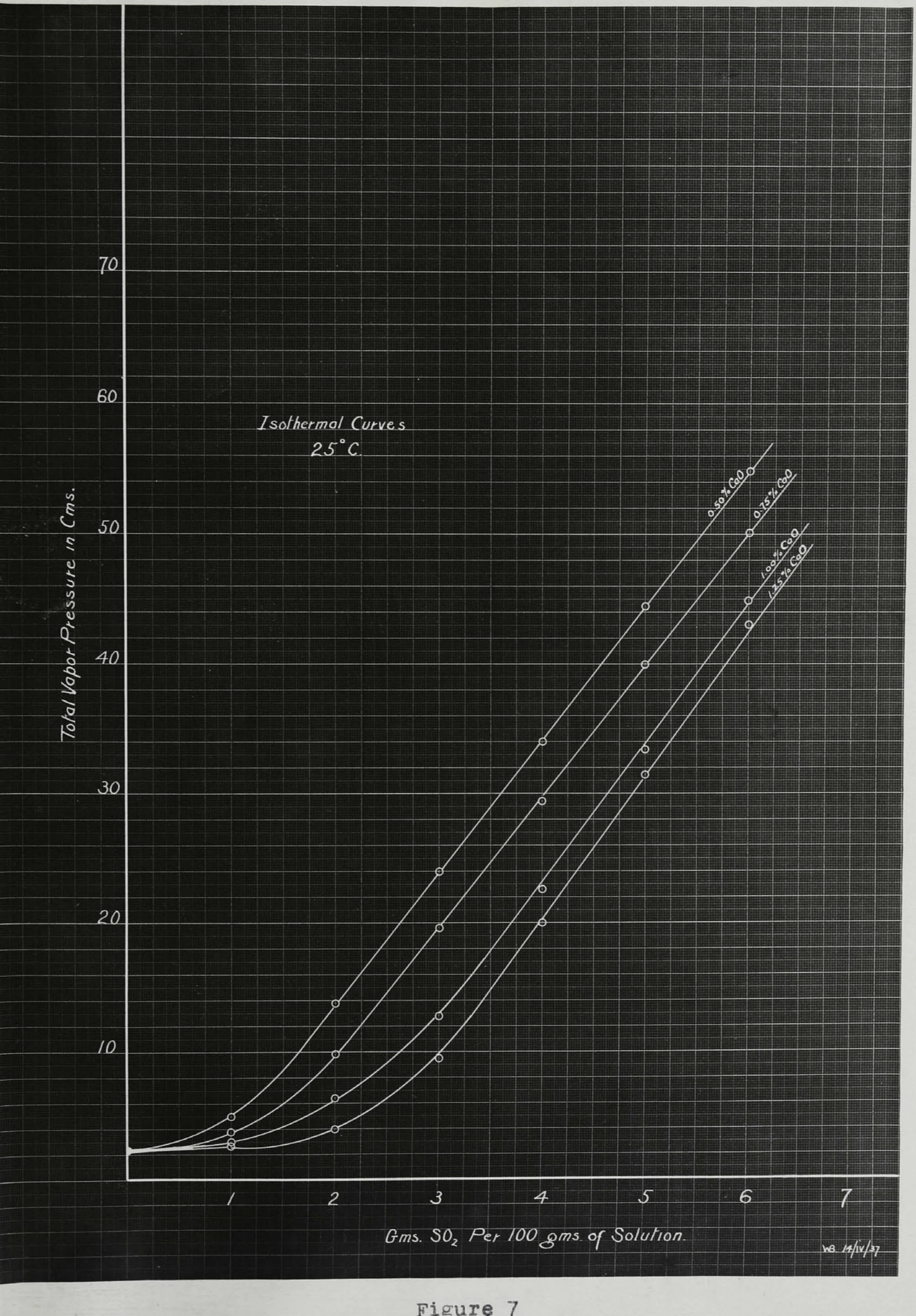

Isothermal Curves
25°C
Total Vapor Pressure in Cms.
70
60
50
40
30
20
10
1
2
3
4
5
6
7
Gms. SO2 Per 100 gms. of Solution.
0.50% CaO
0.75% CaO
1.00% CaO
1.25% CaO
WB. 14/iv/37

Figure 7

TOTAL VAPOR PRESSURES OF THE SYSTEM CaO - SO_2 - H_2O

Temperature		25°	50°	70°	90°	110°	130°
SO_2 %	CaO %	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	0.25	8.0	20.0	43.0	88.0	151	250
1	0.50	5.0	14.5	34.0	69,0	128	222
1	0.75	3.8	10.5	26.0	58.0	120	213
1	1.00	3.0	10.5	24.0	53.5	115	208
1	1.25	2.7	10.5	23.0	50.5	111	205
2	0.0	17.0	45.0	83.0	143	231	353
2	0.25	16.0	41.0	65.0	130	212	339
2	0.50	13.8	33.5	63.0	106	177	303
2	0.75	9.8	22.0	43.0	85.0	156	265
2	1.00	6.4	16.2	37.0	74.5	143	249
2	1.25	4.0	14.2	27.5	67.0	135	241
3	0.0	26.0	64.0	115	190	290	431
3	0.25	25.0	61.0	108	176	280	425
3	0.50	24.0	54.5	96.0	157	253	404
3	0.75	19.6	43.0	76.0	128	218	360
3	1.00	12.8	31.0	60.0	110	191	333
3	1.25	9.5	25.0	50.0	101	176	319
4	0.0	36.0	85.0	147	237	355	518
4	0.25	35.0	82.0	141	226	350	516
4	0.50	34.0	75.0	130	209	329	511
4	0.75	29.4	63.5	110	181	292	456
4	1.00	22.6	51.5	92.0	158	260	424
4	1.25	20.0	44.4	80.0	147	240	405
5	0.0	47.0	106	183	283	420	610
5	0.25	46.0	104	174	275	418	609
5	0.50	44.5	95.0	163	261	405	608
5	0.75	40.0	83.0	145	235	366	550
5	1.00	33.4	73.6	128	211	332	521
5	1.25	31.5	68.2	119	201	313	495
6	0.0	57.0	128	223	330	484	709
6	0.25	56.0	123	206	324	483	709
6	0.50	54.8	116	195	311	481	709
6	0.75	50.1	106	180	288	443	645
6	1.00	44.9	96.1	165	265	410	610
6	1.25	43.0	91.7	155	253	390	580

Table 21

VAPOUR PRESSURES OF THE SYSTEM CaO - SO_2 - H_2O

Temperature		25	50	70	90	110	130
SO_2	CaO	V.P.	V.P.	V.P.	V.P.	F.P.	V.P.
%	%	cm	cm	cm	cm	cm	cm
1	0.0	9	26	52	96	166	275
1	0.5	6	17	40	72	129	235
1	1.0	4	12	30	57	115	212
1	1.5	3	9	22	52	108	203
1	2.0	3	9	22	52	107	202
1	2.5	3	9	22	52	107	202
2	0.0	17	44	82	142	230	353
2	0.5	11	30	62	101	174	303
2	1.0	7	19	42	76	146	263
2	1.5	5	12	25	63	125	240
2	2.0	3	9	22	56	116	220
2	2.5	3	9	22	52	108	210
3	0.0	26	64	104	190	290	431
3	0.5	19	47	88	140	234	375
3	1.0	12	32	62	106	193	325
3	1.5	8	20	43	87	162	295
3	2.0	6	13	35	74	140	275
3	2.5	4	11	31	66	127	256
4	0.0	36	85	148	237	355	518
4	0.5	29	68	119	190	295	462
4	1.0	23	52	91	152	250	409
4	1.5	17	36	67	123	218	372
4	2.0	11	22	53	102	190	340
4	2.5	6	13	36	88	170	314
5	0.0	46	107	180	283	420	610
5	0.5	41	87	155	244	374	560
5	1.0	35	76	130	210	332	516
5	1.5	29	57	102	180	293	467
5	2.0	18	37	80	152	256	420
5	2.5	8	18	63	130	226	377
6	0.0	57	128	223	330	484	709
6	0.5	54	117	198	302	452	675
6	1.0	49	102	175	275	414	655
6	1.5	42	79	140	242	375	580
6	2.0	27	55	110	210	331	516
6	2.5	13	32	86	180	290	450

Table 22

Precipitation Temperatures:

In the fifteen different solutions investigated, nine were found to precipitate at some temperature between 20° and 120°C. Of the remaining six, four remained two-phase throughout the entire run, and two had precipitation temperatures at some point below 20°C. As was previously mentioned, the curves for the nine solutions that precipitated during the runs exhibited "kinks". Table 23 shows the temperatures, as well as the concentrations of sulphur dioxide and calcium oxide at which these kinks occur. Figure 8, which will be found in the section on the discussion of results, shows the result of plotting precipitation temperature against percent total sulphur dioxide for approximately constant lime concentration. The figures beside the points or curves indicate the percent of lime. Some of the results of Russell, Gurd and Gishler are shown on the same graph.

An outline of the theory involved in this phase of the work will be found in the section on the discussion of results.

Run No.	% SO_2	% CaO	$\frac{1}{T}$	Temp.
A 1	1.11	0.514		below 7°
2	1.99	0.510	.002670	101.5°
3	3.60	0.500	.002543	120.1°
4	6.36	0.485		above 95°
B 1	1.53	0.779	.003064	53.3°
2	2.88	0.766	.002733	92.8°
3	2.91	0.771	.002722	94.3°
4	5.41	0.742		above 108°
C 1	2.205	0.997	.003169	28.2°
2	3.36	0.984	.002838	79.2°
3	4.33	0.973	.002640	105.7°
4	5.33	0.951		above 100°
D 1	2.516	1.285		below 19°
2	3.87	1.264	.002955	65.3°
3	6.54	1.225		above 105°

Table 23

DISCUSSION OF THE RESULTS

The system calcuim oxide - sulphur dioxide - water has previously been investigated in this laboratory by Grieve (41) Gurd (42) and Gishler (51). Because of the lack of agreement in the results of these investigators, the relative accuracy of their data and the quality of their experimental technique has been called into question. The vapor pressure data of Gurd and Gishler were combined into one article (59) and will henceforth be referred to as the "Gurd-Gishler" results.

The first discrepancy to be considered is the lack of agreement at low temperatures (25°C) between the results of Grieve and the Gurd-Gishler values. The vapor pressures found by Grieve for low temperatures are considerably lower than those found by Gurd and Gishler. The differences are of the order of seventy-five or one hundred percent in some cases and thus cannot be contributed to experimental error. Secondly, no actual determinations of vapor pressures were made by these investigators at calcium oxide concentrations of less than one percent. The results they give are interpolated values and thus may be subject to considerable error.

There are three probable sources of error in any investigation of the vapor pressures of this three component system: (1) the great tendency the system has toward supersaturation, and thus the necessity of allowing ample time for the attainment of equilibrium. (ii) Because it is necessary to have a manometer that is capable of measureing high pressures, the closed-end type must be resorted to. Extreme care must be taken in calibrating and reading an instrument of this sort if accurate determinations are to be made at relatively low pressures. (iii) The method of introducing the reagents into the cell is most important. Any impurities such as carbonate in the calcium oxide, dissolved air in the water, or sulphur trioxide in the sulphur dioxide must be rigidly excluded because of their effect on the equilibrium pressure. Water and calcium oxide can be weighed into the cell quite readily, but the system for the introduction of the gaseous sulphur dioxide must be capable of determining the weight of this gas with great accuracy.

Each of these three probable sources of error were rigidly investigated before any actual vapor pressure determinations were made. Test runs were made in order to determine just how much time was necessary for the attainment of true equilibrium, and whether the direction of approach had any effect on the value of the equilibrium. It was found that a two phase system came to equilibrium in about two hours, while a three phase system required about ten hours in some cases.

A test run was made with pure water in the cell, and when the vapor pressures were plotted against the temperature the points were found to fall on a curve drawn from data from the International Critical Tables. A second test was made on a three component - three phase system containing about 1.1% sulphur dioxide and 1% lime. The points from this run were found to be on a smooth curve above the curve for water and parallel with it over the whole range at temperatures investigated. The distance between these curves represented a pressure of about one centimetre. These tests prove beyond doubt that the manometer is capable of measuring low and high pressures with accuracy.

The manometer used in this research was the one built and calibrated by Gurd, and used by both Gurd and Gishler.

A test run was made on a sulphur dioxide - water solution the results of which checked with the values of Campbell (22) for a solution of the same sulphur dioxide content. This fact is significant because the results of Morgan (23) check those of Campbell at low temperatures, while the test run under discussion checks Campbell's work at high temperatures.

Table 24 show a comparison between the Gurd-Gishler values and the data from the present investigation over the whole range of temperatures and sulphur-dioxide concentrations at 1.0% calcium oxide.

% CaO	% SO_2	V.p. at 25°	V.p. at 50°	V.p. at 70°	V.p. at 90°	V.p. at 110°	V.p. at 130°
1.0	1	3.0 3.8 - 0.8	10.5 11.9 - 1.4	24.0 29.4 - 5.4	53.5 57.2 - 3.7	115 115 0	208 212 - 4
1.0	2	6.4 7.5 - 1.1	16.2 19.1 - 2.9	37.0 41.7 - 4.7	74.5 75.7 - 1.2	143 147 - 4	249 263 - 14
1.0	3	12.8 12.3 + 0.5	31.0 41.6* -10.6	60.0 61.5 - 1.5	110 106 + 4	191 193 + 2	333 325 + 8
1.0	4	22.6 23.3 - 0.7	51.5 51.9 - 2.0	92.0 91.0 - 2.0	158 152 + 1	260 251 0	424 409 + 5
1.0	5	33.4 35.5 - 2.1	73.6 75.6 - 2.0	128 130 - 2.0	211 210 + 1	332 332 0	521 516 + 5
1.0	6	44.9 49.4 - 4.5	96.1 102.4 - 6.3	165 176 - 11	265 275 - 10	410 414 - 4	610 635 - 25

* Obviously in error.

Table 24

The top figure given for each temperature and concentration represents the result obtained in this present work, while the bottom figure is the Gurd-Gishler value. The agreement is good over the whole range, and definitely shows that the unpublished figures of Grieve which lie below these values are incorrect. If the figures shown in this table are plotted on the log vs. $\frac{1}{T}$ basis, the data from the present investigation is found to fall almost exectly on straight lines. The Gurd-Gishler values show only a slight variation from these straight lines over almost the entire range; The values for 25°C however are for the most part high. The Gurd-Gishler value for 1.0% calcium oxide and 3.0% sulphur dioxide at 50°C is obviously incorrect, due likely to a typographical error.

In this connection it should be noted that in the Gurd-Gishler results no correction was made for the variation in the percentage of calcium oxide which took place from run to run in any given series of runs. This correction was undoubtedly small, but not small enough to be completely neglected.

It was noticed in the present work that when starting a series of runs it required at least six hours of continual stirring to dissolve the last traces of calcium oxide. There was a tendency for the stirrer to pound the lime into a cake in the bottom of the cell which made solution very slow.

In the case of a run which had three phases present at the start this fact could easily pass unnoticed. The presence of uncombined calcium oxide in the cell would of course cause the system to exhibit too high a pressure because of the excess free sulphur dioxide. This fact alone might explain why the Gurd-Gishler values are for the most part higher than the values found in this investigation at low temperatures.

The relative distances between the curves for 1%, 2%, 3%, etc. sulphur dioxide on the log vs. $\frac{1}{T}$ graph for 1% calcium oxide, suggested a method of determining the relative accuracy of the two groups of results.

If the logarithm of the percent sulphur dioxide is plotted against the logarithm of the total pressure for a given temperature, the results of this investigation are found to fall on a much smoother curve than do the Gurd-Gishler values.

It is interesting to note that the curves produced by this method of plotting are straight lines for the range of sulphur dioxide concentration and temperature which result in two phase conditions. In that portion of each isotherm where the sulphur dioxide concentration is low enough or the temperature high enough to result in three phase conditions, the straight line relationship falls off. The straight line portions of the isotherms at 25°, 50°, 70°, 90°, and 110°C are almost exactly parallel.

Table 25 shows a comparison between the Gurd-Gishler values and the data from the present investigation over the whole range of temperatures and sulphur dioxide concentrations at 0.50% calcium oxide. The Gurd-Gishler figures for the most part are lower than the values found in this present research, and when plotted on the log vs. $\frac{1}{T}$ basis do not give as good straight lines. The figures of Gurd-Gishler at this lime concentration are all interpolated values while the figures from this investigation were all experimentally determined and fit in with the values for 0.75% lime which were also experimentally determined. This evidence supports the conclusion that the values obtained in this research are much more accurate than any previously determined.

The discrepancies pointed out in the Gurd-Gishler results are not of great enough magnitude to essentially alter the theory of the equilibria existing in system calcium oxide - sulphur dioxide - water that has been developed in this laboratory during the last few years.

As regards conductivity data for this system, there were no discrepancies in the results of Grieve, Gurd or Gishler and for this reason no further work on conductivity has been included in this investigation.

% CaO	% SO_2	V.p. at 25°	V.p. at 50°	V.p. at 70°	V.p. at 90°	V.p. at 110°	V.p. at 130°
0.50	1	5.0 6.3 - 1.3	14.5 17.2 - 2.7	34.0 40.4 - 6.4	69.0 71.5 - 2.5	128 130 - 2.0	222 235 - 13.0
0.50	2	13.8 11.4 + 2.4	33.5 29.8 + 3.7	63.0 62.1 + 0.9	106 101 5	177 179 - 2	303 303 0
0.50	3	24.0 18.8 + 5.2	54.5 47.0 + 7.5	96.0 87.8 + 8.2	157 140 + 17	253 234 + 19	404 375 + 29
0.50	4	34.0 29.5 + 4.5	75.0 68.2 + 6.8	130 119 + 11	209 190 + 19	329 295 + 34	511 462 + 46
0.50	5	44.5 41.5 + 3.0	95.0 91.6 + 3.4	163 156 + 7	261 245 + 16	405 374 + 31	608 560 + 48
0.50	6	54.8 54.1 + 0.7	116 117 - 1	195 198 - 3	311 302 + 9	481 452 + 26	709 675 + 34

Table 25

Precipitation Temperatures:

For each definite concentration of calcium oxide and sulphur dioxide there is a temperature at which precipitation takes place. This phenomenon is encountered in the sulphite pulping industry as the so-called "liming up" of digesters when the temperature is raised during a cook. Saunderson (57) has shown that this precipitate of calcium sulphite hinders the penetration of the cooking liquor into the chips, which not only leads to non-uniform cooking but often to so-called "burning".

In view of the importance of such data, it is desirable to be able to predict at what temperature a solution of known calcium oxide and sulphur dioxide content will precipitate.

In this connection, the figures obtained in this research are believed to be the most accurate so far obtained. The results of previous investigators have been based upon visual methods, that is, on the actual observation of the precipitate; considering the great tendency this system has to supersaturate it is not surprising that the temperatures they give are all too high. This fact is particularly true if great care if not taken to raise the temperature of the solution slowly and at the same time provide adequate stirring.

The conclusions of this present investigation were based on the following facts:

If vapor pressure measurements are made on a system whose precipitation temperature is low enough to ensure the presence of the solid phase over the entire run, and the log of the total vapor pressure plotted against the reciprocal of the absolute temperature, a straight line results. If a similar run is made on a system of sufficiently high sulphur dioxide content to ensure the absence of the solid phase over the range of temperatures investigated (say up to 130°C.) and the results plotted in the same way, another straight line results. This second straight line however has a smaller numerical slope than the first. If a run is now made on a system having calcium oxide and sulphur dioxide concentration so arranged that two phases only are present during the first part of the run, and three phases present during the latter part (that is, after precipitation has taken place) and the results plotted as before, the result is not a straight line. The curve is composed of two straight lines of different slope; that part of the curve representing the three phase system having a greater numerical slope than the first part.

Since a "three-phase" curve is a straight line, and a "two-phase" curve is also a straight line, one is justified in interpolating the two parts of a curve which represent a system which has undergone precipitation in the course of the run. The intersection of these curves must represent the point of incipient precipitation.

It is noteworthy that the precipitate did not become visible until the temperature had been increased ten or fifteen degrees. This fact alone is sufficient to explain why the temperatures recorded by previous investigators were all higher than the figures obtained in this work for systems having approximately the same calcium oxide and sulphur dioxide content.

The slope of the curve after precipitation had taken place would be expected to be greater, because when precipitation occurs, the equilibria

$$Ca(HSO_3)_2 \rightleftharpoons CaSO_3 + H_2SO_3 \rightleftharpoons CaSO_3 + H_2O + SO_2$$

shift to the right with the production of sulphur dioxide. For each mole of solid calcium sulphite formed, a mole of sulphur dioxide is released to the solution.

From a purely academic point of view the results obtained in the present work will lead to a clearer insight into the phase diagram of this system because of their greater accuracy. From a practical point of view however, the results of the earlier investigators may prove more useful for two reasons: firstly, the presence of colloidal matter in the digester will tend to inhibit precipitation, and secondly, after the point of incipient precipitation has been reached the system will not actually precipitate because of its great tendency to supersaturate.

Rather than precipitation temperatures, these figures should be looked up as the upper limit of safety above which care must be exercised to prevent "liming up". This is particularly true in the case of the heat exchangers commonly employed in the sulphite pulping industry. Solutions are continually passing through this sort of equipment and thus the "time factor" of precipitation is no guard against the formation of the solid calcium sulphite.

Figure 8 shows the result of plotting the precipitation temperature against the percent total sulphur dioxide for definite percentages of calcium oxide. The figures of Gurd and Gishler as well as some of those of Russell are shown on the same graph in order that a comparison may be made. The figures beside the points or curves indicate the lime percentages.

Table 23 (page 105) shows the precipitation temperatures for only those concentrations of calcium oxide and sulphur dioxide that were actually experimentally studied . However, providing the precipitation temperature of any one of the thirty three component systems indicated in Table 21

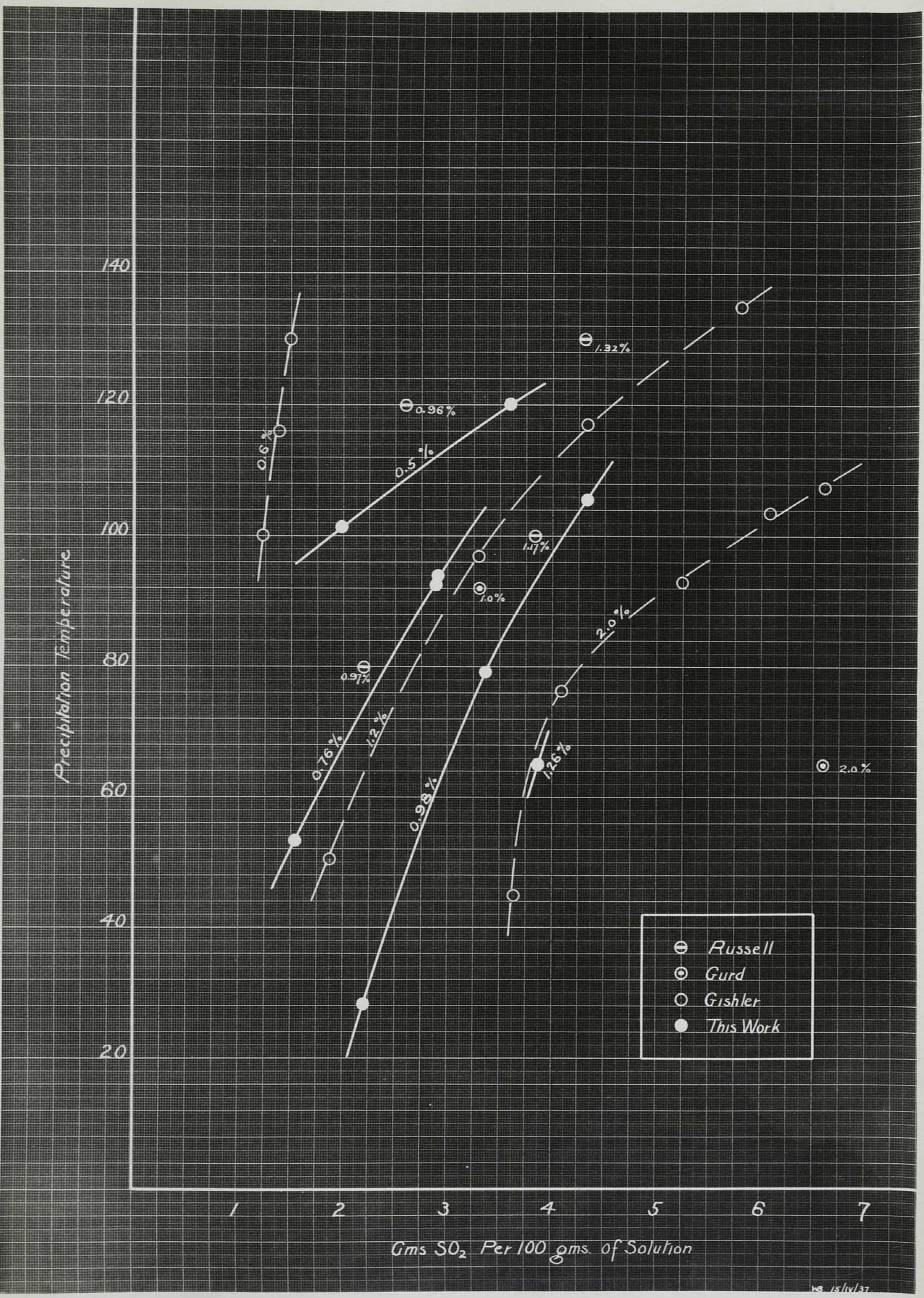

140
120
100
80
60
40
20
Precipitation Temperature
1
2
3
4
5
6
7
Gms SO_2 Per 100 gms. of Solution
0.6%
0.5%
0.96%
1.32%
1.17%
1.0%
0.97%
0.76%
1.2%
0.98%
1.26%
2.0%
2.0%
⊖ Russell
⊙ Gurd
○ Gishler
● This Work
WS 15/IV/37.

Figure 8

(page 102) lies in the temperature range shown in the table. it can be determined by plotting the figures on the log vs. $\frac{1}{T}$ basis and noting where the kinks in the resulting curves appear.

SUMMARY

SUMMARY

This research is a continuation of a general investigation of the equilibria existing in the three component system calcium oxide - sulphur dioxide - water that has been in progress in this laboratory for several years.

Important deductions of a theoretical nature have been made by previous investigators from the results they obtained. Furthermore, although this is considered to be of secondary importance, far reaching conclusions were drawn by the theoretical men of the pulp and paper industry in regard to the practical value of these results.

Unfortunately, the data obtained by Grieve did not agree with those of Gurd and of Gishler. It thus became of paramount importance on both counts to evaluate the relative accuracy of Grieve on the one hand and of Gurd and of Gishler on the other. Extraordinary precautions were therefore undertaken to eliminate possible sources of error; and in particular to determine the "reproducibility" of vapor pressure measurements in a system where time for the establishment of equilibrium plays an important part. By making measurements over time intervals showing definite end values, and by approaching the equilibrium vapor pressures from opposite sides, **confidence** in the reliability of the

results obtained in this investigation has been given.

No claim is made of greater relative accuracy in the determinations made in one particular "run"; however, it can be claimed that within the experimental error of the technique employed, that the error due to the time element has been eliminated.

As a result of this present investigation, the data of Gurd and Gishler has in the main been corrobrated. Concentration ranges in which interpolation had previously been employed have been investigated by actual experiment and here corrections are justified.

In this present investigation, vapor pressure measurements have been made on the system calcium oxide - sulphur dioxide - water at calcium oxide concentrations of 0.5%, 0.75%, 1.0% and 1.25%. For each concentration of calcium oxide a range of sulphur dioxide concentrations from 1% to 6% has been explored. The temperature range covered was from 25°C. to 130°C. Prior to this research no measurements had been made on systems containing less than one percent calcium oxide.

Particular efforts were made to present the data in a convenient form giving vapor pressures of this system at calcium oxide concentrations of from 0% to 1.25% in increments of 0.25%, and sulphur dioxide concentrations from 1% to 6% in 1% increments over the temperature range investigated. Since even in one series of experimental observations, concentrations of sulphur dioxide and calcium oxide varied with the temperature, this proposal was by no means an easy one. To compile the final data as shown in Table 21 (page 102) required the drawing of no less than 150 curves.

A new and accurate method for the determination of the precipitation temperatures of this system has been developed. The results obtained show that all previous determinations of precipitation temperatures have been considerably in error.

A table and the curves showing precipitation temperatures over a considerable range of calcium oxide and sulphur dioxide concentrations are included, as well as data permitting the determination of these temperatures over a much wider range of concentrations.

CLAIMS OF ORIGINAL RESEARCH

CLAIMS TO ORIGINAL RESEARCH

1° Vapor pressure measurements have been made for the first time on the three component system calcium oxide - sulphur dioxide - water at calcium oxide contentrations of 0.5%, 0.75% and 1.25% over a range of sulphur dioxide concentrations from 1% to 6% for each concentration of calcium oxide. The temperature range investigated was from 25° to 130°C. Experimental procedure was carried out in a manner to ensure greater accuracy than had been obtained by previous workers in this field.

2° Similar measurements, over the same temperature range, have been made on systems containing 1% calcium oxide over a range of sulphur dioxide concentrations from 1% to 6% which corroborate, for the most part, the results of Gurd and Gishler, but which indicate that the results of Grieve are considerably in error.

3° Data from systems containing 0.5% calcium oxide show that the figures obtained by Gishler by interpolation for this lime concentration are for the most part too low. In some cases the error being as much as ten percent.

4° Corrections have been made for the first time which take into account the variation in calcium oxide concentration which takes place from run to run in any given series of runs.

5° A new and accurate method for the determination of the precipitation temperatures of this system has been developed.

6° All previous determinations of these precipitation temperatures have been shown to be considerably in error. An explanation is offered to account for the discrepancies in previous results.

BIBLIOGRAPHY

BIBLIOGRAPHY

(1) Sims, - Trans. Chem. Soc. 14, 1, (1862).

(2) Schiff, - Annalen, 107, 312, (1858).

(3) Gerlach, - Zeit. Anal. 8, 292, (1869).

(4) Giles and Shearer, - J. Soc. Chem. Ind. 4, 303, (1885).

(5) Ostwald, - Jour. Prakt. Chemie (2), 32, 314, (1885).

(6) Barth, - Z. Phys. Chemie, 9, 176, (1892).

(7) McCrae and Wilson, - Zeit. anorg. Chemie, 35, 11, (1903).

(8) Walden and Centnerszwer, - Z. Phys. Chemie, 42, 459, (1903).

(9) Drucker, - Z. Phys. Chemie, 49, 579, (1904).

(10) Kerp and Bauer, - Arb. a.d. Kais. Gesundheitsamt, 26, 297, (1907).

(11) Fulda, - Arb. a.d. Kais. Gesundheitsamt, 30, 81, (1909).

(12) Thomsen, - Thermochem. Unters. 1, 169, (1882).

(13) Berthelot, - Ann. chem. et phys. (6), 1, 73, (1884).

(14) Wright, - Trans. Chem. Soc. 105, 2909, (1914).

(15) Baly and Bailey, - Trans. Chem. Soc. 121, 1813, (1922).

(16) Lindner, - Monatshefte, 33, 613, (1912).

(17) Smith and Parkhurst, - J. Amer. Chem. Soc. 44, 1918, (1922).

(18) Oman, - Tekn. Tidskrift Kemi. 54, 81, (1924).

(19) Hudson, - J. Chem. Soc. 127, 1332, (1925).

(20) Enckell, - Papierfabrikant, 23, 633, (1925).

(21) Maass and Maass, - J. Amer. Chem. Soc. 50, 1352, (1928).

(22) Campbell and Maass, - Can. J. Research, 2, 42, (1922).

(23) Morgan and Maass, - Can. J. Research, 5, 162, (1934).

(24) Johnstone and Leppla, - J. Amer. Chem. Soc. 56, 2233, (1934).

(25) Terres and Rühl, - Beiheft Z. Ver. deut. Chem. No. 8; Angew Chem. 47, 331, (1934).

(26) Davis, - Chem. and Met. Eng. 42, 492, (1935).

(27) Bassett, - J. Chem. Soc. 1270, (1934).

(28) Ostwald, - Jour. Prakt. Chemie, 33, 357, (1886).

(29) Cavazzi, - Gazzetta Chimica Italiana, 45, I, 529, (1915).

(30) Miller and Witt, - J. Phys. Chem. 32, 285, (1929).

(31) Whetham, - Theory of Solutions, page 471 (Cambridge Univ. Press 1902).

(32) Maben, - Pharm. J. Trans. (3), 14, 505, (1848).

(33) Lamy, - Compt. Rendu. 86, 333, (1878).

(34) Herzfeld, - Zeit. ver. Rubenzucker. Ind. 818, (1897).

(35) Guthric, - J. Soc. Chem. Ind. 20, 223, (1901).

(36) Moody, - J. Chem. Soc. 93, 1772, (1908).

(37) Haslam, Calingaert and Taylor, - J. Amer. Chem. Soc. 46, 311, (1924).

(38) Smolenski and Zero, - Bull. intern. acad. polonaise, classi. sci. math. nat. 586, (1935) A.

(39) Rodt, - Z. anorg. allgem. Chem. 228, 175, (1936).

(40) Larocque, - Thesis McGill University (1933).

(41) Grieve, - Ph.D. Thesis McGill University (1932).

(42) Gurd, - Ph.D. Thesis McGill University (1932).

(43) Robart, - Bull. d. Assoc. des chim. d. Sucr. et Dist. 31, 108.

(44) Van der Linden, - Arch. Suikerind. 24, 1113, (1916).

(45) Weisberg, - Bull. Soc. Chem. 15, 1247, (1896).

(46) Schwarz and Müller-Clemm, - Z. angew. Chem. 34, 272, (1921).

(47) Farnell, - J. Soc. Chem. Ind. 44, 530, 2T (1925).

(48) Bergman, - Finnish Paper and Trade J. (Special issue) 292 April 1935.

(49) Conrad and Beuschlein, - J. Amer. Chem. Soc. 56, 2554, (1934).

(50) Beuschlein and Conrad, - Paper Trade J. 99, No. 12, 75, (1934).

(51) Gishler, - Ph.D. Thesis McGill University (1935).

(52) Chamot, - Elementary Chemical Microscopy, page 263, (Wiley, 1915).

(53) International Critical Tables, - Vol. I Page 69.

(54) International Critical Tables, - Vol. I Page 69.

(55) International Critical Tables, - Vol. III Page 302.

(56) Russell, - McGill University. Unpublished results, (1931).

(57) Saunderson, - Thesis McGill University (1932).

(58) Gishler and Maass, - Can. J. Research B 13, 370, (1935).

(59) Gurd, Gishler and Maass, - Can. J. Research B 13, 209, (1935).