THE SYSTEM

$CaO - SO_2 - H_2O$

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EQUILIBRIA IN THE THREE-COMPONENT SYSTEM

CALCIUM OXIDE - SULPHUR DIOXIDE - WATER

OVER THE

TEMPERATURE RANGE 25°C. TO 130°C.

A THESIS

by

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To Dr. O. Maass, who directed this research, the writer finds it impossible to make an adequate expression of his appreciation for the encouragement and assistance given throughout the course of this work.

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INTRODUCTION

The investigation to be described deals with the measurement of the vapour pressures and conductivities of the three component system calcium oxide - water - sulphur dioxide, and incidentally of the two component system calcium oxide - water. The investigation covers a large range of variations in temperature and in concentration.

The above is a concise statement of the experimental side of the problem. The development of new experimental technique for making these measurements had, of course, a theoretical objective, viz. an elucidation of the equilibria existing in these systems, especially as there is an intensely practical side to this elucidation. To make this clear it is necessary to elaborate on previous investigations undertaken in this laboratory which culminated in the work to be described.

Some years ago a pulp and paper manufacturing company sent a number of sulphite cooking liquor samples to this laboratory with the request that their physical properties be measured. In an effort to comply with their request a number of conductivity measurements were made on these solutions, and the literature was consulted for previous work. Reference to the literature revealed that data, even on pure sulphur dioxide, was of doubtful value and very incomplete.

Realizing the necessity for physical data, both on pure sulphur dioxide and on its aqueous solutions, Dr. O. Maass and his co-workers commenced in 1923 a primary series of investigations on the properties of pure sulphur dioxide. These were followed later by investigations on its aqueous solutions.

An excellent technique for handling these soluble gas - water systems was developed in the course of the work. This naturally lead to similar researches on the soluble gases ammonia and carbon dioxide. Reference to the scope of this work and the results obtained will be made in a later paragraph.

The properties of pure sulphur dioxide and of its aqueous solutions have been determined, and surprising theoretical deductions made as to the nature of the equilibria existing in the latter at high temperatures. Results obtained in the investigation of the sulphur dioxide - water system, however, have no industrial application except in so far as the free sulphur dioxide in a sulphite cook is concerned. But the properties of the free sulphur dioxide in the sulphite cook are not going to be the same as the properties of the free sulphur dioxide in the experimental system. Both the base, and the bound sulphur dioxide present in the industrial liquor influence the properties of the free sulphur dioxide. The extent to which this is so is of great importance in the sulphite cook. Hence the next logical step in this series of investigations is to determine what effect the addition of a solid third component will have on the properties of the system. Obviously, from the standpoint of importance to sulphite cooking processes, calcium oxide should be the third component.

The work to be described in this thesis is thus a logical continuation of previous work along lines which may produce results of industrial usefulness. Briefly, the problem involved the measurement of vapour pressures and conductivities of solutions of known calcium oxide and sulphur dioxide concentration, the measurements being made at appropriate temperatures between the limits of 25° C. and 130° C. on each solution. The first series of observations were made with solutions containing approximately 1 % calcium oxide and varying concentrations of sulphur dioxide from 0% to about 5.5%. The second series of runs were made with solutions each of which contained approximately 2% calcium oxide and, as before, each run had a different sulphur dioxide concentration. In this series of runs the sulphur dioxide concentration range was from 0% to about 8.6%. A "run" refers to a series of vapour pressure and conductivity measurements made on a single solution of known sulphur dioxide as well as calcium oxide concentrations and in which the variable factor was the temperature.

This three component system may be considered temporarily as consisting of three two-component systems, viz. sulphur dioxide - water, calcium oxide - water, and calcium oxide - sulphur dioxide. The first of these three systems, the sulphur dioxide - water system, has been investigated thoroughly, especially by Dr. Maass and his co-workers. A number of other investigators have worked on this system, usually making vapour pressure, conductivity and density measurements over rather a small range of temperatures and of sulphur dioxide concentrations. The accuracy of most of these measurements was, however, not very great, and very little agreement could be found betwwen the results of separate investigators working on the same phase of the same system. The data of Dr.Maass and his co-workers are accepted as being the most accurate yet obtained on this system. The published data will be reviewed in the following paragraphs.

Sims[1] determined vapour pressures quite accurately over a range of temperatures up to 50°C. and pressures to 200 cms. Smith and Parkhurst[2] also determined vapour pressures of these aqueous solutions, and, in addition, of a few solutions containing varying amounts of bases. Hudson[3] determined the solubility of sulphur dioxide in water at approximately atmospheric pressure and temperatures up to 90°C. Enckell[4] and Oman[5] made less exact solubility determinations up to 90°C. Enckell also made determinations of the solubility of sulphur dioxide in solutions of calcium bisulphite, sodium sulphate, sulphuric acid and sodium sulphate plus hydrochloric acid.

Conductivities have been measured by Ostwald[6] and Barth[7]; freezing-point determinations made by Walden and Centnerszwer[8]; and McRea and Wilson[9] have determined partition coefficients of sulphur dioxide between water and chloroform. Drucker[10], using the results of these four investigators, calculated the dissociation constant. Kerp and Bauer[11] measured freezing points and conductivities. Linder[12] reviews and discusses these papers, and gives data on vapour pressure at 0°C. 25°C. and 50°C. of solutions of four different concentrations. He also gives conductivity data on four solutions over a range of temperatures.

The series of investigations on aqueous sulphur dioxide solutions in this laboratory were made by C.Maass[13], Campbell and O.Maass[14], and Morgan and O.Maass[15]. C.Maass made vapour pressure and conductivity measurements over all possible concentrations at temperatures below 27°C. Morgan and O.Maass greatly improved the experimental technique in handling these systems and made vapour pressure measurements accurate to 0.2% up to atmospheric pressure, and conductivity measurements accurate to 0.1%. The maximum sulphur dioxide concentration they attained was 14.2%. They were able to establish an equilibrium equation between combined and uncombined sulphur dioxide in the liquid phase and to evaluate the constants of this equation at various temperatures.

The work of Campbell and O.Maass[14] was of espacial interest because the work to be described in this thesis deals with the three-component system sulphur dioxide - water - calcium oxide subjected to approximately the same range of temperature and sulphur dioxide concentration variations.

The second two-component system, calcium oxide - water, was the starting point of the work to be described in this thesis. The determination of equilibrium values for the vapour pressures and conductivities of this system over a range of temperatures up to 130°C. was of primary importance. This is more evident if this two-component system is considered as the three-component system with the sulphur dioxide concentration reduced to a value of 0%.

The calcium oxide concentration as well as the temperature will affect the equilibrium of this two-component system. If, however, the calcium oxide concentration is kept above the saturation concentration of the solution at any given temperature with respect to calcium oxide, no change will take place in the equilibrium if more calcium oxide is added. The solution becomes saturated with calcium oxide at quite low concentrations of this substance. Moreover the solubility decreases with a rise in temperature. A 1% addition of calcium oxide was found to leave a considerable quantity of calcium oxide in excess in the solid form even at the 1 lowest temperatures(about 15°C.) at which measurements were made. Since the smallest calcium oxide addition used in this investigation was about 1% the solutions were at all times saturated with respect to this substance.

The vapour pressures and conductivities at various temperatures for a 1% calcium oxide addition are therefore those for a saturated solution and they will be the same as for a 2% calcium oxide addition. These vapour pressures and conductivities were determined accurately at temperatures from 25°C. to 130°C.

It is astonishing that no record of similar measurements over any considerable range of temperatures could be found for this system in the literature. Miller and Witt[16] determined the conductivity at 30°C. while making a solubility determination. A value is also given at 25°C. in Whetham[17]. Values at higher temperatures evidently have not been determined. No record of vapour pressure measurements could be found. The reason may arise from the fact that a true equilibrium value is reached very slowly in these solutions. The great difficulties encountered from this cause will be discussed at greater length in a later paragraph.

Previous investigations of the three-component calcium oxide - water - sulphur dioxide system have also been very limited. The work of Smith and Parkhurst[2] has already been mentioned. Their vapour pressure measurements were made over a very limited range of temperatures and were not very accurate. Schwarz and Mueller-Clemm[25] have determined the ratio of free to combined sulphur dioxide, and Farnell[26] has measured the hydrogen ion concentration in these sulphite solutions.

Enckell's work has been mentioned previously[4]. Conductivity measurements in this system have evidently not been made. The work described in this thesis is apparently the first attempt to measure the physical properties of, and define the equilibria in, this system over any considerable range of temperatures, pressures and concentrations.

In addition to having a theoretical interest insofar as it extends the previous series of investigations, this three-component system has a very real practical importance as has been mentioned previously. Its components are the components used in the preparation of the sulphite liquor for wood cooking by the sulphite process. Moreover, the temperature range over which the system has been investigated includes the temperature range to which the wood and the cooking liquor is subjected in the digesters. Except for the absence of wood then, the experimental conditions parallel the actual industrial conditions. If the results of Campbell and O.Maass[14] proved useful in the industrial process, it is probable that the results to be described later will prove even more useful because they more nearly reproduce the actual conditions to be found inside the digester.

Perhaps the most important phenomenon observed in this research, insofar as its practical application is concerned, was the formation of a precipitate at a definite temperature, as the temperature was gradually increased, for a solution of known calcium oxide and sulphur dioxide concentration. This corresponds in practice to the formation of a precipitate in the digester at a certain stage in the cooking process. This phenomenon is commonly called the "liming up" of the digester.

If the presence of the wood does not cause large changes in the concentration of sulphur dioxide and calcium oxide, the temperature at which this precipitation should take place could be predicted, providing the sulphur dioxide and calcium oxide concentrations of the liquor were known.

The conductivities of the solution undergo very marked changes at this precipitation point. This suggests the possibility of using conductivity measurements as a control method on the digester process.

The problem of precipitation in the digester is one of great importance. Saunderson[18], in a series of investigations on the penetration of the sulphite liquor into wood, has shown that the formation of this precipitate impeded the penetration of the liquor into the wood. It must therefore lengthen the time required to complete a cook. If it could be proved that the presence of this precipitate is in no way beneficial to the process its formation could be avoided by the choice of a solution of suitable calcium oxide and sulphur dioxide concentration. The results to be presented later might prove useful in choosing such concentrations.

The results on these experimental liquors also give data regarding the total pressure in the system and the partial vapour pressure of the sulphur dioxide for a solution of known calcium oxide and sulphur dioxide concentrations at any temperature between 25°C. and 130°C.

It must be admitted that the results obtained are for an "ideal" liquor, i.e., there is no wood present to cause complications. If concentration changes due to the presence of the wood are small however, the results obtained could be applied directly to the industrial process, and they would give an accurate picture of what really takes place inside the digester in the cooking process.

The most important contribution of this whole investigation is that an experimental method has been developed whereby such complicated systems can be directly studied. The next step is to introduce wood into the "experimental liquor" and see how its presence modifies the equilibria as determined for the pure "experimental liquor". This should not present any additional experimental difficulties, and would require only minor alterations in the present apparatus. Unfortunately there was insufficient time even to make preliminary experiments of this nature.

The development of a satisfactory experimental technique for handling these systems proved to be a difficult undertaking. Many months were spent in designing and building the apparatus. Finally, having perfected the apparatus, it was thought that a large number of runs could be completed in a short period of time. Unfortunately, at certain concentrations, long periods of time were required for the systems to come to equilibrium. This was especially true of the two-component calcium oxide - water system and also of the runs in the three-component system in which the sulphur dioxide concentrations were low. The equilibrium values of the vapour pressures seemed to be reached fairly rapidly, but the conductivity was very slow in approaching its true equilibrium value. The conductivity measurements were made with great precision. Since they are a very sensitive type of measurement they naturally would be a better means of following the changes in the system, and consequently of revealing when true equilibrium was reached.

This delayed equilibrium was undoubtedly due to the slow rate at which the solid phase in these systems went into, or came out of, solution (depending on whether the temperature were lowered or raised). For confirmation of this fact it is only necessary to consult the literature for the solubility of calcium oxide in water over a range of temperatures. Mellor[19] gives a table of solubilities compiled from various sources in which the solubilities at higher temperatures sadly disagree with those at lower temperatures. Even at low temperatures data from other sources do not agree. Since detailed solubility data were required for the calculation of the degree of ionization and the dissociation constants of the calcium oxide - water system at various temperatures, a comprehensive search of the literature for these solubilities was made. The solubility references will be given in a later section on the discussion of this two-component system. It is probable that these discrepancies are due to the fact that the solubility determinations were carried out on solutions in which the solute had not had time to reach equilibrium with the solvent. Miller and Witt[16] doubted the accuracy of previous determinations at 30°C. and proceeded to make a determination by using conductivity measurements as a criterion of true equilibrium. They found that the conductivity underwent a regular variation until equilibrium was reached, and that it required about thirty hours to get the system to equilibrium. Moreover they found that the final value for the solubility depended to a slight extent on the manner in which the calcium oxide was put into solution. It is possible that true equilibrium is delayed by a secondary equilibrium existing between large and small particle solubilities.

It is not surprising therefore to find such poor agreement among the various solubility determinations. In addition to the equilibrium time factor in these solutions there are two other factors which add to the difficulty of determining solubilities accurately, viz., (1) the solutions rapidly absorb carbon dioxide, and (2) the solubility decreases with a rise in temperature. This latter factor makes low temperature solubility determinations very difficult.

Even under the most ideal conditions, as has been pointed out above, some thirty hours at least would be required to get the system to equilibrium at each temperature point of each run. This would require a tremendous amount of time for the completion of each run and consequently such a procedure was entirely out of the question. Considerable time was therefore spent in devising a method whereby the true equilibrium values could be approximated without actually waiting for equilibrium to be attained. This method will be described in a later section. Even with this shortened procedure each run often required about twenty four hours of continuous observations. This, together with the time necessary to prepare for the next run made the whole a tedious and lengthy procedure resulting in the completion of fewer actual experimental measurements than had originally been intended.

Calculation of results from the experimental data also required a great deal of time. About six weeks were spent in calculating the data obtained. The calculations, while not difficult, involved the application of many correction factors and were very lengthy.

The following is a brief summary of the work completed. Vapour pressures and conductivities of the calcium oxide - water system (0% sulphur dioxide) were measured at appropriate temperature intervals between the temperatures 25^oC. and 130^oC. A series of six runs, all having a calcium oxide concentration of approximately 1%, and having sulphur dioxide concentrations of approximately 0.2%, 0.3%, 0.9%, 1.75%, 3.3%, and 5.5% respectively, were next made. This series was followed by a second series of runs each having approximately 2% calcium oxide and sulphur dioxide concentrations of 1.25%, 2.4%, 3%, 5%, 6.6%, and 8.6% respectively.

The section immediately following this introduction will contain a detailed description of the apparatus. The technique involved in the manipulation of the apparatus and the preparation of the solutions will next be described. This will be followed by a section on results and the calculation of results, and finally, the results will be discussed in detail and a summarized conclusion made.

EXPERIMENTAL SECTION

PART A APPARATUS AND PROCEDURE

To facilitate the description of the apparatus a brief general discussion of its constituent parts will precede the detailed description. The following is a summary of the headings of subsequent sections describing the apparatus, its purpose and its manipulation.

I <u>General</u>
II <u>Detailed description of apparatus</u>
  (a) Gas purification system.
  (b) Gas Measuring and Introduction System.
  (c) The Reaction Cell, Manometer System.
    (1) The Cell.
    (2) The Manometer.
    (3) The Calibration of the Manometer.
  (d) The Frozen Mercury Seal.
  (e) The Reaction Cell Heating Bath.
III <u>Conductivity Measurements</u>
IV <u>Preparation of pure Calcium Oxide</u>
V <u>Procedure for the Preparation of Solutions</u>
VI <u>Procedure in Making a "Run"</u>
VII <u>Factors to be considered in the Calculation of Results</u>

I General

The apparatus may, for the sake of convenience, be considered as consisting of four major constituent parts, viz., a gas supply and purification system, a gas measuring and introduction system, a frozen mercury seal-off, and a reaction cell and manometer system. These systems are marked off in plate (A).

The gas supply and purification system had as its purpose the extraction of the sulphur dioxide from the supply cylinder and its purification. An effective evacuating unit formed part of this system. The gas measuring and introduction system provided a means whereby an amount of the purified gas could be accurately measured and introduced into the reaction cell system. The reaction cell - manometer system was the system in which the actual experimental observations were made. It consisted of a reaction cell, into which the calcium oxide, water and sulphur dioxide were introduced, joined to a manometer for measuring the vapour pressure of the solution. Electrodes were placed in the reaction cell so that conductivity and vapour pressure measurements could be made simultaneously. The frozen mercury seal-off provided an effective means of sealing off the sulphur dioxide introduction system from the cell-manometer system after a sulphur dioxide introduction had been made. It could be considered as a form of stop-cock capable of standing high pressures.

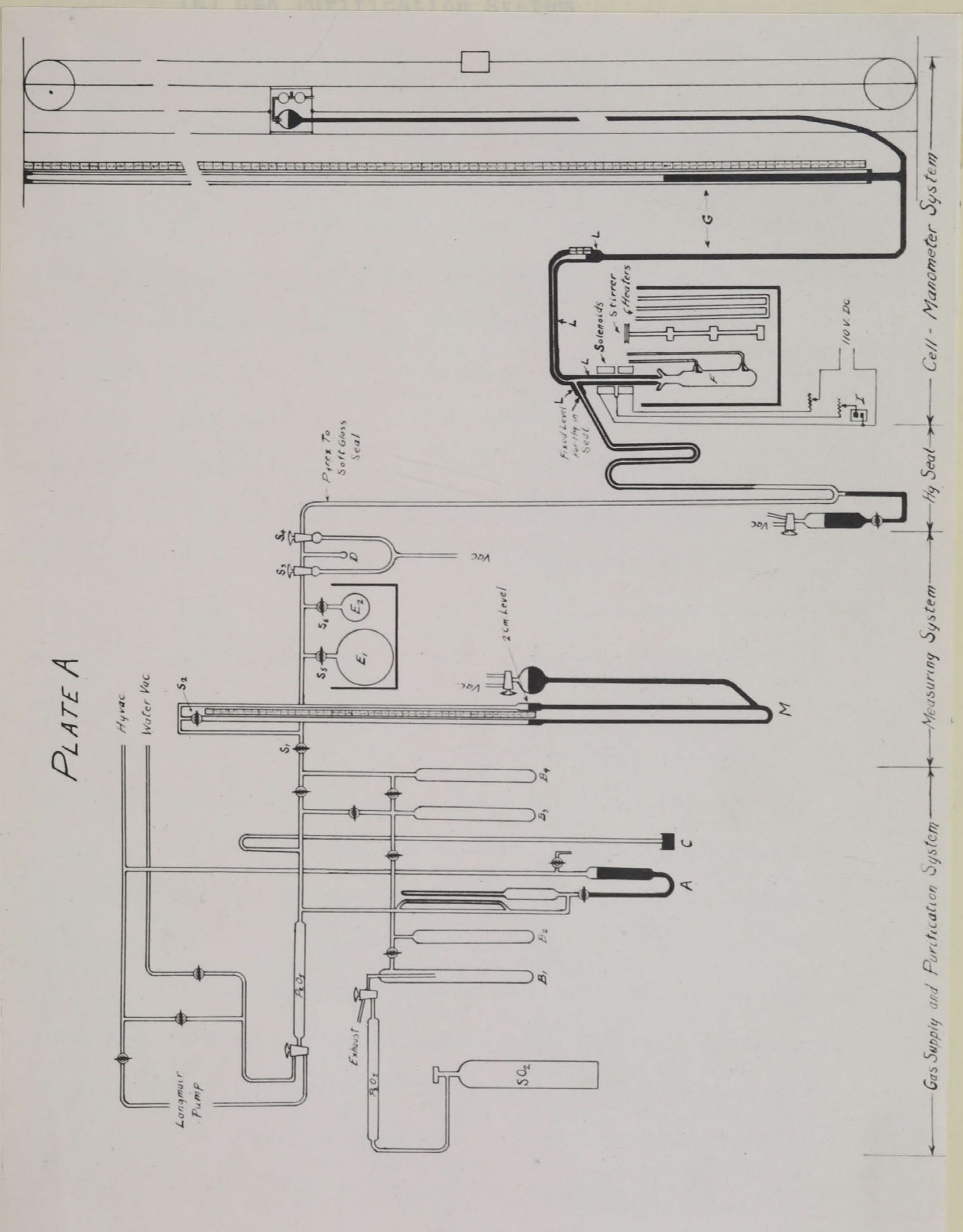


PLATE A

Hyvac
Water Vac
S2
S1
S5
S6
E1
E2
S3
S4
D
Vac
2 cm Level
Vac
M
B4
B3
C
A
B2
B1
P2O5
Exhaust
P2O5
SO2
Longmuir Pump
Pyrex To Soft Glass Seal
Vac
Fixed Level for Hg in Seal
L
L
L
L
Solenoids
Stirrer & Heaters
F
110 V. DC
I
G
Gas Supply and Purification System
Measuring System
Hg Seal
Cell - Manometer System

II Detailed description of apparatus.

(a) Gas Purification System

Reference will be made frequently to plate (A).

This entire system was made of soft glass, and a satisfactory seal was made to the sulphur dioxide supply cylinder by the use of De Khotinsky cement. Gas extracted from the cylinder was dried by passing over phosphorus pentoxide and condensed in the bulb (B_1) by surrounding the bulb with a mixture containing carbon dioxide snow and acetone. The whole system had previously been thoroughly dried and evacuated. Successive low temperature distillations of the liquid sulphur dioxide were then made from B_1 to B_2, B_2 to B_3 and B_3 to B_4. In each distillation the first and last portions of the distillate were ejected back through the exhaust tube. A mercury trap in this exhaust tube prevented air entering the system. B_4 served as a storage bulb for the purified sulphur dioxide. The sulphur dioxide was procured from the Matheson Co. and was found to be almost completely free from sulphur trioxide. The above method of purification gave very pure sulphur dioxide.

The evacuating system was a flexible one and was arranged so that a water vacuum pump, a Cenco Hyvac pump, or a Langmuir mercury diffusion pump backed by the Hyvac pump could be used to evacuate the entire apparatus or portions of it. The arrangement is shown in the diagram. A McLeod Gauge (A) was used to test the efficiency of the evacuating system and to detect slow leaks in the system. The simple manometer (C) was used for rough pressure measurements and also acted as a safety valve when gas was admitted from the supply cylinder.

(b) Gas Measuring and Introduction System

This system consisted of the volumes (E_1) and (E_2), and the connecting tubing bounded by the stopcocks (S_1), (S_2), (S_4) and a fixed level of 2.0 cm. on the right hand tube of the manometer (M). The left hand tube of this manometer was completely evacuated and (S_2) was closed. By applying air or vacuum to the mercury well on this manometer the mercury in the right hand column could always be adjusted to the 2.0 cm. level. The difference in the mercury levels in these two columns was read on a calibrated glass scale and gave (after a suitable glass scale temperature correction had been applied) the gas pressure in this gas measuring system.

(E_1) and (E_2) were totally immersed in a water bath, the temperature of which was read by a calibrated thermometer. Three other calibrated thermometers were placed in contact with the connecting tubing at appropriate points to determine the temperature of the gas in this portion of the volume.

(E_1) and (E_2) were calibrated up to the stopcocks (S_5) and (S_6) by weighing them empty and then filled with water and applying the necessary corrections. The connecting tubing volume was determined in two ways:

First Method: The whole volume system was filled with dry air, the pressure and temperatures were recorded, (S_5) and (S_6) were closed, the rest of the system was completely evacuated, then the air closed off in (E_1) and (E_2) was allowed to expand into the evacuated connecting tubing and the pressures and temperatures were read again. If p_1 is the pressure at the beginning, V_1 the combined volume of (E_1) plus (E_2), and p_2 is the final pressure, then

$$p_1V_1 = p_2(V_1 + x)$$

where x is the volume of the connecting tubing. This equation is only true if the temperatures remain constant. The appropriate corrections can be made if the temperature does not stay constant.

Second Method: A small glass bulb was blown onto the system just past (S_4), temporarily replacing the tube leading to the cell system. Both it and the connecting tubing were then evacuated and (S_4) closed. Sulphur dioxide was now allowed to fill the connecting tubing ((S_5) and (S_6) were closed) to about atmospheric pressure. The pressure and temperatures were read. The sulphur dioxide was then condensed out in the small glass bulb by immersing the bulb in liquid air. The bulb was then sealed off, weighed, the tip broken off and the sulphur dioxide allowed to escape, and the empty bulb and tip weighed. The volume of the tubing was then calculated from the Gas Law equation using the sulphur dioxide molecular weight data of Cooper and O.Maass[20]. The values for the volume as determined by two such experiments checked very closely and agreed well with the volume as determined by the first method. The following are the values for the three volumes found from a number of determinations:

Volume of (E_1)	587.82 cc.
Volume of (E_2)	126.80 cc.
Volume of connecting tubing	82.25 cc.

A known amount of sulphur dioxide was taken from this gas measuring system and introduced into the reaction cell system in the following manner: Pure sulphur dioxide was allowed to enter the gas measuring system from the storage bulb (B_4) until the gas pressure as registered on manometer (M) was about atmospheric pressure. The gas measuring system was then closed off by its boundary stop-cocks (S_1) (S_2) (S_4), and (M) adjusted until the right hand side was at the 2.0 cm. level. The pressure and the temperatures were then recorded. A portion of the sulphur dioxide in this system was now condensed in the small tube (D) and the pressure stop-cock (S_3) closed. (Note that both (S_3) and (S_4) are pressure stop-cocks. (S_4) was previously closed). The sulphur dioxide in this small tube was then allowed to warm up until sufficient pressure was developed to cause it to go over into the cell system with a rush when (S_4) was opened. (S_4) was then closed again, (S_3) opened, and the gas allowed time to come to a uniform temperature in the tubing and volumes. The pressure and temperatures were recorded as before and the weight of sulphur dioxide introduced into the reaction cell calculated from the loss in weight of the sulphur dioxide in this gas measuring system by using the simple Gas Law equation.

If W is the weight of sulphur dioxide introduced into the reaction cell system, then

$$W = w_1 - w_2$$

where w_1 is the original weight of gas in the system before injection and w_2 is the weight of gas in the system after injection.

Then

$$w_1 = \frac{p_1 . v_1 . M_1}{R . T_1} + \frac{p_1 . v_2 . M_2}{R . T_2}$$

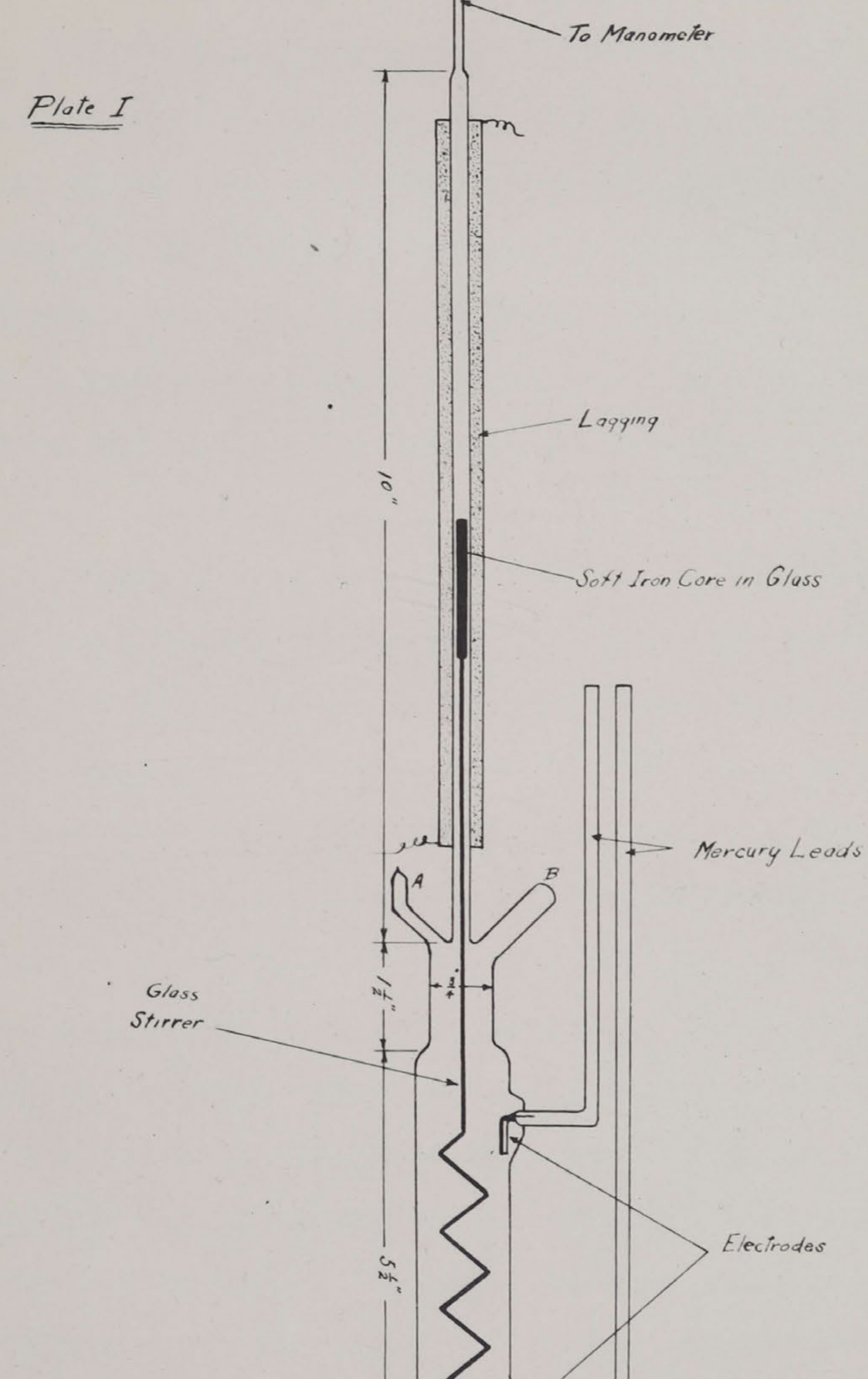
and

$$w_2 = \frac{p_1^1 . v_1 . M_1^1}{R . T_1^1} + \frac{p_1^1 . v_2 . M_2^1}{R . T_2^1}$$

where p_1 is the pressure of the gas in the system before injection.
p'_1 is the pressure of gas in the system after injection.
v_1 is the volume of (E_1) plus (E_2).
v_2 is the volume of the connecting tubing.
T_1 is the temperature of v_1 before injection.
T'_1 is the temperature of v_1 after injection.
T_2 is the mean temperature of v_2 before injection.
T'_2 is the mean temperature of v_2 after injection.
M_1 is the molecular weight of the gas at T_1 and p_1.
M'_1 is the molecular weight of the gas at T'_1 and p'_1.
M_2 is the molecular weight of the gas at T_2 and p_1.
M'_2 is the molecular weight of the gas at T'_2 and p'_1.
R is the gas constant = .08209

T_2 and T'_2 were mean temperatures calculated from the temperatures recorded on the three thermometers in contact with the connecting tubing. T_2 and T'_2 generally differed from T_1 and T'_1. This necessitated the division of the whole system into two parts with the application of the Gas Law equation to each part separately. The molecular

Plate I


To Manometer
Lagging
10"
Soft Iron Core in Glass
Mercury Leads
A
B
1½"
¾"
Glass Stirrer
Electrodes
5½"
1¼"

weight data was due to Cooper and O.Maass[20].

(c) The Reaction Cell and Manometer System.

Plate A shows the general arrangement of this system. The system was composed of a reaction cell (F) joined to a constant level manometer (G) capable of measuring high pressures. This whole system was made of pyrex glass. The reaction cell will first be described in detail, and later a separate sub-section will be devoted to the description of the manometer.

(1) The Cell.

Plate I is a detailed drawing of the cell giving its approximate dimensions. Adequate stirring of the solution was obtained by an electromagnetically operated all-glass stirrer. A small iron core was sealed in the upper end of a glass tube, the lower end of which was bent in a form capable of producing effective agitation of the liquid in the main body of the cell. A solenoid consisting of a large number of turns of ennunciator wire and tapped out in the centre was placed around the vertical tube leading from the top of the cell inside which the upper end of the stirrer could slide freely up and down. By passing a current through the solenoid and adjusting its position the stirrer could be lifted from the bottom of the cell. The upper portion of the solenoid, from the centre tap to the upper end, was then intermittently short circuited by a make and break device which resulted in a continuous up and down movement of the stirrer. Variable resistances in these circuits (as shown in plate A) made it possible for the "jump" or thrust of this stirrer to be adjusted to give a good stirring action and also to prevent it from striking the bottom of the cell when the upper half of the solenoid was partially short-circuited. The make and break device (I in Plate A) was a motor-driven eccentric wheel on the outer surface of which an arm rested. One end of the arm was fixed, the other had a contact which intermittently dipped into a mercury well as the eccentric wheel rotated. This end of the arm made an up and down motion. The frequency of the make and break could be varied by varying the motor speed, thus varying the stirring rate.

Some difficulty was experienced with overheating of the solenoids. This was due to the lagging (L) heated to about 150°C. surrounding the vertical tube from the top of the cell. This heated lagging came very close to the inside windings of the solenoid. The difficulty was overcome by winding a thin copper tube around the lagging and then winding the solenoid on top of this tube. A small amount of spacing was left between the lagging and the cooling coil. Water was circulated through this cooling coil.

The conductivity electrodes were made of thin platinum foil and were sealed in the pyrex glass according to the method devised by Housekeeper[21]. Special mention of the form of these electrodes and the shape of the recesses in the cell in which they were placed should be made. In the first type of cell some difficulty was encountered with solid material, present in some of the runs, accumulating in these recesses and covering the electrodes. After a number of modifications in the design of these recesses had been made the type shown in Plate I finally proved satisfactory. The electrode surface in this cell faces the stirrer and is thus swept free from solid. The recesses were very shallow and the back walls of the recess were so nearly perpendicular that there was no pocket in which the solid could settle.

Side tube (B) (Plate I) at the top of the cell is the opening through which calcium oxide was introduced into the cell. Side tube (A) is for the introduction of water. Water was introduced into the cell by joining a distillation bulb to the cell at this point, weighing the water into this bulb, freeing it from air, and then distilling it into the cell and sealing off the tube leading to the distillation bulb at point (A). This procedure will be described in detail later.

To prevent condensation of the vapour phase in the vertical tube leading from the top of the cell (and this also applies to the rest of the tubing and the mercury surface of the manometer in this cell - manometer system) this tube always had to be kept at a higher temperature than the cell. This was accomplished by winding an electrical heating unit on the tubing. A thin layer of asbestos paper was wrapped around the tube.

Fine nichrome resistance wire having a resistance of about three ohms per foot was then wound on this asbestos. The turn spacing was about one sixteenth of an inch. A coating of asbestos packing cement was then placed over the wire to prevent heat radiation. A variable resistance placed in series with the heating unit so formed served to control the current and consequently the temperature. Heating units so constructed will be called "lagging" throughout this description. Such a "lagging" was wound on the vertical tube from the top of the cell. It extended almost to the point where the cell was joined to the rest of the system as is shown in Plate I.

The oil bath in which the cell was immersed will be described in a separate section. The cell constant determinations will be given in the section on Conductivity Measurements.

(2) The Manometer.

A detailed drawing of the manometer is to be found in Plate III. In many ways this manometer had some rather unusual features, and, as was the case in the design of the reaction cell, this final form was the result of many improvements made on the manometer as it was originally constructed. The measurement of pressures up to about eight atmospheres in a room about four meters high necessitated the construction of a "closed tube" type of manometer. This closed tube, in which air was trapped above the mercury surface, was about 380 cm. high, and about 1 cm. in diameter. This

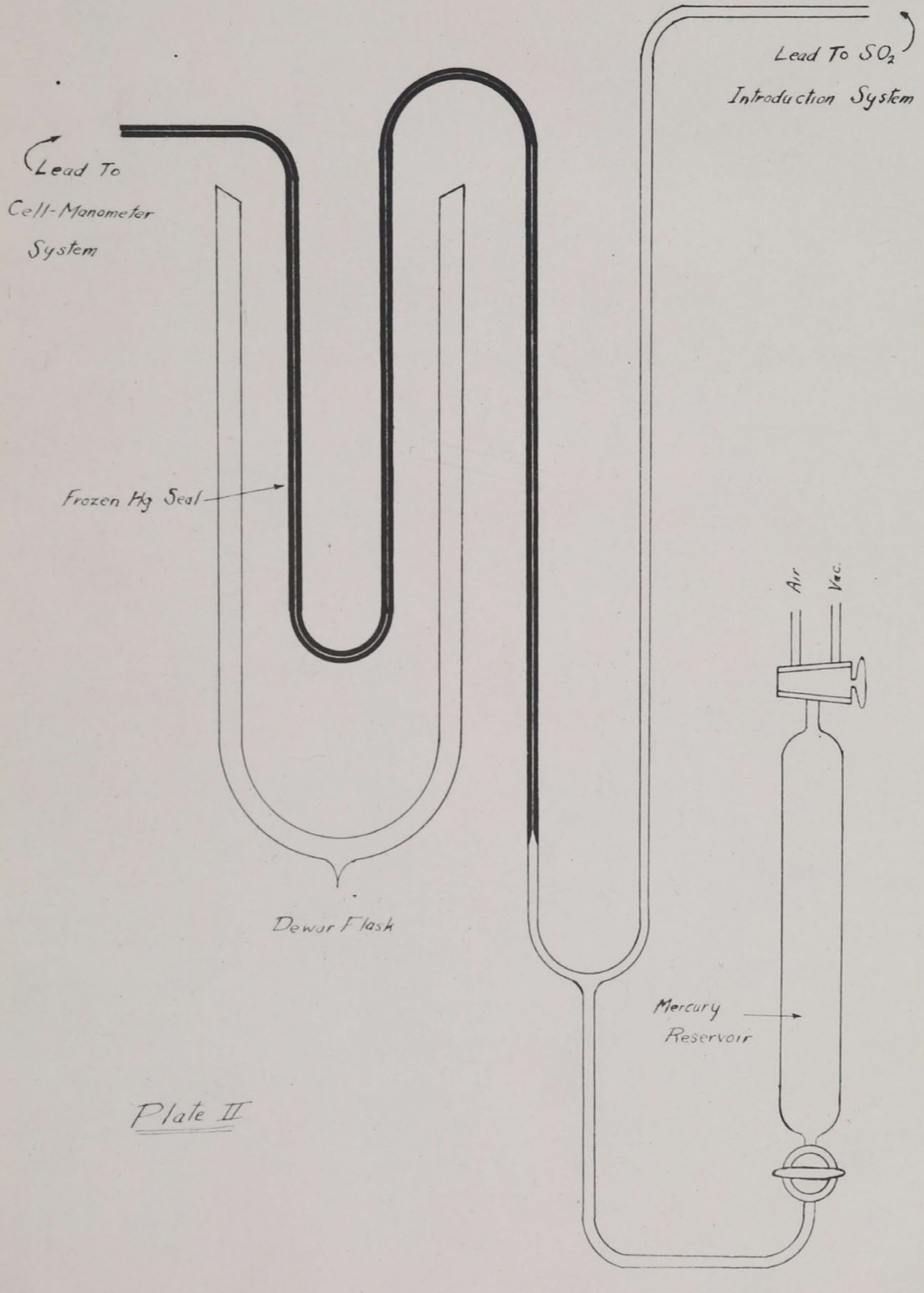

Lead To SO₂
Introduction System
Lead To
Cell-Manometer
System
Frozen Hg Seal
Air
Vac.
Dewar Flask
Mercury
Reservoir

Plate II

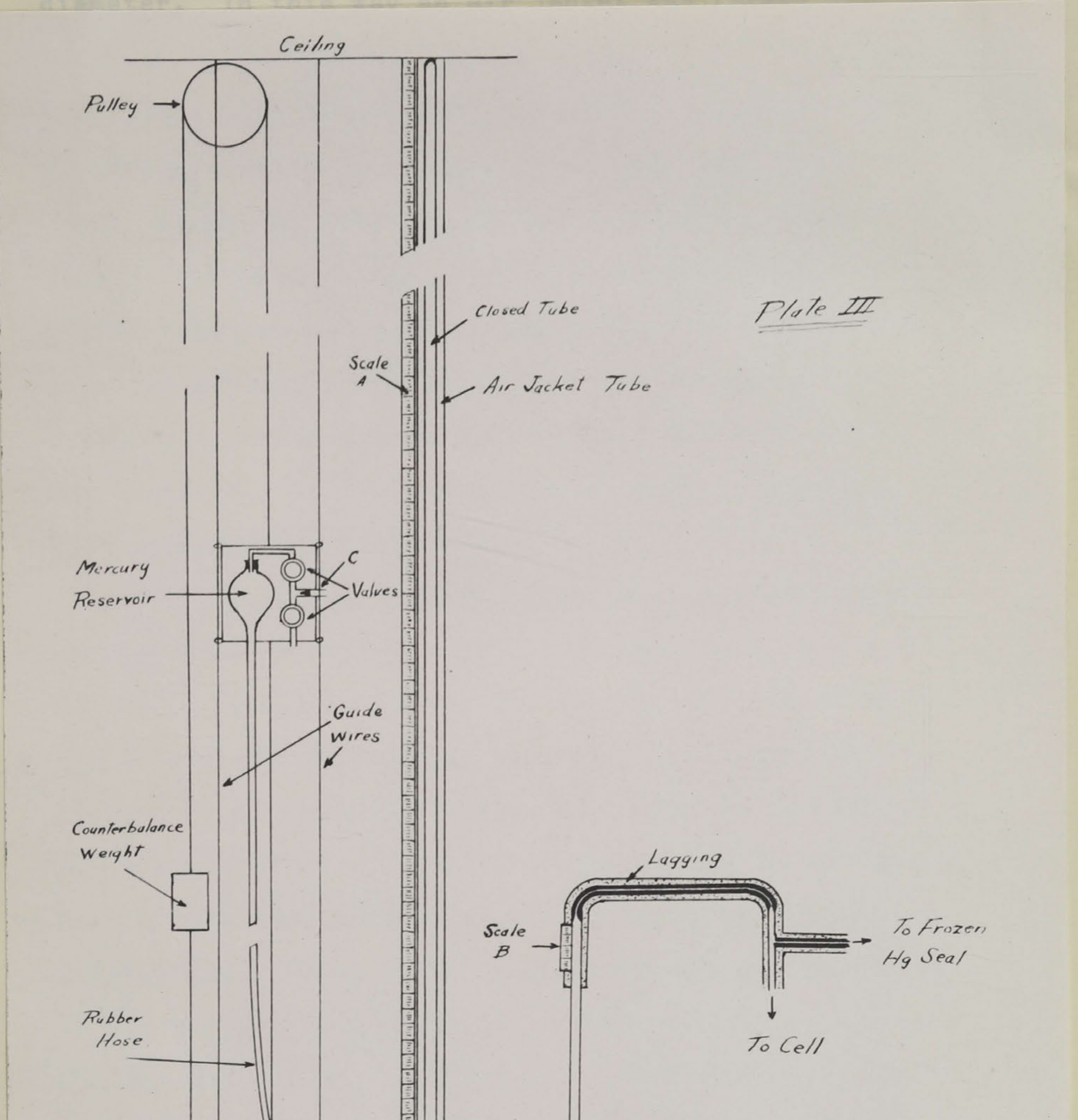

Ceiling
Pulley
Closed Tube
Scale A
Air Jacket Tube
Mercury Reservoir
C
Valves
Guide Wires
Counterbalance Weight
Lagging
Scale B
To Frozen Hg Seal
To Cell
Rubber Hose
Pulley
Floor

Plate III

tube was surrounded by a second tube about 2.5 cm. in diameter. In this way an air jacket was formed about the inner tube thus protecting the air trapped inside the closed tube from sudden temperature changes. The temperature of the trapped air was read from three standardized thermometers placed against this inside tube at suitable points. The air pressure inside this closed tube was about three quarters of an atmosphere when the mercury level stood near the bottom of the tube. The scales placed beside this tube were wooden meter sticks. They were calibrated when in position by a standardized brass scale.

The first type of manometer had a stationary mercury reservoir joined to this closed tube, and all of the levelling device to the left of the manometer scale in Plate III was not present. The top of the reservoir was joined by a fine bore tube to the cell. The reservoir and the tubing of course had to be "lagged". This type of manometer was quite simple, but it had one serious fault, viz. as the pressure increased the level of the mercury in the reservoir fell and the volume of the gas phase (this includes the gas volume above the liquid in the cell, in the connecting tubing to the manometer, and above the mercury in the reservoir of the manometer) greatly increased. An increase of volume in this gas phase , or "dead space", caused sulphur dioxide to come out of solution and thus it greatly depleted the concentration of the sulphur dioxide in the liquid phase.

The ideal type of manometer system was one in which this gas phase volume was as small as possible and approximately constant at all times. The modified form of manometer as shown in Plate III met these requirements.

A tube 1 cm. in diameter was lead up from the bottom of the closed tube to a height suitable for joining onto the cell. A capillary tube joined the top of this tube to the tubes leading from the mercury seal and the cell. All this tubing was "lagged". Scale (B) was placed at the top of the tube leading from the bottom of the manometer and the lagging continued to a point just below this small scale. A small window was left in the lagging beside this scale for observing the mercury level. The scale was graduated from 0.0 cm. in the centre to about 3 cm. above and below this point. A thermometer was inserted under the asbestos paper of the lagging against the tube near the upper end of this scale. Another thermometer was placed in the connecting tubing to the cell in a similar manner. These thermometers gave the temperature of the gas in this tubing. This had to be known before a calculation of the weight of sulphur dioxide in the gas phase could be made. After the cell was joined to the tube leading from the manometer the section of the tube where the join was made had to be lagged. The lagging unit on the vertical tube from the top of the cell was connected in series with the lagging on the tube to the manometer, forming one electrical heating circuit. The other circuit was the portion of the lagging around the scale up to the beginning of the capillary tubing. Resistances in each of these circuits allowed their temperatures as read on the two thermometers embedded in the lagging to be adjusted so as to be the same.

To maintain the mercury level at approximately zero on scale (B), regardless of the pressure, a moveable mercury reservoir was also attached to the closed tube. The reservoir was mounted on a board capable of being raised and lowered in two wire tracks by a counterbalanced rope leading over pulleys at the ceiling and floor of the room. The reservoir was joined to the closed tube by heavy oxygen hose. If the pressure in the cell system increased, the reservoir had to be raised to maintain the mercury level at zero on scale (B) and vice versa.

Since the room was only about four meters high some arrangement had to be devised whereby pressure could be applied to the mercury in the reservoir when pressures of six or seven atmospheres were to be measured. For this purpose a copper tube was tightly sealed into the top of the reservoir bulb. Two brass needle valves were joined to this copper tube. A bicycle tire valve stem (C) was soldered to the tubing between these two valves, and the valve inside left in the stem. By closing the lower valve, opening the upper, and attaching a pump at (C) the air pressure on the mercury surface in the reservoir could be greatly increased. Sufficient pressure could be developed by a small foot pump to measure pressures up to about seven atmospheres without danger of bursting the glass reservoir. The two valves were also convenient in releasing the pressure in this reservoir. They could be opened and closed alternately thus preventing any sudden decrease in pressure.

Considerable care had to be taken to maintain the level at about zero on B. If this level was not closely watched, especially when the temperature of the cell was being raised or lowered, mercury would be either forced over into the cell or else the mercury would drop below the lagged portion of the tube, be cooled, and condensation would take place on its surface.

The zero reading on scale (B) was determined in terms of scale (A) by means of a cathetometer.

Reading on (B) = 0.0 cm. = 291.92 cm. on scale (A)

(3) Calibration of the Manometer.

Since the manometer was of the closed tube type, the volume of air trapped above the mercury had to be known for any position of the mercury surface in this closed tube. This necessitated a calibration of this tube before the manometer was connected to the system.

The closed tube with its air jacket tube, and the scales, were rigidly mounted on the board which supported them. At this time none of the other tubes leading to the bottom of the manometer had been attached. The manometer tube was thus closed at the top end and open at the bottom end. This whole assembly was now turned upside down and the calibration carried out by pouring small weighed portions of mercury down the tube and recording the scale reading after each addition. Where joins occurred in the tube three additions, one on either side and one in the centre of the join, were made. The appropriate temperature corrections were made. The following table gives the weight of mercury in the tube, the corresponding scale reading, and the corrected volume. The volume for any scale reading was found by interpolating between these values.

Weight of mercury	Corrected volume	Scale reading
41.0117 gms.	3.0303 cc.	3.90
82.8885	6.1244	7.85
377.3938	27.884	36.15
673.1103	49.734	65.05
913.4496	67.493	87.85
940.1780	69.467	90.30
964.6547	71.275	92.38
1261.514	93.210	120.30
1558.118	115.21	148.50
1867.970	138.02	178.00
1894.228	139.96	180.50
1907.604	140.95	181.68
1924.666	142.21	183.25
2221.091	164.11	211.50
2520.937	186.26	240.45
2835.571	209.52	271.15
2847.252	210.38	272.15
2866.916	211.83	273.82
3165.754	233.91	301.25
3459.742	255.63	328.63
3810.852	281.58	360.90
3829.647	282.96	362.51
3842.609	283.92	363.43
3855.860	284.91	364.61
3916.185	289.35	370.49

The scale readings in this table have not been corrected.

The meter scales were calibrated with a standardized scale and the following table of corrections obtained. The units are centimeters.

Wood Scale Reading	Standard Scale	Correction to be added
0.00	0.00	0.00
50.00	50.03	0.03
90.00	90.05	0.05
100.00	100.25	0.25
101.00	101.35	0.35
150.00	150.35	0.35
190.00	190.35	0.35
199.00	199.35	0.35
200.00	200.45	0.45
201.00	201.65	0.65
230.00	230.64	0.64
260.00	260.63	0.63
290.00	290.62	0.62
299.00	299.62	0.62
300.00	300.77	0.77
301.00	301.89	0.89
350.00	350.89	0.89

The simple Gas Law equation can now be applied to the air trapped above the mercury in the closed tube. A known pressure, say atmospheric pressure, was applied to the manometer by leaving open the tube joined to the cell. The mercury was brought up to 0.0 on scale (B) and the mercury level in the closed tube read. The volume is known, and the average temperature of the trapped air was found by calculation from the temperatures as read on the three thermometers. The pressure exerted by the trapped air was equal to atmospheric pressure minus the corrected difference in heights between 291.92 cm. on (A) (0.0 cm. on (B)) and the mercury level read on (A). The manometer constant k was then calculated.

k was determined at complete evacuation, at atmospheric pressure and at a fairly high pressure in this manner and determinations checked exceedingly well. The final value assigned to it was

Manometer Constant k = 49.93

The constant had the dimensions of centimeters of mercury and cubic centimeters.

If k, the volume, and the temperature are known then the pressure due to this trapped air can be calculated. This pressure added to or subtracted from the pressure due to the difference in mercury levels, depending on the relative positions of the mercury levels in (A) and (B), gives the pressure in the cell system.

(d) The Frozen Mercury Seal.

When the calcium oxide, water, and sulphur dioxide had all been introduced into the reaction cell it was necessary to seal off the reaction cell system from the gas introduction system. Moreover this seal had to be capable of standing pressures of about eight atmospheres. Obviously a stop-cock between these two systems would not do. In a number of preliminary experimental runs the system was sealed off by drawing down the glass tube leading to the gas introduction system at a point close to where it joined the tube from the cell to the manometer. The disadvantage of this procedure was that the cell had to be cut away from the system, cleaned out, and the whole tedious process of water distillation and lime addition repeated every time a run was made on a solution of higher sulphur dioxide concentration.

The frozen mercury seal shown in Plate II overcame this difficulty. The tube from the gas introduction system to the cell system was constructed as is shown in the diagram. A portion of it was capillary tubing. It was made entirely of pyrex glass as was the cell - manometer system. A pyrex to soft glass seal was inserted in the tube leading to the gas introduction system just before stop-cock (S_4) in plate A. When vacuum is applied to the mercury reservoir all mercury is drawn down out of these tubes and sulphur dioxide may be introduced into the cell. When the introduction is completed, air is allowed to enter the mercury reservoir forcing mercury into this tube. Enough mercury is allowed to enter so that the mercury rises to a fixed point in the capillary tubing leading to the cell just where the lagging commences as shown in Plate A. A solid carbon dioxide - acetone mixture in a Dewar flask is then carefully placed around the capillary tubing where it is bent in the form of a U. The mercury freezes, giving a seal capable of standing tremendous pressures.

If a run has been completed and more sulphur dioxide is to be added, the seal is allowed to melt by removing the Dewar. The mercury is then drawn back into the reservoir and the gas introduced. Occasionally the mercury thread in the capillary tube breaks and all of the mercury is not drawn back into the reservoir. This mercury can easily be driven out of the capillary tubing back to the reservoir by warming up the cell system. The increased vapour pressure of the solution in the cell quickly forces the mercury out of the bend in the capillary.

This seal made it possible to make runs on any number of solutions with increasingly greater sulphur dioxide concentrations and the same calcium oxide and water concentrations. Thus in a series of five or six runs the system was set up only once. Calcium oxide and water were introduced into the cell, a sulphur dioxide addition was made, and the system taken over a range of temperatures, completing one run. More sulphur dioxide was added to this system and the next run made, etc. When it is considered that it took about three days to make the original set up for a run, i.e. clean and dry the cell, add calcium oxide, free the water from air and distil it into the cell, the amount of time saved by the use of this seal can be appreciated.

(e) The Reaction Cell Heating Bath.

The reaction cell was immersed in a Glycoline oil bath to a point where the side tubes (A) and (B) were just covered. The bath was of pyrex glass and was 8.5 inches in diameter and 18 inches high. The bath was vigorously stirred by a motor driven stirrer. There were two separate electrical heating units in the bath; both were of quite large heating capacity, and their heating speed could be varied. Two separate units are necessary if the temperature is to be maintained constant at a fairly high temperature. One of the units, the heating rate of which was controlled by an external variable resistance in series with it, was regulated so that it would all but maintain the desired temperature. It was left on continuously and was not connected in the thermoregulator circuit. The other unit, the heating rate of which was varied by tap-outs to a series of switches, was connected through the thermoregulator circuit and set at as low a heating rate as it was possible to use in order to maintain the desired temperature. By manipulation of the heating units in this manner temperatures could be maintained to ± .05°C. at any temperature from 25°C. to 150°C.

The thermoregulator was a liquid expansion type using glycoline oil and mercury. It had three bulbs, two of which were filled with copper gauze to accelerate the heat transfer. It was connected in a low voltage relay circuit in the usual manner and controlled the current in only one of the bath heater units as stated above.

A copper cooling coil through which water was circulated facilitated the cooling of the bath and was also useful in maintaining the bath at temperatures of about 25°C. and lower.

Since fairly high gas pressures were developed at the higher temperatures at which observations were made there was some danger of the cell exploding. Accordingly a box-like enclosure, made of wood, was built around all of the apparatus except the manometer. This wooden enclosure had heavy glass windows built into the front so that temperatures etc. could be read. At low temperatures when there was no danger of an explosion taking place, the front and the top of this enclosure could be removed.

III Conductivity Measurements.

The construction of the reaction cell, which also served as the conductivity cell, has been described in detail in Section II(c), part (1).

The conductivity measuring apparatus consisted of a Leeds and Northrup Kohlrausch slide-wire bridge, a Curtiss-wound non inductive resistance box (0 to 1000 ohms in 1 ohm steps), a pair of good quality high resistance ear-phones and a Vreeland oscillator. The oscillator was operated at a frequency of 1000 cycles per second. The ordinary type of bridge hook-up was used and a low capacity variable condenser was shunted across the resistance terminals to balance out any capacity effects and give a sharper balance point. Amplification in the phone circuit was tried but was found unnecessary.

Since thin platinum foil was used in the construction of the electrodes and in the seal through the pyrex glass, these platinum leads would have an appreciable resistance. The conductivity bridge was set up several feet from the cell system and the copper lead wires from the bridge to the cell would also contribute slightly to the "lead resistance". This total "lead resistance" was determined by filling the cell with mersury and determining the actual resistance by using the conductivity bridge.

Lead resistance = .39 ohms.

The electrodes were platinized in the usual manner and the cell constant determined with both N/50 and N/10 potassium chloride solutions. These solutions, and their specific conductivities were after Kohlrausch, Holborn and Diesselhorst[22]. The electrodes were covered with solution at all times to a sufficient depth so that a slight variation in the depth caused no appreciable change in the cell constant. The cell constant was determined before and after the observations on the whole series of solutions were made and the best value is:

Cell Constant = 2.097

IV Preparation of Pure Calcium Oxide.

The calcium oxide used in this research had to be of the highest purity possible. The presence of carbonates, in particular, had to be avoided as carbon dioxide would be formed in the solution, escape into the gas phase, and cause both the vapour pressure and conductivity measurements to be in error.

An analysis of various samples of C.P. calcium oxide showed them to contain carbonates and silicates in quantities large enough to make them useless in this work. Consequently a method had to be developed to prepare this substance in a high state of purity and also to handle and store it in such a way that the pure material would have no opportunity of absorbing carbon dioxide and water vapour from the air.

Clear, select, natural crystals of Iceland Spar (calcium carbonate in a very pure form) were obtained from the Eimer and Amend Company. These were broken up and placed in an electrically heated muffle furnace in a platinum dish. A current of dry air was passed over the carbonate during the heating process. The muffle was maintained at a high temperature and the heating continued for about a week. Spar treated in this manner was found to give pure calcium oxide entirely free from carbonate.

The hot dish containing the oxide was quickly transferred from the muffle to a vacuum dessicator, the bottom of which was divided into two sections, one containing fused potassium hydroxide and the other containing phosphorus pentoxide. The dessicator was then quickly evacuated. To open the dessicator, air was admitted through a train composed of, first a mercury trap, second a saturated solution of potassium hydroxide, and lastly through concentrated sulphuric acid. The oxide was quickly transferred to weighing bottles, which were then stored in the dessicator. When calcium oxide was introduced into the cell, the weighing bottles were kept for the least possible time in the air and opened only for a few seconds to remove the sample. In this procedure no appreciable amounts of water vapour or carbon dioxide were absorbed by the solid oxide.

Samples of this calcium oxide were subjected to two test procedures capable of detecting the least trace of carbonate. In the first method[23], a quantity of the solid was placed on a microscope slide and a warm gelatin solution poured over it. The slide was then immediately chilled, causing the gelatin to set. The solid particles were now brought into focus under moderately high power, and a drop of hydrochloric acid was touched to the gelatin. The acid diffused in, and if carbonate was present the carbon dioxide bubbles formed were caught in the gelatin mass and could easily be observed. In the second method a quantity of the solid was placed in a small distillation bulb together with some carbon dioxide free water and a few cc. of chloroform. This distillation bulb was connected by a delivery tube to a small bubbling tube in which was placed a barium hydroxide solution. The whole apparatus was air tight and was so arranged that a gentle stream of carbon dioxide free air could be sucked through the distilling bulb and the bubbling tube. Acid was now drained from a burette protruding into the distillation flask. Any carbonate present was decomposed and the carbon dioxide formed swept over into the barium hydroxide by the current of air and also by the chloroform vapour produced by gently warming the distillation flask. The absence of any cloudiness in the barium hydroxide solution proved the absence of carbonate in the sample.

Samples of calcium oxide prepared from the spar as above gave negative tests for the presence of carbonate with both of these test procedures.

V Procedure for the Preparation of Solutions.

The final object of the procedure to be described was to get known amounts of pure calcium oxide, water and sulphur dioxide into the reaction cell. Parts of this procedure have been described in previous sections but will be briefly reviewed here for the sake of clarity.

The clean, dry cell was sealed to the tube from the manometer and the lagging put in place over this join. A pyrex distillation bulb of about 200 cc. capacity was joined to the side tube (A) of the cell by a short length of glass tubing. This tube was constricted at the point where it was sealed on to facilitate the process of sealing off at this point (A) after the water had been introduced. A second tube leading into the top of this distillation bulb admitted the tip of the weight pipette from which water was introduced. This tube, and the cell side tube (B) were now temporarily sealed off, and the whole system completely dried and evacuated by the diffusion pump.

Dry, carbon dioxide-free air was then slowly admitted to the cell-manometer system and side tube (B) and the top of the distillation bulb blown open. A known amount of the pure calcium oxide was then quickly introduced into the cell through side tube (B) using glazed paper, and then this tube was sealed off. A known amount of water was then drained from a large weight pipette into the water distillation bulb through the tube in the top of this bulb. This tube was then sealed off and the water in this distillation bulb quickly, but carefully, frozen by a carbon dioxide snow - acetone mixture. The cell-manometer system was then completely evacuated. Since the vapour pressure of water at the temperature of this freezing mixture is so low, no appreciable quantity of water vapour was removed by the evacuation.

The next few steps in the procedure had as their object the freeing of the water from dissolved gases. When the system had been completely evacuated (S_4) was closed, the Dewar containing the freezing mixture taken from around the distillation bulb, and the ice allowed to melt. In this melting process a large amount of the dissolved gas came out of solution under the reduced pressure. When the ice was completely melted it was again frozen and time allowed for the water vapour to condense from the gas phase. The system was again evacuated, (S_4) closed again and the melting process repeated. This procedure was repeated until no more gas bubbles came out of the water when the ice was melted. This usually required about four freezings and thawings.

When this "out-gassing" process was completed, the cell was temporarily surrounded by an ice bath and the water distilled from the distillation bulb into the cell by gently warming the bulb. When the distillation was complete the tube was sealed off at (A) where a constriction was previously made. During this distillation process the mercury was run up into the mercury seal-off to prevent diffusion of the water vapour into that part of the apparatus.

Sulphur dioxide was now taken from the cylinder, purified by successive distillations, and stored in the bulb (B_4). A portion of this was allowed to enter the previously evacuated gas introduction and volume measuring system, and a known amount taken from this system and introduced into the cell-manometer system as described in Section II (c). After the introduction was completed the mercury was forced up into the mercury seal just to the point where the lagging begins and the mercury was then frozen. A small amount of sulphur dioxide was trapped between the stop-cock (S_4) and the surface of the mercury in the mercury seal. This was taken back into the gas measuring system by closing (S_3), opening (S_4), and placing a carbon dioxide - acetone freezing mixture around the tube (D). (S_4) was then closed, (S_3) opened, and the gas allowed time to come to the tubing temperature before the final temperature and pressure measurements in the gas introduction system were made. Since the vapour pressure of the sulphur dioxide at the temperature of solid carbon dioxide is low, and the tubing volume is small, the amount of sulphur dioxide left in this tube after this condensation was not appreciable.

After a "run" had been completed on a solution prepared as described above, another solution, having the same amount of water and calcium oxide but a larger sulphur dioxide content, could then be prepared as follows: the mercury seal was allowed to melt, the mercury drawn out of the tube, and sulphur dioxide again introduced as previously described. The seal was then made again and the solution was ready for the next run. This process was continued until the desired sulphur dioxide concentration range was completely covered. If a different calcium oxide concentration was desired, the whole procedure of "setting up the run", i.e., introducing calcium oxide, distilling in water etc., had, of course, to be repeated.

VI Procedure in Making a "Run".

A "run" was previously defined as a series of vapour pressure and conductivity measurements made on a single solution of known sulphur dioxide as well as calcium oxide concentrations and in which the variable factor was the temperature.

After the solution had been prepared as described above, the oil bath, thermoregulator, bath thermometer etc. were put in place, and both the bath and the electromagnetic cell stirrers started.

Vapour pressure and conductivity measurements were then made at about 20°C. intervals from 25°C. to 130°C. The choice of temperatures at which readings were made depended to a large extent on the behaviour of the system. The solution was stirred vigorously at all times.

It was pointed out in the introduction that solutions in which the sulphur dioxide concentration was low, especially those in which a solid phase was present, required a long period of time to come to true equilibrium. The method adopted for determining the equilibrium value without waiting for the system to reach true equilibrium was as follows. Suppose that readings were to be made at 25°C, 50°C, 70°C, 90°C, 110°C, and 130°C. The bath was heated up to 25°C. and regulated to ±.05°C. A conductivity reading was immediately taken and the time recorded. Conductivity readings were then made at 15 minute intervals for a period of one hour. At the end of this period the conductivity changes were quite small. Vapour pressure readings were taken at the half hour and the final reading at the end of the hour. The bath temperature was then raised to 50°C, 70°C etc. and this process repeated, care being taken not to exceed the temperature at which the readings were to be made. After the highest temperature had been reached, the temperature was raised several degrees for a few minutes, then lowered to this temperature again and another series of readings taken as before. readings were taken at exactly the same temperatures on this decreasing temperature run as on the increasing temperature run, and the solution held at these temperatures approximately the same time.

This method gave two sets of data, one for increasing and the other for decreasing temperature. With one or two exceptions the vapour pressures in these two sets of data were the same (within the experimental error), and were considered to be the equilibrium vapour pressures. The ascending conductivities, usually however, differed considerably from the descending conductivities. Unless there was some definite reason for not doing so, the equilibrium conductivity values were found by plotting these two sets of data and interpolating a curve between these two curves.

The mercury level in the manometer was kept close to 0.0 on the small scale in order to keep the gas volume in the cell system approximately constant throughout the entire run. The temperatures of this gas volume, of the air in the closed tube in the manometer, and of the mercury columns in the manometer were all read and recorded as each vapour pressure reading was made. A typical series of readings will be given in the section on Experimental Results.

The experimental procedure in the treatment of the calcium oxide-water system (0.0% SO_2), and in one or two systems with very low sulphur dioxide concentrations, had to be modified slightly. It was found that there was too great a difference between the ascending and descending conductivity readings in these runs to interpolate a curve between these two curves. By increasing the temperature exactly 2°C. above the temperature at which the reading was to be made, holding it there for twenty minutes, then lowering it 2°C. again, on the ascending temperature run, and just reversing this process on the descending temperature run, the interval between the two sets of readings was found to be much smaller and the equilibrium curve could easily be drawn in.

In the runs with solutions of high sulphur dioxide concentration, where no solid phase remained in the cell at low temperatures, only one set of measurements was made, viz., the observations taken with the temperature ascending. Equilibrium in these true solutions was reached almost immediately and moreover, if a solid precipitated out of these solutions at high temperatures as was usually the case, observations made with the temperature descending would have no significance because the solid re-entered solution very slowly.

VII Factors to be considered in the calculation of results.

The purpose of this section is to indicate the various calculations connected with the experimental work, and to point out where corrections have to be made.

The weight of calcium oxide introduced into the cell requires no corrections. The weighing of the water in air requires the application of the usual buoyancy corrections and also a small correction for the weight of water vapour trapped off in the distillation bulb when this is sealed off from the cell. The calculation of the weight of sulphur dioxide introduced requires the application of corrections of the mercury heights read on a glass scale to 0°C., and also of corrections to the various thermometers. The weight of the gas introduced was calculated as described in section II (b).

Calculation of vapour pressures were carried out as indicated in Section II (c), part (3). The mercury column height measured on wooden scales was corrected to 0°C. by application of the formula in Critical Tables[24]. Since a short length of the mercury column was heated by the lagging to a high temperature a special correction had to be applied to this portion of the mercury column. A distance of 5.5 cm. below 0.0 cm. on the small scale (B) (292.47 cm. on Scale (A)) was chosen as a fixed point. Above this point the mercury in this tube was considered as heated to the temperature recorded on the thermometer embedded in the lagging, and corrections made to 0°C. for the length of the column above this point. The temperature of the column below this point down to a level of 345.00 cm. on the manometer was all considered to be at a temperature given by a thermometer placed against the tube at the appropriate point. This section of the column was also corrected to 0°C. The length of the mercury column above 345.00 cm. in the closed tube of the manometer was corrected to 0°C. Below 345.00 cm. both the closed tube column and the column in the tube leading to the cell system were considered to be at the same temperature, consequently the corrections balanced out. The corrected heights found in this manner are now added or subtracted, depending on the relative positions of the columns, and the correct pressure due to the mercury column thus determined.

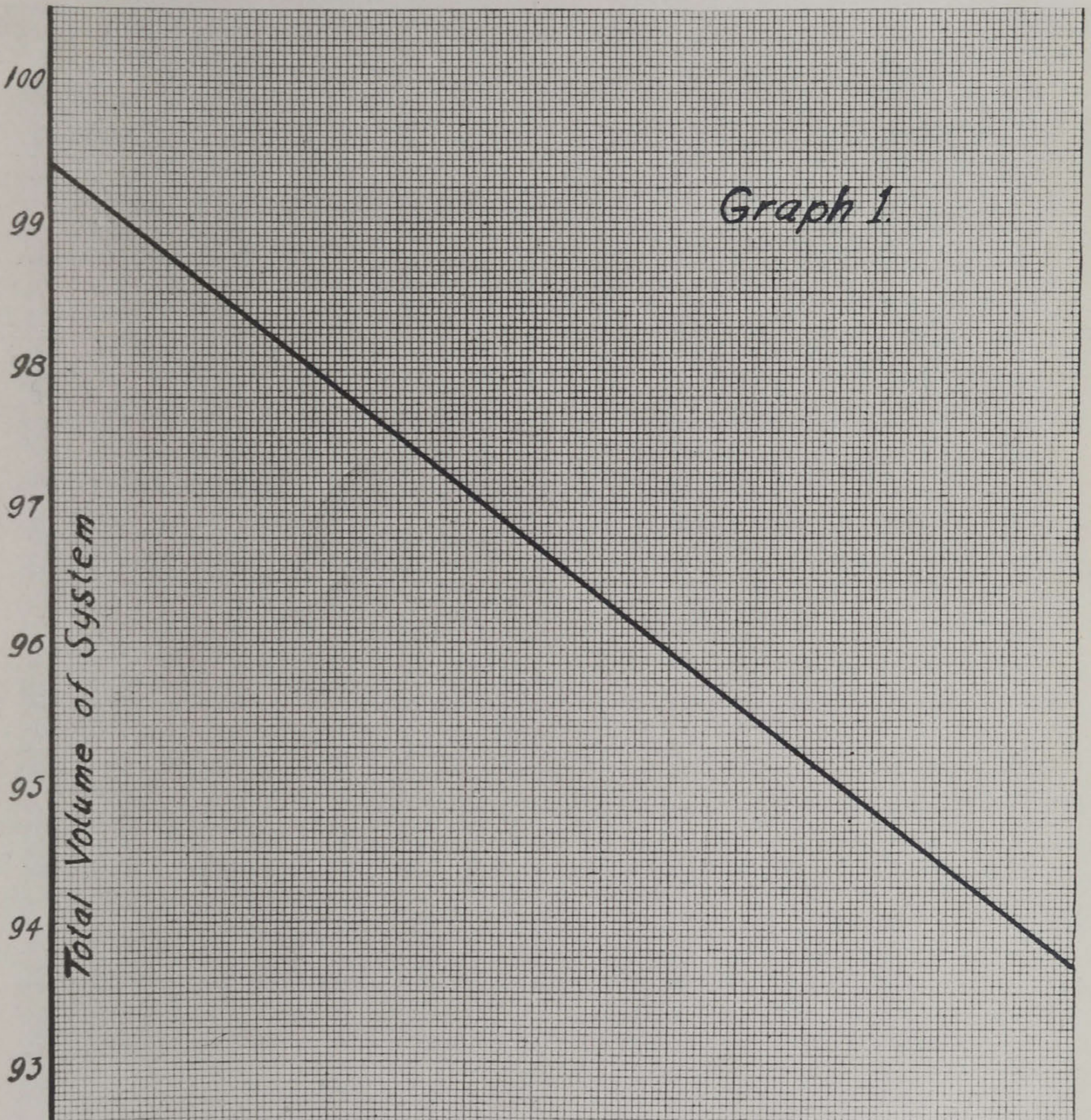
Two bath thermometers, one reading from 0°C. to 100°C. and the other from 100°C. to 150°C., were standardized by comparison with standard thermometers. Where necessary the following equation for emergent stem corrections was applied:

$$T = T_1 + .00156 \times 1 \times (T_1 - T_2)$$

where T = the corrected temperature.
T_1 = the observed temperature.
1 = the length, in degrees, of the mercury thread not at the temperature being measured.
T_2 = the temperature of the middle point of the emergent thread taken by another thermometer.

In order to determine the true weight of water and sulphur dioxide in the solution, the weights of these two substances in the vapour phase, above the liquid in the cell and in the connecting tubing to the manometer, must first be known. The volume of this vapour phase must consequently be known. It is dependent on two factors: first, the level to which the mercury is raised as registered on scale (B), and second, on the amount of liquid in the cell. As the mercury is always raised to the same level in the capillary tube of the mercury seal and frozen there no volume change takes place at that point.

The volume of the empty cell and the connecting tubing for various levels of the mercury on scale (B) was determined by the pressure change method described in Section II (b) (First Method). The calibrated volumes of the Gas Measuring and Introduction system were used in this calibration. The volumes at various levels on (B) were determined for the whole cell-manometer system plus the tubing of the mercury seal and the lead to the stopcock (S_4). The cell-manometer system was then temporarily sealed off at that point to which the mercury of the seal was raised and the volume of the tubing of the seal and the lead to (S_4) determined. By subtracting this volume from the former the volumes of the cell-manometer system only were obtained. The accompanying graph (Graph I)


Graph I.
Total Volume of System
100
99
98
97
96
95
94
93
92
-3·0
-2·0
-1·0
0·0
+1·0
+2·0
+3·0
Reading of Scale B in Cms.

gives the volume of this system at any scale reading of (B). Care was taken in breaking off and sealing on the cell to maintain this volume constant by blowing out the join about the same amount each time a seal was made.

Since the total volume of the system is known, the volume of the gas phase may be determined by subtracting the volume occupied by the solution. This can be found accurately enough by using the density data of Campbell and O.Maass[14] for aqueous sulphur dioxide solutions. Knowing the gas volume, the temperature of this gas (read from the thermometers in the lagging), and calculating the partial pressure of the sulphur dioxide by subtracting the partial pressure of the water vapour from the total pressure at any given temperature, the weight of sulphur dioxide in the gas phase can easily be calculated. The values used for the partial vapour pressures of the water were the vapour pressures as determined for the two component system calcium oxide - water. These values for the partial pressure of water are probably slightly higher than the actual partial water vapour pressure in the three component system. The differences, however, would be so small that they need not be taken into account in these calculations. Since part of this gas volume was at the temperature of the bath, and the remainder at the temperature of the lagged tubes the volume was divided into two sections and the simple gas law applied to each. The weight of sulphur dioxide in the gas phase is given by the following equation:

$$W = \frac{(p - p_1).V_1.M_1}{R.T_1} + \frac{(p - p_1).V_2.M_2}{R.T_2}$$

where

p is the total vapour pressure.
p_1 is the partial pressure of water vapour.
V_1 is the volume of the gas phase at the lagging temperature T_1.
V_2 is the volume of the gas phase at the bath temperature T_2 above the liquid in the cell.
M_1 is the molecular weight of SO_2 at T_1 and $(p - p_1)$.
M2 is the molecular weight of SO_2 at T_2 and $(p - p_1)$.

$V_1 + V_2$ is the total volume of the gas phase. It was determined as described above. Values for V_1 and V_2 were obtained by finding V_2 and subtracting it from the total volume. V_2 was found by subtracting the volume occupied by the liquid in the cell from the volume 83.2 cc., which was the total volume of that part of the cell immersed in the oil bath. The weight of water in the vapour phase was such a small fraction of the total weight of water that no correction needed to be applied.

At the conclusion of the following section on Experimental results, a complete type calculation will be given to indicate the way in which the weight of sulphur dioxide added to the system and the vapour pressures were calculated.

The specific conductivities were calculated in the usual manner, viz.

$$k = \frac{C}{(R - r)}$$

where k is the specific conductivity in ohms^{-1}.

C is the cell constant (2.097).

R is the total resistance of the system as measured by the bridge.

r is the lead resistance (0.39 ohms).

Since the slide wire of the bridge was divided into 1000 divisions, the total resistance R is given by

$$R = \frac{A}{1000 - A} \times B$$

where A is the bridge reading!

B is the reading of the resistance box in the bridge circuit.

The values of $\frac{A}{1000 - A}$ were read from tables.

EXPERIMENTAL SECTION (Contd.)

Part B Results

The experimental data consist of thirteen complete "runs", i.e. the measurement of conductivities and vapour pressures at appropriate temperatures between the temperatures 25°C. and 130°C. on each of thirteen solutions having different sulphur dioxide concentrations. These thirteen runs are divided into three "series" of runs: Series C, Series F and Series G. Two runs were made in series C, and five were made in Series F. Series C and F had almost the same calcium oxide concentration, approximately 1%. There were six runs in Series G and the calcium oxide addition was approximately 2% in this series. Series C, run No.1 was the two-component system calcium oxide - water, there being no sulphur dioxide present in this run. Since a 1% addition of calcium oxide to water leaves some solid in excess, the results are for a system in which the water is saturated with calcium oxide.

Reference to Plate IV (page 76) shows the number of experimental observations that must be made in each run. It will readily be realized that it is impossible to record all this data for each run. Consequently only the temperatures, vapour pressures, ascending and descending conductivities, and the mean values of the conductivities will be given. This is the whole of the actual experimental data from a run, and it will constitute one of two tables (the "a" table) given for each run. The experimental values of the vapour pressures and the conductivities were both plotted against the temperature using a large scale. The mean values for the conductivities were obtained from an equilibrium conductivity curve drawn between the ascending and descending experimental curves as described in Experimental, Part A, Section VI. In the second, or "b" table, for each run, values of the equilibrium vapour pressures and conductivities read from these experimental curves at selected temperatures are given. In this same table the calculated values of the partial pressures of sulphur dioxide and the weight of sulphur dioxide present in the liquid phase (See Experimental, Part A, Section VI) are also given at these selected temperatures. Knowing the weight of sulphur dioxide in the liquid phase, its percentage in the liquid phase, calculated on a basis of the total weight of water plus calcium oxide plus sulphur dioxide, may be found. The concentrations of sulphur dioxide in the liquid phase may also be expressed on the basis of the number of mols. of sulphur dioxide per mol. of calcium oxide. Concentrations expressed in these two ways are included in this "b" table for these selected temperatures.

Series F, Runs 4 and 5, and Series G, Runs 5 and 6 required measurements only with ascending temperatures.

Consequently there was but one set of conductivity data for these runs. In Series F, Runs 1,2 and 3, and in Series G, Runs 1,2,3 and 4, the equilibrium values for the conductivities were found by interpolating the equilibrium curve between the two experimental curves as indicated above. In Series C, Runs 1 and 2 the equilibrium values were also found by interpolation, but, as was pointed out in Experimental, Part A, Section VI, the extra 2°C. change in temperature was necessary in order to bring the two experimental curves closer together so that the equilibrium curve could be interpolated more accurately.

The data are summarized in the following sets of tables arranged in the order in which the runs were made. Preceding the tables for each run, the total weight of water, the weight of calcium oxide and the weight of the sulphur dioxide introduced are recorded.

Following these tables, two plates, Plate IV and Plate V are to be found. As was previously mentioned Plate IV is a complete table of all the experimental observations made in a single run. In Plate V, part (1), a typical calculation for the weight of sulphur dioxide introduced into the cell is given. Part (2) is a single vapour pressure calculation. The experimental readings used in this calculation are taken from observation No.2 Series G, Run No.1, Plate IV.

Series C Run No. 1.

(The system Calcium Oxide - Water)

Total Weight of Water	70.0661 gms.
Weight of Calcium Oxide	0.6889 gms.
Weight of Sulphur Dioxide	0.0 gms.

Table I (a)

		Specific Conductivity in Ohms^{-1}		
Temp.	V.P. in cm.	Ascend. Temp.	Descend. Temp.	Equilib.
24.6	2.3	.00864		
				.00848
24.6			.00832	
49.9	9.2	.00974		
				.00966
49.8			.00958	
60.0	14.9	.00993		
				.00982
59.9			.00971	
70.0	23.3	.00975		
				.00973
70.0			.00972	
90.5	53.6	.00905		
				.00910
90.5			.00915	
129.9	200.1	.00713		
				.00713
129.9			.00714	

The equilibrium conductivities are plotted vs. temperature in Graph 2.

Table I (b)

Temp. oC.	Specific Cond. in Ohms^{-1}	Total V.P. in cm.
25.0	.00850	2.3
50.0	.00966	9.2
70.0	.00972	23.3
90.0	.00913	52.5
105.0	.00843	90.5
110.0	.00820	107.0
120.0	.00767	148.5
130.0	.00712	200.5

Series C Run No.2.

Total Weight of Water	70.0661 gms.
Weight of Calcium Oxide	0.6889 gms.
Total weight of Sulphur Dioxide	0.1451 gms.

Table 2(a)

		Specific Conductivities in Ohms^{-1}		
Temp.	V.P. in cm.	Ascend. Temp.	Descend. Temp.	Equilib.
24.7	2.5	.00820		
				.00808
24.7			.00796	
49.9	9.3	.01017		
				.00960
49.8			.00923	
60.0	15.0	.01016		
				.00977
60.0			.00939	
70.0	23.5	.00991		
				.00966
70.0			.00935	
90.5	53.6	.00913		
				.00899
90.5			.00886	
135.1	233.4	.00677		
				.00670
135.1			.00680	

The equilibrium conductivities are plotted vs. temperature in Graph 2.

Table 2(b)

Temp. °C.	Sp.Cond. in Ohms^{-1}	Total V.P.	Part. V.P. SO_2	Wt.SO_2 in.Liq. Phase	%SO_2 in Liquid Phase	Mols.SO_2/ Mol.CaO
25.0	.00810	2.5	.2	.1451	.205	.1844
50.0	.00961	9.4	.3	.1451	.205	.1844
70.0	.00966	23.5	.2	.1451	.205	.1844
90.0	.00900	52.6	.1	.1451	.205	.1844
111.0	.00804	107.2	.2	.1451	.205	.1844
120.0	.00752	148.8	.3	.1451	.205	.1844
130.0	.00697	200.9	.4	.1451	.205	.1844

Series F Run No.1.

Total Weight of Water	69.8535 gms.
Weight of Calcium Oxide	0.7151 gms.
Total Weight of Sulphur Dioxide	0.2215 gms.

Table 3(a)

		Specific Conductivities in Ohms^{-1}		
Temp.	V.P. in cm.	Ascend. Temp.	Descend. Temp.	Equilib.
24.9	2.5	.00794		
				.00777
24.9			.00760	
49.6	9.5	.00995		
				.00947
49.6			.00900	
60.1	15.3	.01007		
				.00967
60.0			.00905	
69.9	23.6	.01038		
				.00952
70.0			.00899	
90.4	53.7	.00946		
				.00868
90.5			.00849	
109.3	104.9	.00756		
				.00770
109.3			.00766	
129.9	200.6	.00637		
				.00660
129.9			.00657	

The equilibrium conductivities are plotted vs. temperature in Graph 2.

Table 3(b)

Temp.	Sp.Cond. in Ohms^{-1}	Total V.P.	Part. V.P. SO_2	Wt.SO_2 in Liq. Phase	%SO_2 in Liquid Phase	Mols.SO_2/Mol.CaO
25.0	.00778	2.5	.2	.2215	.313	.271
50.0	.00949	9.5	.3	.2215	.313	.271
70.0	.00952	23.7	.4	.2215	.313	.271
90.0	.00870	52.9	.4	.2215	.313	.271
110.0	.00769	107.5	.5	.2215	.313	.271
120.0	.00715	149.0	.5	.2215	.313	.271
130.0	.00661	201.1	.6	.2215	.313	.271

Series F Run No.2.

Total Weight of Water	69.8535 gms.
Weight of Calcium Oxide	0.7151 gms.
Total Weight of Sulphur Dioxide	0.6444 gms.

Table 4(a)

		Specific Conductivities in Ohms^{-1}		
Temp.	V.P. in cm.	Ascend. Temp.	Descend. Temp.	Equilib.
24.7	3.0	.00347		
				.00303
24.7			.00259	
49.8	10.0	.00528		
				.00468
49.8			.00409	
60.3	16.0	.00599		
				.00540
60.3			.00481	
69.9	24.3	.00662		
				.00605
69.9			.00548	
90.3	54.2	.00792		
				.00734
90.3			.00676	
109.3	106.7	.00875		
				.00835
109.3			.00795	
130.3	206.6	.00896		
				.00884
130.3			.00872	

Table 4(b)

Temp.	Sp.Cond. in Ohms^{-1}	Total V.P.	Part. V.P. SO_2	Wt.SO_2 in Liq. Phase	%SO_2 in Liquid Phase	Mols.SO_2/ Mol.CaO
25.0	.00305	3.0	.7	.6444	.905	.789
50.0	.00470	10.0	.8	.6444	.905	.789
70.0	.00605	24.5	1.2	.6444	.905	.789
90.0	.00732	53.5	1.0	.6444	.905	.789
110.0	.00840	109.2	2.2	.6444	.905	.789
120.0	.00871	152.1	3.6	.6444	.905	.789
130.0	.00881	205.2	4.7	.6444	.905	.789

Note- The data of this run do not seem to agree with data forthe other runs of this series. Ths discrepancy will be discussed in greater detail later.

Series F Run No.3.

Total Weight of Water	69.8535 gms.
Weight of Calcium Oxide	0.7151 gms.
Total Weight of Sulphur Dioxide	1.2441 gms.

Table 5(a)

Ascending Temperatures			Equilibrium Values	
Temp.	V.P.	Sp.Cond. in ohms^{-1}	V.P.	Sp.Cond. in ohms^{-1}
24.7	6.0	.01488	6.0	.01470
49.8	16.5	.02241	16.5	.02159
70.0	(33.9)M	(.02847)M	35.5	.0262
90.4	(68.2)M	(.03422)M	72.5	.02908
109.3	134.0	.03167	134.0	.02966
119.8	184.2	.03116	184.2	.02883
130.06	247.9	.02958	247.9	.02703
Descending Temperatures				
106.2	125.8	.02777		
80.2	53.2	.02645		
49.8	17.4	.02077		
24.7	-	.01452		

The equilibrium conductivity values are plotted vs. the temperature in Graph 3.

Table 5(b)

Temp.	Sp.Cond. in ohms^{-1}	Total V.P.	Part. V.P. SO_2	Wt.SO_2 in Liq. Phase	%SO_2in Liquid Phase	Mols.SO_2/ Mol.CaO
25.0	.01480	6.0	3.7	1.241	1.728	1.519
50.0	.02163	16.5	7.3	1.239	1.726	1.516
70.0	.02620	(34.0)M 35.5	(10.7)M 12.2	1.237	1.723	1.514
90.0	.02904	(67.2)M 71.3	(14.7)M 18.8	1.235	1.720	1.511
110.0	.02963	136.9	29.9	1.227	1.708	1.502
120.0	.0288	185.2	36.7	1.224	1.704	1.498
130.0	.0270	247.5	47.0	1.220	1.699	1.493

Series F Run No.4.

Total Weight of Water	69.8535 gms.
Weight of Calcium Oxide	0.7151 gms.
Total Weight of Sulphur Dioxide	2.4814 gms.

Table 6(a)

Temp.	Vap.Press.	Sp.Cond. in ohms^{-1}
24.7	18.0	.02518
49.8	40.6	.03504
70.0	72.0	.04330
90.5	123.4	.05169
109.4	207.2	(.05284)
119.9	273.5	.04871
129.8	352.3	.04688

The conductivities are plotted vs. the temperature in Graph 3.

Table 6(b)

Temp.	Sp.Cond. in ohms^{-1}	Total V.P.	Part. V.P. SO_2	Wt.SO_2 in Liq. Phase	%SO_2 in Liquid Phase	Mols.SO_2/ Mol.CaO
25.0	.02510	18.2	15.9	2.469	3.38	3.023
50.0	.03520	40.8	31.6	2.459	3.37	3.010
70.0	.04335	72.1	48.8	2.449	3.35	2.998
90.0	.05143	121.6	69.1	2.440	3.34	2.986
110.0	.05050	210.5	103.5	2.424	3.32	2.967
120.0	.04868	274.1	125.6	2.415	3.31	2.955
130.0	.04680	354.2	153.7	2.401	3.29	2.938

Series F Run No.5.

Total Weight of Water	69.8535 gms.
Weight of Calcium Oxide	0.7151 gms.
Total Weight of Sulphur Dioxide	4.1398 gms.

Table 7(a)

Temp.	Vap.Press.		Sp. Cond. in ohms^{-1}	
24.7	40.4		.03278	
49.8	89.3		.04028	
70.0	151.0		.04648	
90.6	243.1		.05305	
104.1	317.5	M	.05717	M
109.4	350.5		.05869	
119.9	429.2		.06153	
123.8	436.5		.06297	

The conductivities are plotted against the temperature in Graph 3.

Table 7(b)

Temp.	Sp.Cond. in ohms^{-1}		Total V.P.		Part. V.P. SO_2		Wt.SO_2 in Liq. Phase	%SO_2 in Liquid Phase	Mols.SO_2/Mol.CaO
25.0	.03290		40.8		38.5		4.111	5.50	5.032
50.0	.04047		89.8		80.6		4.082	5.47	4.997
70.0	.04657		151.0		127.7		4.059	5.44	4.968
90.0	.05265		240.2		187.7		4.043	5.41	4.949
110.0	.0588	M	354.5	M	247.5	M	4.006	5.36	4.903
120.0	.0618		430.0		281.5		4.001	5.35	4.897

Series G Run No.1.

Total Weight of Water	69.8805 gms.
Weight of Calcium Oxide	1.4892 gms.
Total Weight of Sulphur Dioxide	0.8972 gms.

Table 8(a)

		Specific Conductivities in Ohms^{-1}		
Temp.	V.P. in cm.	Ascend. Temp.	Descend. Temp.	Equilib.
24.7	2.6	.00869		
				.00832
24.7			.00794	
49.8	9.4	.01003		
				.00965
49.8			.00939	
60.0	15.1	.01014		
				.00982
60.0			.00951	
70.3	23.8	.01004		
				.00972
70.3			.00940	
90.5	53.7	.00922		
				.00905
90.5			.00895	
110.4	109.0	.00793		
				.00804
110.4			.00804	
130.2	203.4	.00688		
				.00692
130.2			.00694	

The equilibrium conductivities are plotted vs. the temperature in Graph 2.

Table 8(b)

Temp.	Sp.Cond. in Ohms^{-1}	Total V.P.	Part. V.P. SO_2	Wt.SO_2 in Liq. Phase	%SO_2 in Liquid Phase	Mols.SO_2/Mol.CaO
25.0	.00833	2.7	.4	.8972	1.24	.527
50.0	.00966	9.5	.3	.8972	1.24	.527
70.0	.00972	23.6	.3	.8972	1.24	.527
90.0	.00907	52.9	.4	.8972	1.24	.527
105.0	.00833	91.1	.6	.8972	1.24	.527
120.0	.00751	150.3	1.8	.8972	1.24	.527
130.0	.00693	202.2	1.7	.8972	1.24	.527

Series G Run No.2.

Total Weight of Water	69.8805 gms.
Weight of Calcium Oxide	1.4892 gms.
Total Weight of Sulphur Dioxide	1.7826 gms.

Table 9(a)

		Specific Conductivities in Ohms^{-1}		
Temp.	V.P. in cm.	Ascend. Temp.	Descend. Temp.	Equilib.
24.7	2.9	.00534		
				.00491
24.7			.00447	
49.8	10.1	.00820		
				.00759
49.9			.00697	
60.3	16.1	.00928		
70.0	24.7	.01022		.00959
				.00959
70.0			.00896	
90.5	55.8	.01187		
				.01132
90.5			.01076	
110.4	112.7	.01269		
				.01231
110.4			.01193	
130.0	208.7	.01260		
				.01244
130.0			.01229	

The equilibrium conductivities are plotted vs. the temperature in Graph 3.

Table 9(b)

Temp.	Sp.Cond. in Ohms^{-1}	Total V.P.	Part. V.P. SO_2	Wt.SO_2 in Liq. Phase	%SO_2in Liquid Phase	Mols.SO_2/ Mol.CaO
25.0	.00494	3.0	.7	1.7826	2.44	1.048
50.0	.00761	10.1	.9	1.7826	2.44	1.048
70.0	.00960	24.8	1.5	1.7826	2.44	1.048
90.0	.01130	54.8	2.3	1.7826	2.44	1.048
105.0	.01217	93.7	3.2	1.7826	2.44	1.048
120.0	.01250	155.0	6.5	1.7826	2.44	1.048
130.0	.01245	208.8	8.3	1.7826	2.44	1.048

Series G Run No.3.

Total Weight of Water	69.8805 gms.
Weight of Calcium Oxide	1.4892 gms.
Total Weight of Sulphur Dioxide	2.1967 gms.

Table 10(a)

		Specific Conductivities in $Ohms^{-1}$		
Temp.	V.P. in cm.	Ascend. Temp.	Descend. Temp.	Equilib.
24.7	4.2	.01417		
				.01401
24.7			.01385	
49.9	12.6	.02131		
				.02082
49.9			.02032	
70.0	30.9	.02542		
				.02489
70.0			.02436	
90.5	68.3	.02731		
				.02687
90.5			.02666	
110.4	134.2	.02714		
				.02693
110.4			.02671	
130.0	238.5	.02562		
				.02546
130.0			.02530	

The equilibrium conductivities are plotted vs. the temperature in Graph 3.

Table 10(b)

Temp.	Sp.Cond. in $Ohms^{-1}$	Total V.P.	Part. V.P. SO_2	Wt.SO_2 in Liq. Phase	%SO_2 in Liquid Phase	Mols.SO_2/ Mol.CaO
25.0	.01410	4.2	1.9	2.196	2.99	1.291
50.0	.02088	12.7	3.5	2.196	2.99	1.291
70.0	.02490	30.9	7.6	2.191	2.98	1.288
90.0	.02685	67.2	14.7	2.187	2.98	1.286
105.0	.02710	112.8	22.3	2.183	2.97	1.283
120.0	.02640	183.0	34.5	2.179	2.96	1.281
130.0	.02545	238.8	38.3	2.176	2.96	1.279

Series G Run No.4.

Total Weight of Water	69.8805 gms.
Weight of Calcium Oxide	1.4892 gms.
Total Weight of Sulphur Dioxide	3.8731 gms.

Table 11(a)

		Specific Conductivities in Ohms^{-1}		
Temp.	V.P. in cm.	Ascend. Temp.	Descend. Temp.	Equilib.
24.7	14.6	.03662		
				.03569
24.7			.03476	
49.8	(33.9)M	(.05423)M		
				.04815
49.8			.04709	
70.0	82.8	.05436		
				.05323
70.0			.05209	
90.5	155.5	.05412		
				.05327
90.5			.05241	
110.4	260.6	.05138		
				.05039
110.4			.04939	
129.9	402.9	.04659		
				.04565

The equilibrium conductivities are plotted vs. the temperatures in Graph 3.

Table 11(b)

Temp.	Sp.Cond. in Ohms^{-1}	Total V.P.	Part. V.P. SO_2	Wt.SO_2 in Liq. Phase	%SO_2 in Liquid Phase	Mols.SO_2/ Mol.CaO
25.0	.03581	14.8	12.5	3.864	5.14	2.271
50.0	.04822	41.2	32.0	3.855	5.12	2.266
70.0	.05323	82.8	59.5	3.834	5.10	2.254
90.0	.05330	153.1	100.6	3.811	5.07	2.240
105.0	.05140	227.5	137.0	3.792	5.04	2.229
120.0	.04820	327.2	178.7	3.774	5.02	2.218
130.0	.04563	403.5	203.0	3.762	5.00	2.211

Series G Run No.5.

Total Weight of Water	69.8805 gms.
Weight of Calcium Oxide	1.4892 gms.
Total Weight of Sulphur Dioxide	5.1578 gms.

Table 12(a)

Temp.	Vap. Press.	Spec. Cond. in ohms^{-1}
24.7	32.9	.04087
49.8	71.8	.05846
70.0	(122.4)M	(.07284)M
90.5	233.6	.06372
105.2	330.4	.06068
119.9	447.9	.05694

The conductivities are plotted vs. temperature in Graph 3

Table 12(b)

Temp.	Sp.Cond. in ohms^{-1}	Total V.P.	Part. V.P. SO_2	Wt.SO_2 in Liq. Phase	%SO_2 in Liquid Phase	Mols.SO_2/ Mol. CaO
25.0	.04107	33.3	31.0	5.135	6.71	3.018
50.0	.05871	72.2	63.0	5.115	6.69	3.007
70.0	.06820	(122.4)M	(99.1)M	5.095	6.66	2.995
90.0	.06360	230.7	178.2	5.054	6.61	2.970
105.0	.06025	329.2	238.7	5.032	6.58	2.957
120.0	.05690	449.1	300.6	4.999	6.54	2.938

Series G Run No.6.

Total Weight of Water	69.8805 gms.
Weight of Calcium Oxide	1.4892 gms.
Total Weight of Sulphur Dioxide	6.8832 gms.

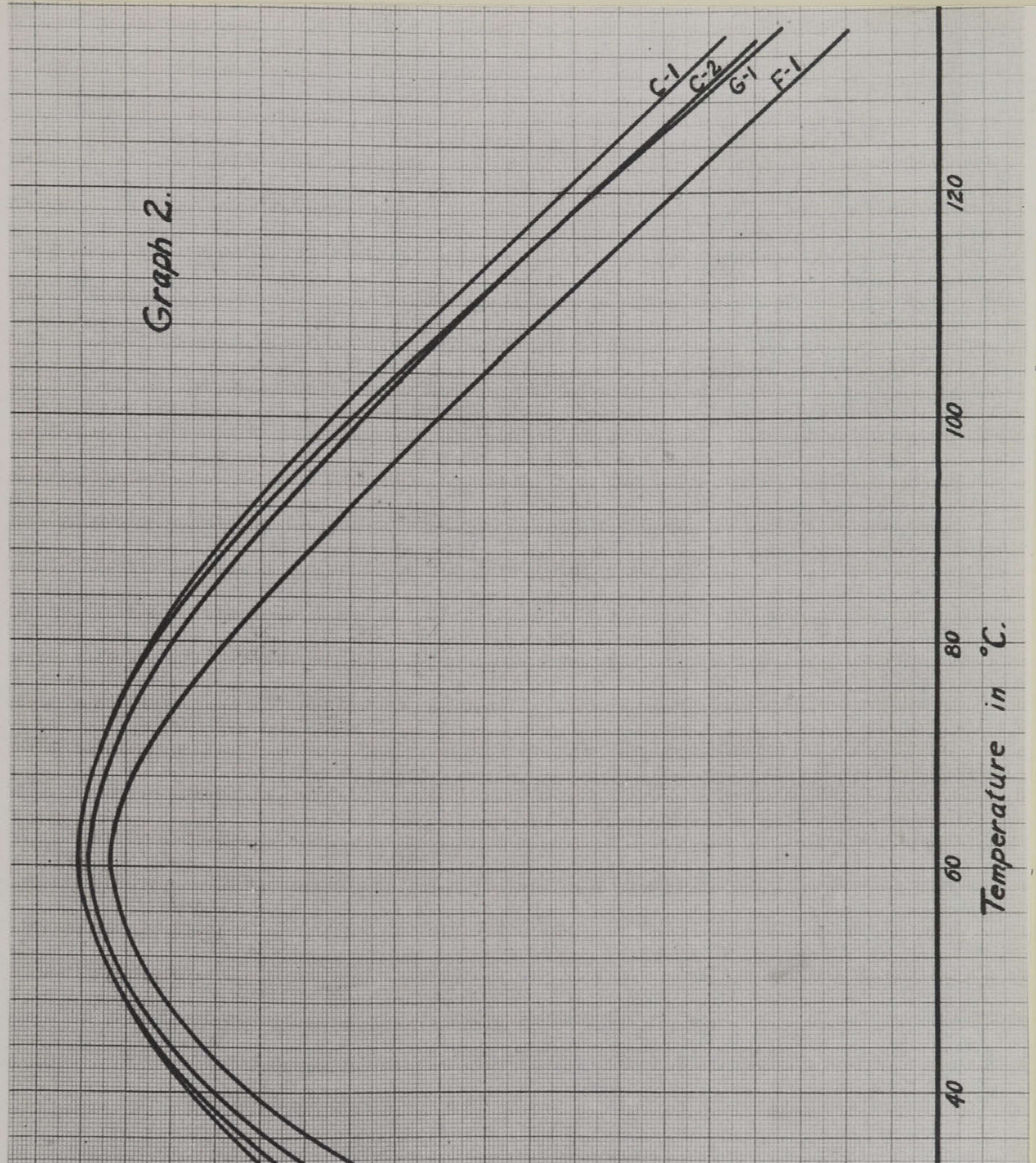
Table 13(a)

Temp.	Vap.Press.	Spec. Cond. in $ohms^{-1}$
24.7	59.0	.04449
49.8	126.6	.06021
70.0	209.2	.07299
90.5	(327.1)M	(.08542)M
102.0	(447.7)	(.07226)

The conductivities are plotted vs. the temperature in Graph 3.

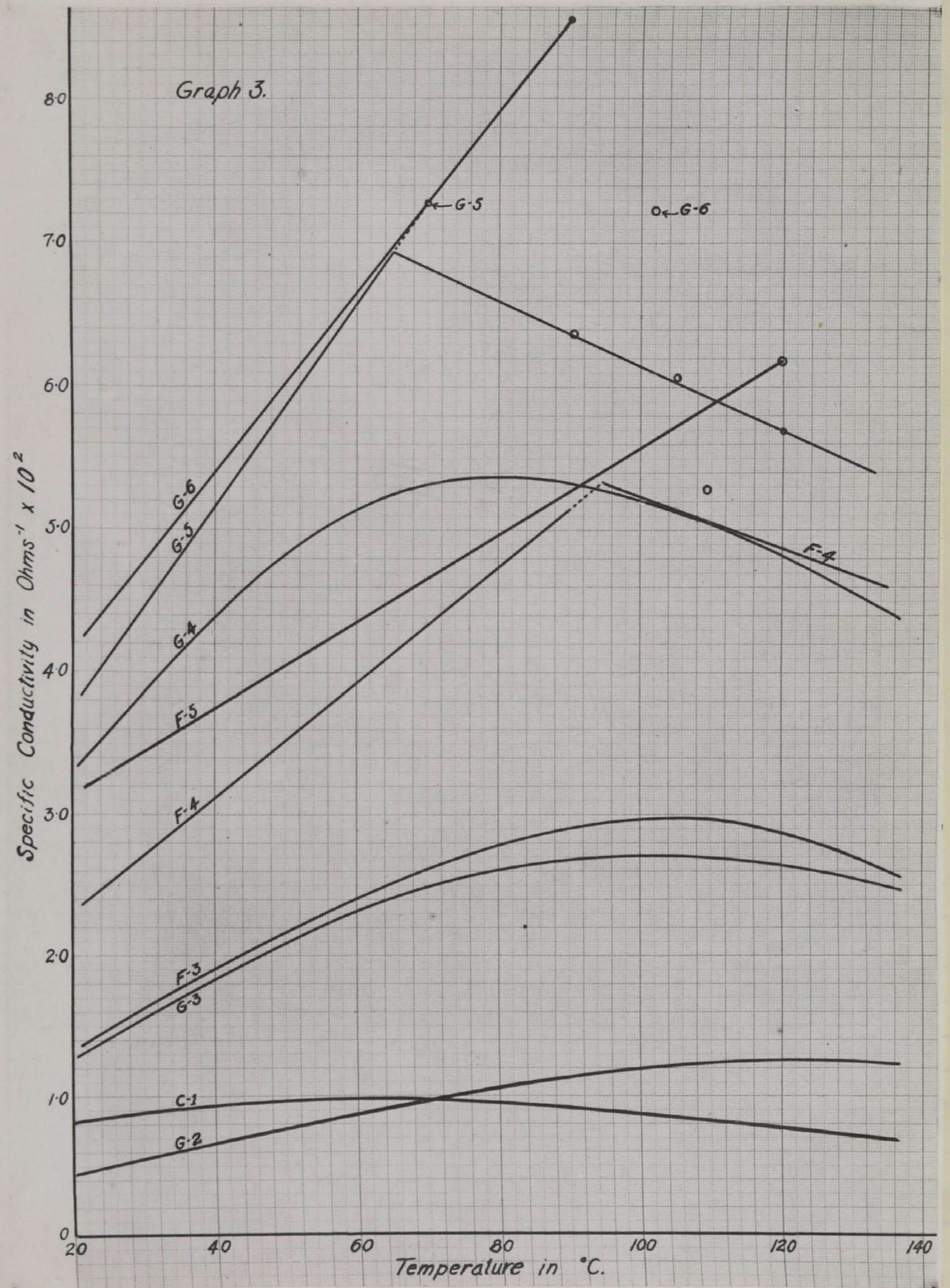
Table 13(b)

Temp.	Sp.Cond. in $ohms^{-1}$	Total V.P.	Part. V.P. SO_2	Wt. SO_2 in Liq. Phase	% SO_2 in Liquid Phase	Mols. SO_2/ Mol.CaO
25.0	.04463	59.8	57.5	6.843	8.77	4.022
50.0	.06030	127.2	118.0	6.792	8.70	3.992
70.0	.0728	209.2	185.9	6.775	8.68	3.982
90.0	(.0853)M	(323.8)M	(271.3)M	6.740	8.64	3.962
105.0		(444.0)M	(353.5)M	6.701	8.59	3.939



Graph 2.

C-1
C-2
G-1
F-1
Temperature in °C.
20
40
60
80
100
120
0·6
0·7
0·8
0·9
1·0
Specific Conductivity in Ohms^{-1} x 10^2


Graph 3.
Specific Conductivity in Ohms⁻¹ x 10²
Temperature in °C.
0
1·0
2·0
3·0
4·0
5·0
6·0
7·0
8·0
20
40
60
80
100
120
140
G-6
G-5
G-4
F-5
F-4
F-3
G-3
C-1
G-2
←G-5
o←G-6
F-4

Feb 8/32.

Series G.- Run No. 1.

PLATE IV

Reading No.	Time of V.P. Reading	Temperature of Bath	Stem Immersion	Temperature of Stem	Stem Correction	Thermometer Correction	Corrected Temperature	Temp of Hg. Col. Below Scale B	Tubing Temp. at Scale B	Tubing Temp.	Reading of Scale B	Manometer Scale Reading (Scale A)	Manom Temp. Bottom	Manom Temp. Middle	Manom Temp. Top	Time-Conductivity Readings (1)	(2)	(3)	(4)	Resistance Box	Specific Conductivity Ohms^{-1}	Vapour Pressure Cms.
1.	11^{13}A	25.0	11	24	0	-.33	24.7	21.8	58	80	-1.85	345.23	20.5	21.6	22.0	10^{35}A 545	11^{10}A 544.5	11^{35}A 545.5	11^{40}A 547.0	200	.008694	2.6
2	11^{56}A.	25.0	11	24	0	-.33	24.7	22.2	58	90	-1.85	345.27	20.7	21.8	22.1							
3.	2^{48}P	49.95	12	28	+.13	-.29	49.8	24.2	152	157	-2.0	339.7	21.3	22.6	23.0	2^{25}P 499.0	2^{40}P 508.5	2^{55}P 509.0	3^{10}P 511.5	200	.010033	9.4
4	3^{10}P.	49.95	12	28	+.13	-.29	49.8	24.4	151	156	-2.0	339.72	21.7	22.9	23.3							
5.	3^{43}P	60.0	13	31	+.21	-.26	60.0	25.2	151	156	-1.8	334.78	22.0	23.3	23.8	3^{25}P 500	3^{40}P. 501.0	3^{55}P 506.	4^{10}P 509.	200	.01014	15.1
6.	4^{09}P	60.0	13	31	+.21	-.26	60.0	25.4	150	155	-1.75	334.77	22.2	23.6	24.0							
7.	4^{50}P	70.25	13	30	+.36	-.35	70.3	26.1	154	159	-1.3	326.98	22.5	23.8	24.3	4^{25}P. 499.	4^{40}P. 507	4^{55}P. 511	5^{10}P. 512.0	200	.01004	23.8
8	5^{08}P.	70.25	13	29	+.36	-.35	70.3	26.2	153	158	-1.2	326.98	22.7	24.0	24.6							
9.	5^{50}P	90.0	13	35	+.66	-.17	90.5	27.6	153	156	-1.2	302.08	22.9	24.2	24.9	5^{30}P. 514.0	5^{45}P. 524.0	6^{00}P 529	6^{15}P 532.5	200	.009222	53.7
10.	6^{14}P	90.0	13	35	+.66	-.17	90.5	27.9	153	154	-1.12	302.03	23.2	24.6	25.3							
11.	8^{25}P	111.0	—	—	—	-.65	110.4	29.9	162	159	-0.7	257.67	23.7	24.3	25.0	8^{05}P 454	8^{20}P. 466	8^{35}P. 468.0	8^{50}P. 469.0	300	.007925	109.0
12.	8^{49}P.	111.0	—	—	—	-.65	110.4	29.7	163	161	-0.7	257.63	23.9	24.6	25.1							
13.	9^{37}P	130.2	118	81	+.09	-.15	130.2	31.2	174	168	-0.3	189.5	24.0	24.7	25.4	9^{10}P. 500.	9^{25}P. 504.5	9^{40}P. 504.5	9^{55}P. 504.5	300	.006875	203.4
14.	9^{53}P	130.2	118	82	+.09	-.15	130.2	31.0	174	166	-0.25	189.5	24.0	24.8	25.6							
		Taken up to 135°C, Held there for 15 Minutes, and then the Descending Temperature Run Commenced.																				
15.	11^{03}P.	130.2	118	83	+.09	-.15	130.2	31.0	171	167	-0.3	189.45	24.2	24.8	25.6	10^{20}P. 505	10^{35}P. 503.5	10^{50}P. 502.5	11^{05}P. 502.0	300	.006944	
16.	12^{13}A.	111.0	—	—	—	-.65	110.4	29.4	161	159	-0.8	257.41	24.0	24.6	25.4	11^{30}P. 472	11^{45}P. 467.5	12^{00}M. 466.0	12^{15}A. 465.5	300	.008038	
17.	1^{14}A.	90.0	13	32	+.7	-.17	90.5	27.0	156	154	-1.0	301.7	23.7	24.5	25.0	12^{30}A. 549	12^{45}A 542.5	1^{00}A 540.5	1^{15}A 540.0	200	.008946	
18	3^{08}A	70.25	13	31	+.36	-.35	70.3	25.3	156	157	-1.1	326.78	22.6	23.8	24.5	2^{25}A. 536	2^{40}A 529.0	2^{55}A 528	3^{10}A 527.5	200	.009404	
19.	4^{09}A.	60.0	13	29	+.23	-.26	60.0	24.3	157	158	-1.65	334.67	22.0	23.5	24.1	3^{25}A. 533.0	3^{40}A. 528.5	3^{55}A. 526.5	4^{10}A. 525.0	200.	.009506	
20.	5^{09}A.	49.95	12	28	+.13	-.29	49.8	23.5	158	160	-1.9	339.68	21.7	23.1	23.9	4^{25}A 536.0	4^{40}A 533.0	4^{55}A 528.5	5^{10}A 528.0	200.	.009387	
21.	6^{48}A.	25.0	11	24	—	-.33	24.7	22.2	60	107	-1.35	345.05	21.6	23.0	23.8	6^{05}A 573.5	6^{20}A 572.0	6^{38}A 570.0	6^{50}A. 569.5	200	.007937	

PLATE V

Type Calculation - Series G Run No. 1

(1) Sulpher Dioxide Introduction

	L.Man	R.Man	Tubing Temp. No4	Tubing Temp. No7	Bath T*3	Corrected Pressure
Before Introduction	69.8	2.0	21.4°C	21.4°C	19.8°C	67.55 Cm.
After "	38.3	2.0	21.4°C	21.4°C	19.8°C	36.17 Cm.

$$\text{Wt. } SO_2 \text{ Introd} = \left\{\frac{67.55\times .71462\times 65082}{76\times .08209\times 292.9} + \frac{67.55\times .08225\times 65.061}{76\times .08209\times 294.5}\right\} - \left\{\frac{36.17\times .71462\times 64605}{76\times .08209\times 292.9} + \frac{36.17\times .08225\times 64.594}{76\times .08209\times 294.5}\right\}$$

$$= (1.7192 + .19674) - (.91384 + .10459)$$

$$= .8975 \text{ Gms.}$$

Correction For SO_2 Trapped in Tubing = -.0003 Gms.

Final Corrected Wt. SO_2 Introduced = .8972 Gms.

(2) Vapour Pressure - Reading No. 2 in Table.

Scale Reading = 345.27
Scale Correction = + .89
Corrected Reading = 346.16 Cms.

Volume

$$\begin{array}{ccc} \text{Cms} & & \text{Ccs.} \\ 361.79 & \longrightarrow & 281.58 \\ \underline{346.16} & & \underline{-12.57} \\ 15.63 & & 269.01 \end{array} \qquad \underline{\underline{V = 269.01 \text{ ccs.}}}$$

Temperature	Bottom	Middle	Top
	20.7	21.8	22.1
Corrected	20.5	21.8	21.9

$$\begin{array}{r} 21.8 \\ \underline{-20.5} \\ \frac{1.3}{17}\times 5 = .4 \end{array} \qquad \begin{array}{r} 21.8 \\ \underline{-\ .4} \\ \boxed{21.4} \end{array} \qquad \begin{array}{r} 21.9 \\ \underline{21.8} \\ \frac{.1}{14}\times 2.5 = 0 \ \boxed{21.9} \end{array} \qquad \begin{array}{r} 21.9 \\ \underline{21.4} \\ 43.3 \end{array} \qquad \begin{array}{r} 21.7 \\ \underline{273.1} \\ 294.8 \end{array} \qquad \underline{\underline{T = 294.8}}$$

$$\text{P. Due to Enclosed Air} = \frac{K\times T}{V} = \frac{49.93\times 294.8}{269.01} = \underline{\underline{54.72 \text{ Cms.}}}$$

$$\text{Reading Scale B} = -1.85 = \begin{array}{r} 291.92 \\ \underline{+\ 1.85} \\ 293.77 \end{array} \text{ Cm. on Scale A.}$$

Heated to -5.5 on Scale B = 291.92 + 5.5 = 297.42 on Scale A

$$\text{1st. Portion Heated to } 58°C = \begin{array}{r} 297.42 \\ \underline{-293.77} \\ 3.65 \text{ Cms.} \end{array} \quad \text{Correction } \begin{array}{r} 3.65 \\ \underline{-\ .04} \\ 3.61 \end{array} = 3.61 \text{ Cm at } 0°C$$

$$\text{2nd. Portion at } 22.2°C \text{ to } 346.16 \text{ Cms} - \begin{array}{r} 346.16 \\ \underline{297.42} \\ 48.74 \end{array} \quad \text{Correction } \begin{array}{r} 48.74 \\ \underline{-\ .19} \\ 48.55 \end{array} - 48.55 \text{ Cms at } 0°C$$

Total Hg Column Height - 52.16 Cms at 0°C

$$\therefore \text{The Vapour Pressure} = \begin{array}{r} 54.72 \\ \underline{-52.16} \\ 2.56 \end{array} = \underline{2.6 \text{ Cms.}}$$

Results Derived from Experimental Data

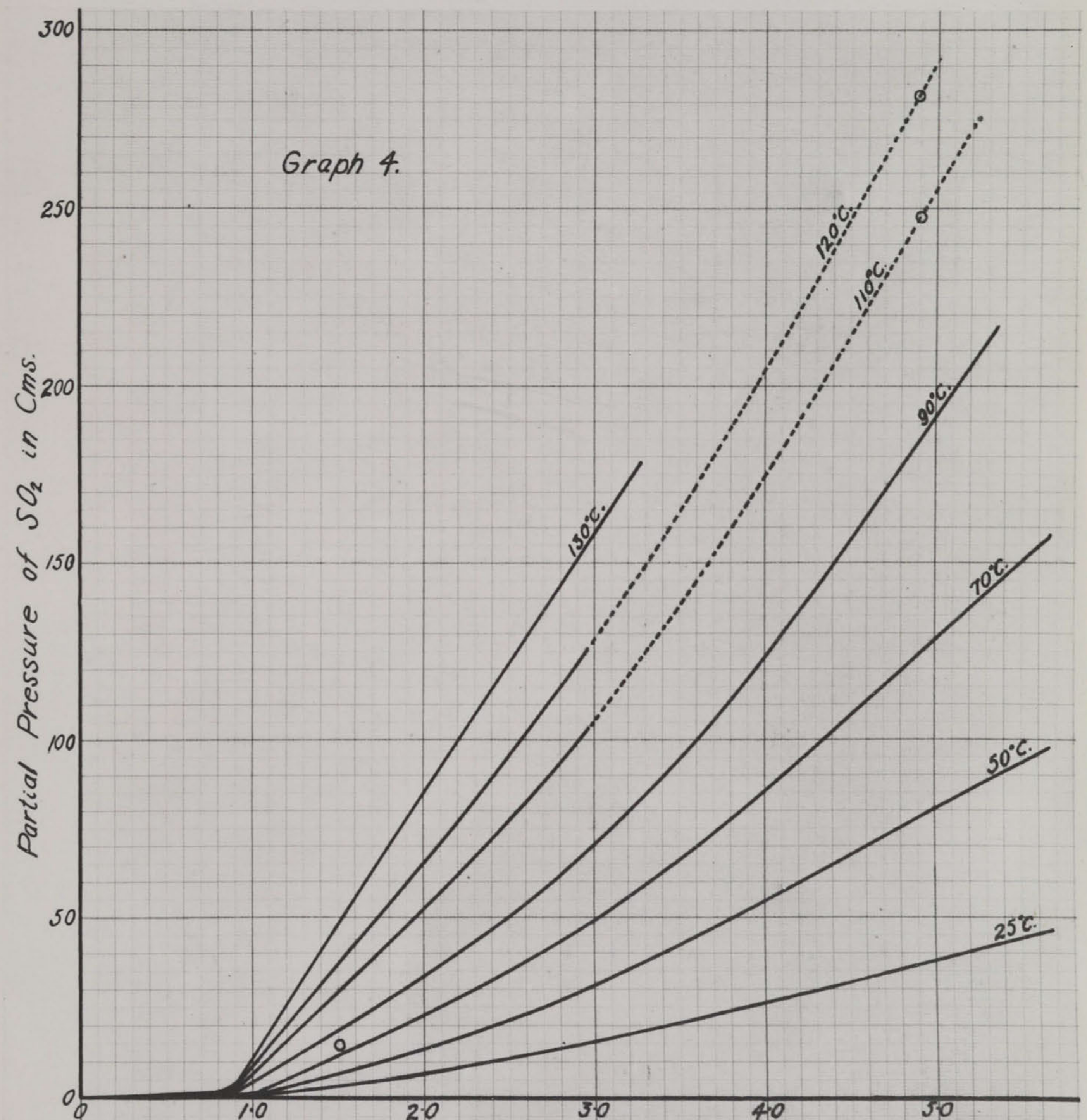
From a theoretical standpoint, the most useful results obtained in the experimental observations are the values of the specific conductivities and the partial pressures of sulphur dioxide at definitely known concentrations of sulphur dioxide with respect to calcium oxide. In order to inter-relate the data from a series of the runs (e.g. the runs in Series F) both the partial pressures and the conductivities at a selected temperature are compared with the mol. ratio of sulphur dioxide to calcium oxide. In this way two sets of isothermal curves are obtained for this series. In one set the partial pressures are plotted vs. the number of mols. of sulphur dioxide per mol. of calcium oxide, and in the other the conductivities are plotted against the relative concentrations expressed in the same way.

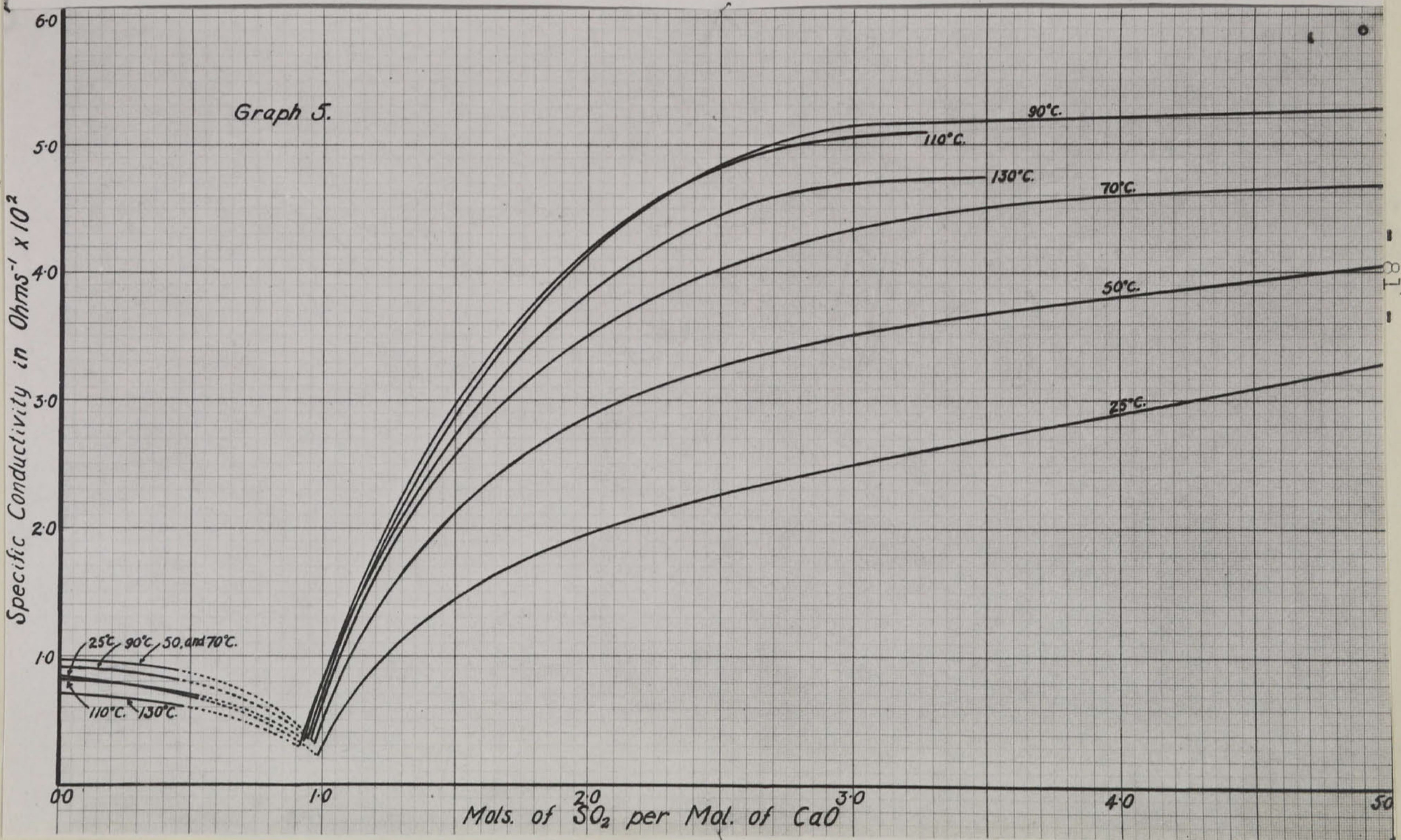
Series C and Series F both had calcium oxide concentrations of about 1%. (Actually the calcium oxide concentrations in these two series are slightly different. The two series may be combined here however without introducing any appreciable errors). The data from these two runs were combined and two sets of isothermal curves constructed from it. In Series G the calcium oxide concentration was approximately double that in the first two series. Two similar sets of isothermal curves were constructed from the data for this Series. Since Series C, Run No.1 was the system calcium oxide - water (i.e. 0.0 mols. of sulphur dioxide per mol. of calcium oxide) it enters into the sets of curves for both the 1% and 2% calcium oxide concentrations.

The data from which these isothermal curves were constructed are tabulated below. They are derived directly from the "b" tables given previously for each run. The first column gives the Series and the number of the run in the Series from which the data were taken. The second column is the concentration of sulphur dioxide expressed in mols. of sulphur dioxide per mol. of calcium oxide, and the third and fourth columns are the specific conductivity and the partial vapour pressure of sulphur dioxide respectively.

For the 1% calcium oxide series, isothermal curves at 25°,50°,70°,90°,110°,120° and 130°C. were constructed. The partial pressure of sulphur dioxide vs. mol. of sulphur dioxide per mol. of calcium oxide curves are plotted in Graph 4, and the specific conductivity vs. mol. of sulphur dioxide per mol. of calcium oxide curves are plotted in Graph 5.

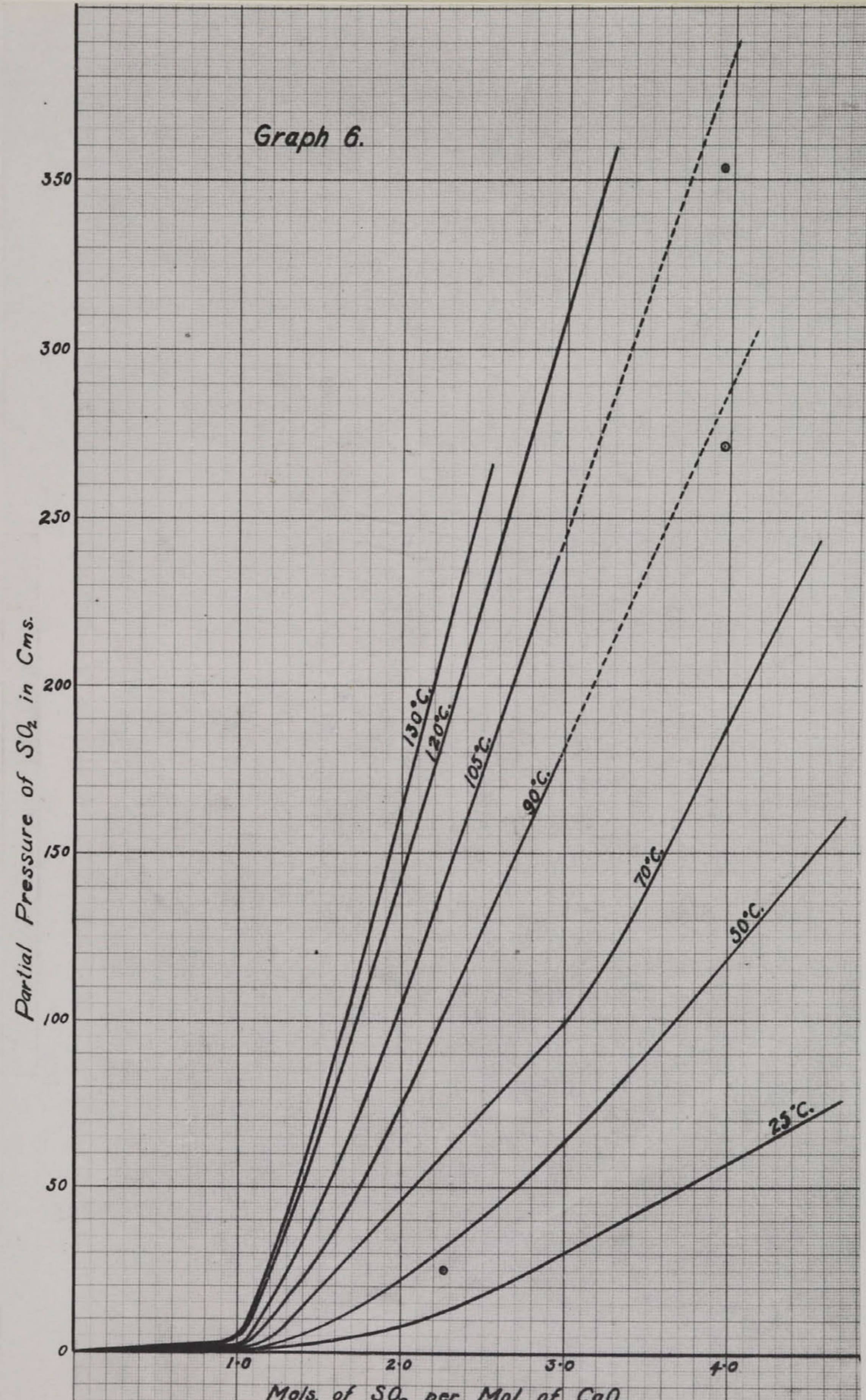
For the 2% calcium oxide series, isothermals were constructed at 25°,50°, 70°, 90°, 105°, 120°, and 130°C. The partial pressure curves are plotted in Graph 6, and the conductivity curves in Graph 7.

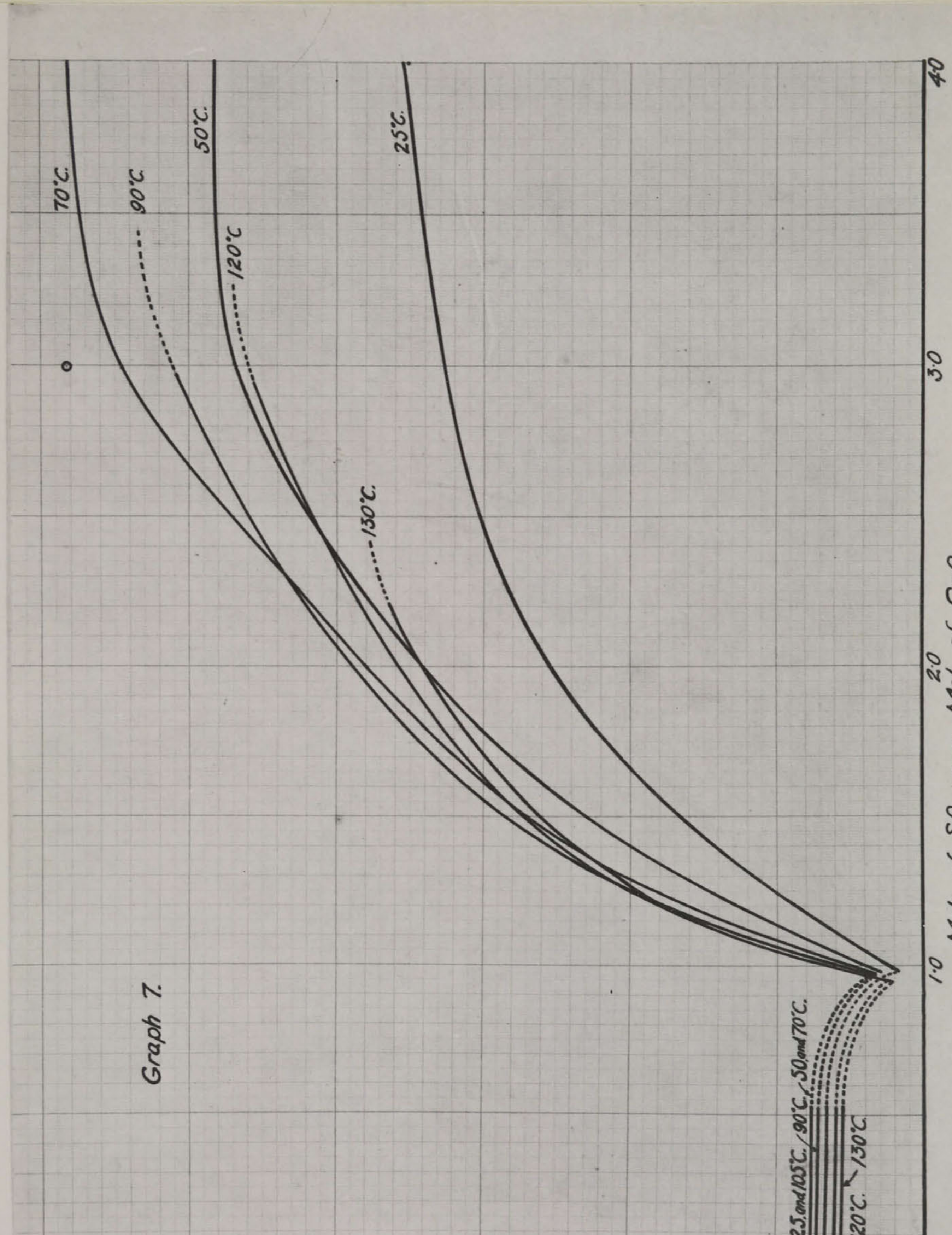

Graph 4.
Partial Pressure of SO_2 in Cms.
Mols. of SO_2 per Mol. of CaO
300
250
200
150
100
50
0
0
1·0
2·0
3·0
4·0
5·0
130°C.
120°C.
110°C.
90°C.
70°C.
50°C.
25°C.



Graph 5.

Specific Conductivity in Ohms^{-1} x 10^2
6·0
5·0
4·0
3·0
2·0
1·0
0·0
1·0
2·0
3·0
4·0
5·0
Mols. of SO_2 per Mol. of CaO
90°C.
110°C.
130°C.
70°C.
50°C.
25°C.
25°C.
90°C.
50, and 70°C.
110°C.
130°C.


Graph 6.
Partial Pressure of SO_2 in Cms.
Mols. of SO_2 per Mol. of CaO
0
50
100
150
200
250
300
350
1·0
2·0
3·0
4·0
130°C.
120°C.
105°C.
90°C.
70°C.
50°C.
25°C.


Graph 7.
70°C.
90°C
50°C.
120°C
25°C.
130°C.
25 and 105°C.
90°C.
50 and 70°C.
120°C.
130°C.
0
2·5
5·0
7·5
0
1·0
2·0
3·0
4·0
Mols. of SO₂ per Mol. of CaO
Specific Conductivity in Ohms⁻¹ x 10²

Isothermal Tables for the 1% (approx.) CaO Series

Series and Run No.	Mols. SO_2/ Mol. CaO	Spec. Cond. in $ohms^{-1}$	Part. V.P. of SO_2
Temperature 25°C.		Table (a)	
C - 1	0.0	.00850	0.0
C - 2	0.184	.00810	0.2
F - 1	0.271	.00778	0.2
(F - 2)	(0.789)	(.00305)	(0.7)
F - 3	1.519	.01480	3.7
F - 4	3.023	.02510	15.9
F - 5	5.032	.03290	38.5
Temperature 50°C.		Table (b)	
C - 1	0.0	.00966	0.0
C - 2	0.184	.00961	0.2
F - 1	0.271	.00949	0.3
(F - 2)	(0.789)	(.00470)	(0.8)
F - 3	1.516	.02163	7.3
F - 4	3.010	.03520	31.6
F - 5	4.997	.04047	80.6
Temperature 70°C.		Table (c)	
C - 1	0.0	.00972	0.0
C - 2	0.184	.00966	0.2
F - 1	0.271	.00952	0.4
(F - 2)	(0.789)	(.00605)	(1.2)
F - 3	1.514	.02620	12.2
F - 4	2.998	.04335	48.8
F - 5	4.968	.04657	127.7
Temperature 90°C.		Table (d)	
C - 1	0.0	.00913	0.0
C - 2	0.184	.00900	0.1
F - 1	0.271	.00870	0.4
(F - 2)	(0.789)	(.00732)	(1.0)
F - 3	1.511	.02904	18.8
F - 4	2.986	.05143	69.1
F - 5	4.949	.05265	187.7

Series and Run No.	Mols. SO_2/ Mol. CaO	Spec. Cond. in ohms^{-1}	Part. V.P. SO_2
	Temperature 110°C.	Table (e)	
C - 1	0.0	.00820	0.0
C - 2	0.184	.00804	0.2
F - 1	0.271	.00769	0.5
(F - 2)	(0.789)	(.00840)	(2.2)
F - 3	1.502	.02963	29.9
F - 4	2.967	.05050	103.5
F - 5	4.903	(.0588)M	(247.5)M
	Temperature 120°C.	Table (f)	
C - 1	0.0	.00767	0.0
C - 2	0.184	.00752	0.3
F - 1	0.271	.00715	0.5
(F - 2)	(0.789)	(.00871)	(3.6)
F - 3	1.498	.02880	36.7
F - 4	2.955	.04868	125.6
F - 5	4.897	-	(281.5)M
	Temperature 130°C.	Table (g)	
C - 1	0.0	.00712	0.0
C - 2	0.184	.00697	0.4
F - 1	0.271	.00661	0.6
(F - 2)	(0.789)	(.00881)	(4.7)
F - 3	1.493	.0270	47.0
F - 4	2.938	.04680	153.7

Isothermal Tables for the 2%(approx) CaO Series

Series and Run No.	Mols. SO_2/ Mol. CaO	Spec. Cond. in ohms^{-1}	Part. V.P. of SO_2
	Temperature 25°C.	Table (h)	
C - 1	0.0	.00850	0.0
G - 1	0.527	.00833	0.4
G - 2	1.048	.00494	0.7
G - 3	1.291	.01410	1.9
G - 4	2.271	.03581	12.5
G - 5	3.018	.04107	31.0
G - 6	4.022	.04463	57.5
	Temperature 50°C.	Table (i)	
C - 1	0.0	.00966	0.0
G - 1	0.527	.00966	0.3
G - 2	1.048	.00761	0.9
G - 3	1.291	.02088	3.5
G - 4	2.266	.04822	32.0
G - 5	3.007	.05871	63.0
G - 6	3.992	.0603	118.0
	Temperature 70°C.	Table (j)	
C - 1	0.0	.00972	0.0
G - 1	0.527	.00972	0.3
G - 2	1.048	.00960	1.5
G - 3	1.288	.02490	7.6
G - 4	2.254	.05323	59.5
G - 5	2.995	.06820	(99.1)M
G - 6	3.982	.07280	185.9
	Temperature 90°C.	Table (k)	
C - 1	0.0	.00913	0.0
G - 1	0.527	.00907	0.4
G - 2	1.048	.01130	2.3
G - 3	1.286	.02685	14.7
G - 4	2.240	.05330	100.6
G - 5	2.970	.06360	178.2
G - 6	3.962		(271.3)M

Series and Run No.	Mols.SO$_2$/ Mol. CaO	Spec.Cond. in ohms^{-1}	Part.V.P. SO$_2$
	Temperature 105°C.	Table (l)	
C - 1	0.0	.00843	0.0
G - 1	0.527	.00833	0.6
G - 2	1.048	.01217	3.2
G - 3	1.283	.02710	22.3
G - 4	2.229	.05140	137.0
G - 5	2.957	.06025	238.7
G - 6	3.939	-	(353.5)M
	Temperature 120°C.	Table (m)	
C - 1	0.0	.00767	0.0
G - 1	0.527	.00751	1.8
G - 2	1.048	.01250	6.5
G - 3	1.281	.02640	34.5
G - 4	2.218	.04820	178.7
G - 5	2.938	.05690	300.6
	Temperature 130°C.	Table (n)	
C - 1	0.0	.00712	0.0
G - 1	0.527	.00693	1.7
G - 2	1.048	.01245	8.3
G - 3	1.279	.02545	38.3
G - 4	2.211	.04563	203.0

Critical Survey of Results

It will be observed that some of the readings in the preceding tables are bracketed and followed by the letter "M". The purpose of this notation is to indicate that the reading is not a true equilibrium reading, and that the system was at that time in a metastable condition. In spite of the vigorous agitation, maintained at all times, to which the solution in the cell was subjected, there seemed to be an unusually great tendency for the system to persist in a metastable state. This was particularly noticeable in one or two cases. The concise criticisms of each experimental run contained in the following paragraphs will point out where such metastability existed and will also give an estimate of the value of the experimental data of that run.

Series C, Runs Nos. 1 and 2. No difficulty was experienced with tendencies toward metastability in these two runs. The temperature-conductivity curves for the ascending and descending portions of the run are both smooth curves and in each case the equilibrium conductivity curve was easily interpolated. The system was slow in approaching equilibrium, requiring the special 2°C. procedure in both runs, undoubtedly due to the slow rate at which the solid phase went into, or came out of, solution.

Series F, Run No.1. As in the above runs there was no tendency toward metastability. The system approached equilibrium more rapidly than in the two previous runs, and did not require the application of the extra 2°C. rise in temperature mentioned previously. This may be attributed to the fact that the sulphur dioxide content of this solution was higher than in Series C, Runs 1 and 2, and that the increased concentration of this substance was responsible for the increase in rate at which the system came to equilibrium. The equilibrium conductivity curve was easily interpolated between the two smooth experimental curves.

Series F, Run No.2. Unfortunately, the data of this run do not agree with the data of either the preceding or following runs. Consequently it was not plotted in Graph 3, nor was it used in the construction of Graphs 4 and 5. It was recorded in the tables of isothermals and bracketed, merely for the sake of continuity. The discarding of this data is justified by a comparison of both the conductivities and partial pressures of this run with those of Series G, Run No.2. In this latter case the conductivities and partial pressures were considerably lower than in F-2 even though the concentration of sulphur dioxide was greater in G-2 than in F-2. Surprisingly, the conductivities at 25°C. and 50°C. do appear to agree with those of Series C, Runs 1 and 2, and Series F, Run 1. Above these temperatures they do not, and the maximum in the conductivity vs. temperature curve appears at about 130°C. instead of at about 60°C. as would be expected from a comparison with the other curves for solutions having a sulphur dioxide concentration less than one mol. per mol. of calcium oxide. It is possible that the precipitation of the solid phase that should accompany a rise in temperature in these runs did not take place. This would account for these discordant results.

Series F, Run No.3. This is the first run in which the tendency toward metastability was well defined. In spite of the fact that a small amount of the solid phase was still present in the solution in the beginning of this run, the conductivity increased with temperature in a linear manner until the temperature slightly exceeded 90°C. Undoubtedly, solid should have been coming out of solution continuously as the temperature was raised, giving a smooth ascending temperature-comductivity curve with a maximum at about 105°C. This run affords an excellent example of the great tendency of this system to persist in a metastable condition. The equilibrium conductivity values were obtained by making the shape of the equilibrium curve conform with the descending temperature curve. Slight modifications also had to be made in the vapour pressure curve at 70°C. and 90°C. The true equilibrium values at these temperatures were obtained in a similar manner to that in which the equilibrium conductivities were obtained.

Series F, Run No.4. This is the first run in this Series in which there was no solid phase present in the solution at the beginning of the run. The conductivity increased in a linear manner with the temperature until the temperature exceeded 90°C. whereupon a solid precipitated out of solution and the conductivity underwent a sharp decline with further increase in temperature. No descending temperature conductivity run was made. The back interpolation of the high temperature portion of the curve indicates that precipitation should take place about 95°C. The bracketed value in Table 6(a) is a little too high, due to the fact that insufficient time was allowed for precipitation to be completed before this reading was taken.

Series F, Run No.5. The conductivity-temperature curve, obtained for this run experimentally, is a straight line. It is exceedingly probable, however, that precipitation should have occurred between 90°C. and 110°C. and that above these temperatures the conductivities should have fallen off as in Run 5. The failure of this solution to precipitate out a solid can be attributed to metastability. Unfortunately the pressures became too high to attempt to cause precipitation by increasing the temperature and consequently the degree of supersaturation. The evidence in favour of the existence of metastability at high temperatures in this run is further enhanced by the form of the isothermal curves.

Series G, Runs Nos. 1,2 and 3. These three runs behaved in a manner similar to Series F Run 1. No difficulty was experienced in interpolating the equilibrium conductivity curve. The maximum in the conductivity temperature curve in Run 1 occurred at the same point as in Series C, Run 1 (See Graph 2). The maxima in Runs 2 and 3 occurred at approximately 120°C. and 105°C. respectively.

Series G, Run No.4. The 49.8°C. point in this Run with ascending temperatures was a metastable point. Evidently the same type of metastability existed at this one point of this run as was discussed in Series F, Run 3. Unlike Series F, Run 3 metastability did not persist over a large temperature range. Both the conductivity and vapour pressure readings at this temperature differed from the true equilibrium values. As previously, the true equilibrium values were obtained from the equilibrium curves.

Series G, Run No.5. This run has its counterpart in Series F, Run 4. A back extrapolation of the high temperature portion of the conductivity-temperature curve indicates that precipitation should have taken place at approximately 65°C. This would make the 70°C. point a metastable point, but the degree of metastability is so small that it can readily be understood why precipitation did not take place at this point. The vapour pressure reading at this point is also not a true equilibrium value. It is probable, however, that it differs only slightly from the equilibrium value since the degree of supersaturation of the solution is small.

Series G, Run No.6. This run was similar to Series F, Run 5 except that at about 102°C. precipitation did take place. Unfortunately the pressures were so high at this temperature that it was thought unsafe to take the solution beyond this temperature. A reading was therefore made at this temperature and the conductivity was found to have dropped to a comparatively low value. It was impossible, however, to keep the system at this temperature for a long enough time for equilibrium to be reached. It may be concluded therefore that there is a very strong tendency toward metastability in these runs with high sulphur dioxide concentration, and that precipitation will take place when the degree of metastability of the system becomes very great. When precipitation does take place the conductivity undergoes a marked decrease, and where it is possible to establish a conductivity-temperature curve after precipitation has taken place the back extrapolation of this curve, where it cuts the other portion of the curve for the run, indicates the temperature at which precipitation should have first taken place.

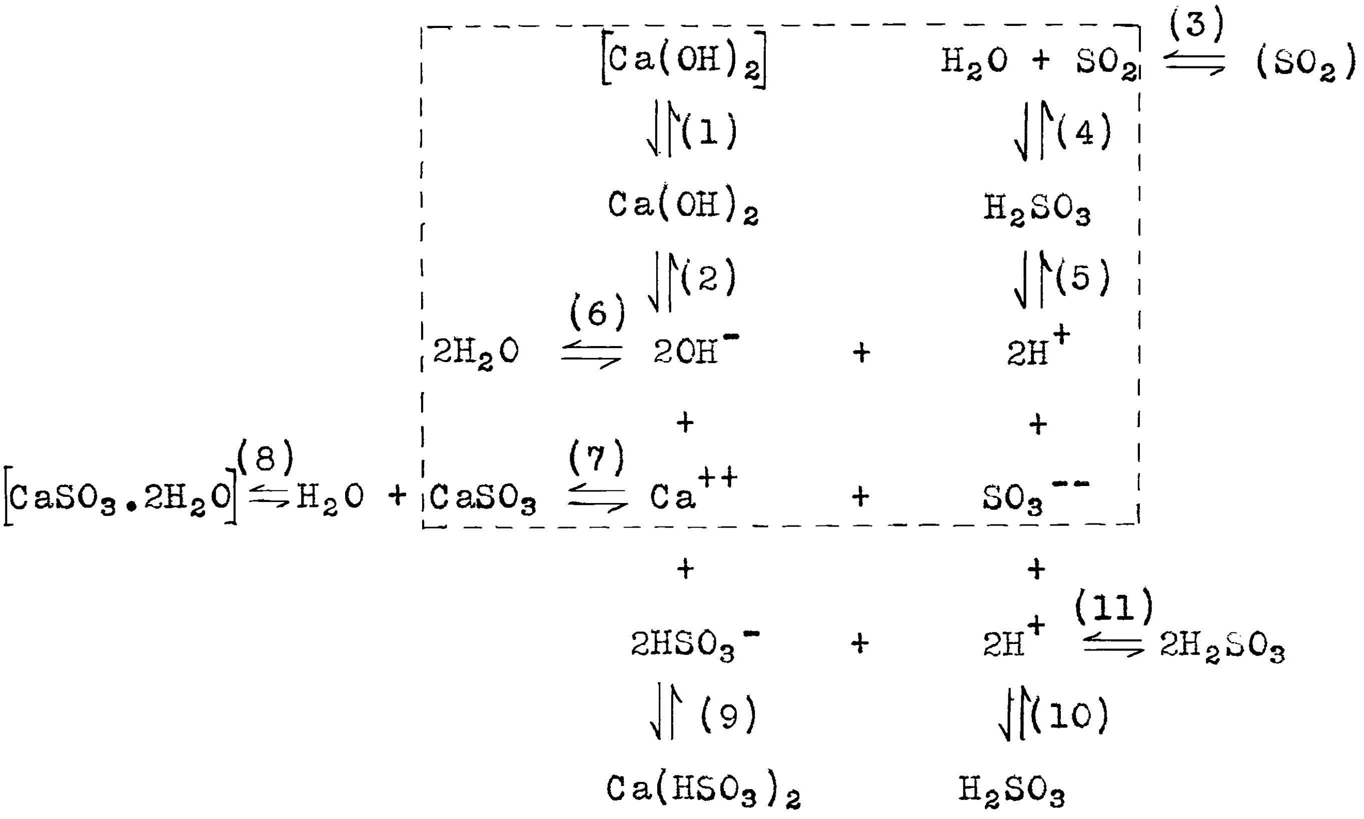
NOTE

The writer is aware that the treatment of the subject matter of this thesis is somewhat more detailed than is perhaps necessary. It was considered advisable, however, not to sacrifice clarity by attempting to present too concise a discussion of such a complicated system.

DISCUSSION OF RESULTS

(a) General.

The complexity of the equilibria existing in this three component system will be appreciated when the following reaction chart is studied. It is believed that all of the important equilibria which exist in this system are included in the chart.



Formulae enclosed in [ ] brackets represent the substance as being present in the solid state. Formulae in ( ) brackets indicate the substance to be in the gaseous state. Formulae not enclosed represent the substance in true solution.

Essentially there are two two-component equilibria involved in this system, viz., the equilibria in the systems calcium oxide - water and sulphur dioxide - water. Their combination constitutes the basis of the three component system as is shown in the reaction chart. There is one other possible system: the system calcium oxide - sulphur dioxide. It is obviously of no interest in relation to the equilibria involved in these aqueous solutions. Equilibria (1),(2),(3),(4),(5),(6),(7) and (8) could appropriately be classed as "fundamental" equilibria. Of these equilibria those enclosed by the dotted lines are all stoichiometrically balanced. In addition to these fundamental equilibria there exist the equilibria merely indicated by (9),(10) and (11) which further complicate the system, consequently hindering any attempt at its complete elucidation. The contribution made by this research is but one step in many yet required for the complete solution of such a complicated system.

If, as a first simplification, the discussion is confined to a system in which there is no possibility of the formation of appreciable amounts of the bisulphite ion, only the "fundamental" equilibria mentioned above will be involved. This condition would exist provided that the concentration of the sulphite ion formed from the sulphur dioxide in solution as sulphurous acid does not exceed the concentration of the calcium ion formed from the calcium hydroxide. As long as hydroxyl ion is being formed from calcium hydroxide no appreciable quantity of free hydrogen ion can go to form the bisulphite ion because of the very small ionization of water.

A consideration of the two important two-component equilibria affords a good basis for a discussion of the other equilibria in this fundamental system. The two-component sulphur dioxide - water system represented by equilibria (3),(4) and (5) has been the subject of several previous investigations made in this laboratory by C.Maass and O.Maass[13], Campbell and O.Maass[14], and Morgan and O. Maass[15](see introduction). These investigators have succeeded in evaluating the constants in equilibria (3),(4) and (5) over a considerable range of temperatures and concentrations. Data concerning the properties of the second two-component system,viz., calcium oxide - water (equilibria (1) and (2)) were almost entirely lacking in the literature. The determination of the properties of this system over a large range of temperatures at saturation concentration was consequently the first work undertaken in this research. A full discussion of equilibria (1) and (2) as evaluated from the measurements made on this system will be presented in the following section.

One other equilibrium in this "fundamental" system is accurately known, i.e.,equilibrium (6) for the ionization of water. A discussion of this equilibrium can be found in almost any text book of Physical Chemistry.

(b) Equilibria in the system Calcium oxide - water.

The equilibria existing in this system may be represented thus;

$$\underset{\text{solid}}{Ca(OH)_2} \rightleftharpoons \underset{\text{dissolved}}{Ca(OH)_2} \rightleftharpoons Ca^{++} + 2OH^-$$

and $$C(1-\alpha) = C\alpha + C\alpha$$

where α is the degree of ionization

C is the concentration in equivalents per liter.

Application of the Law of Mass Action to this equilibrium gives

$$\frac{[Ca^{++}]\,[OH^-]^2}{\underset{\text{dissolved}}{[Ca(OH)_2]}} = K$$

where K is the dissociation constant,

and

$$\frac{C\alpha.(C\alpha)^2}{C(1-\alpha)} = \frac{C^2.\alpha^3}{1-\alpha} = K$$

If C and α are known at any temperature the dissociation constant at that temperature can be evaluated from the above expression.

α at any temperature t is given by

$$\frac{\Lambda_{c,t}}{\Lambda_{o,t}} = \alpha_t$$

where $\Lambda_{c,t}$ is the equivalent conductivity at the temperature t and the concentration C.

$\Lambda_{o,t}$ is the equivalent conductivity at the temperature t and infinite dilution

$$\Lambda_{o,t} = (l_0^+ + l_0^-)_t$$

where l_0^- is the limiting equivalent ionic conductivity at temperature t for the anion.

l_0^+ is the limiting equivalent ionic conductivity at temperature t for the cation.

Now

$$l_0^+ = l_{0,18^\circ}^+ + l_{0,18^\circ}^+ \times b_1 \times (t - 18^0)$$

and

$$l_0^- = l_{0,18^\circ}^- + l_{0,18^\circ}^- \times b_2 \times (t - 18^0)$$

where $l_{0,18^\circ}^-$ is the limiting equivalent ionic conductivity of the anion at 18°C.

$l_{0,18^\circ}^+$ is the limiting equivalent ionic conductivity of the cation at 18°C.

b_1 is the temperature coefficient of l_0^+

b_2 is the temperature coefficient of l_0^-

l_0^+ for $1/2\ Ca^{++}$ = 51

b_1 for $1/2\ Ca^{++}$ = .0247

l_0^- for OH^- = 173.8

b_2 for OH^- = .018

These values are taken from the International Critical Tables[27].

$$\Lambda_{c,t} = \left(\frac{1000 \times k}{C}\right)_t$$

where k is the specific conductivity in $Ohms^{-1}$ at the concentration C and the temperature t.

C is expressed in equivalents per liter.

It is evident from the above that if C and k are known, both the degree of ionization α and the dissociation constant K may be calculated.

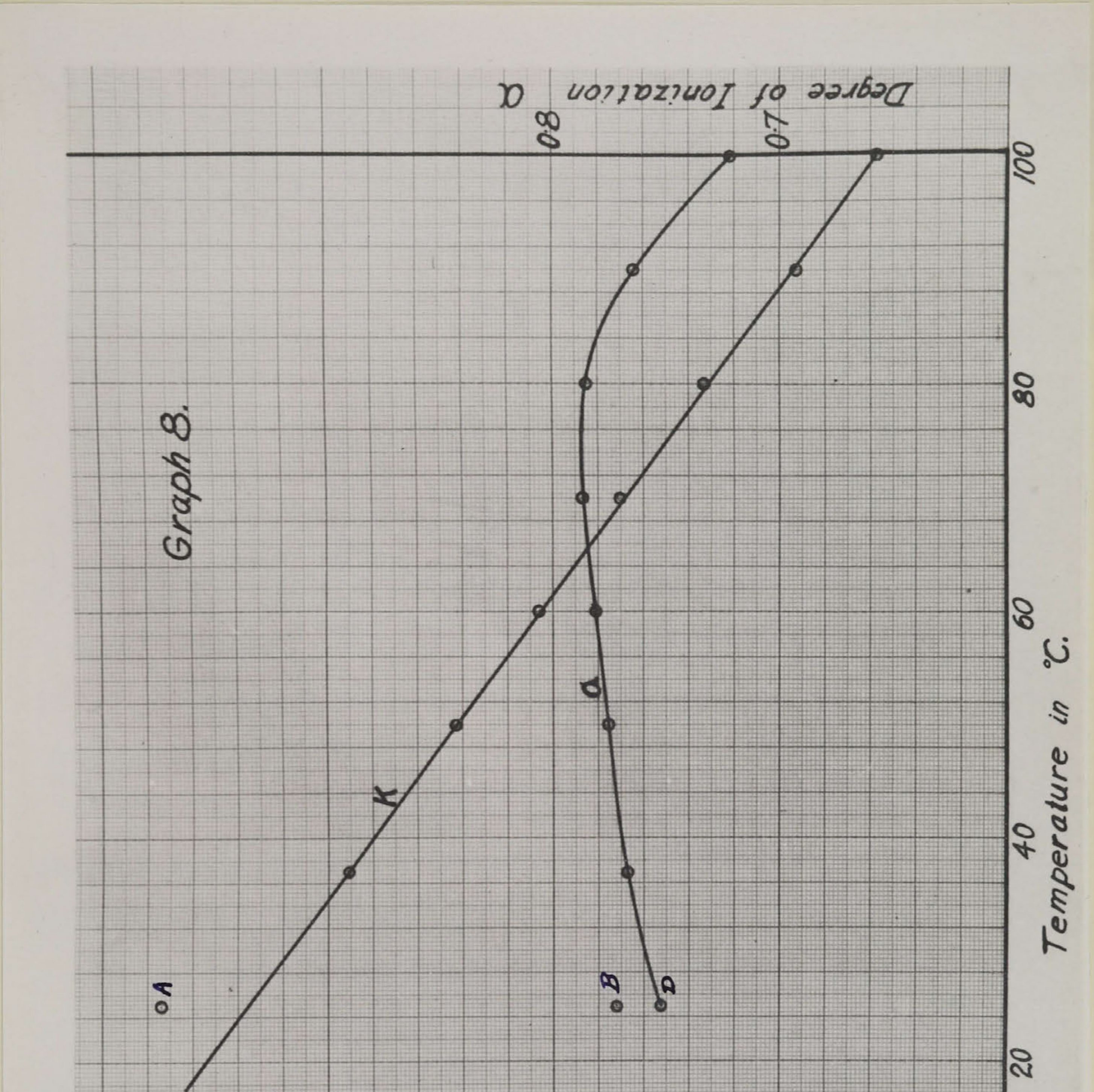
Since the solubility of calcium hydroxide in water is so low (less than 0.2% at 25°C. and decreasing with increasing temperature) the constants K and α were only evaluated for saturated solutions of this substance. K and α were determined for the saturated solution over a temperature range from 25°C. to 100°C.

A great many determinations of the solubility of calcium oxide in water have been made. Unfortunately there is very poor agreement in the data obtained by various investigators, especially at high and low temperatures. Above 100°C. the data are practically worthless. Consequently no attempt was made to calculate K and α at temperatures above 100°C. although the specific conductivities were measured up to 130°C. Between 25°C. and 100°C. the solubilities used in the calculations for K and α were obtained in the following manner; the values for the solubilities as determined at various temperatures, from a number of sources considered to be reliable, were plotted an a large scale graph. A smooth curve was now drawn through the average of these plotted values, due consideration being made for the continuity of any set of points from a single source. The data were taken from the following sources: International Critical Tables[28], Landolt Bornstein[29], Landolt Bornstein Ergänzungsband[30], Miller and Witt[16], Lamy[31], Maben[32], Herzfeld[33], Guthrie[34], and Moody[35]. Where the transposition of concentration units was necessary the solutions were assumed to have the same density as water. The error introduced in this assumption is very small, compared to some of the solubility discrepancies which in a few cases amounted to 5%.

The solubility curve can be reconstructed from the following table of data:

Temp. °C.	Solubility Gms. CaO/liter
0.0	1.350
10.0	1.322
20.0	1.254
25.0	1.208
37.0	1.086
50.0	0.958
60.0	0.861
70.0	0.764
80.0	0.681
90.0	0.620
100.0	0.578

The values calculated for α and K at various temperatures and for a saturated solution are tabulated below. The concentration C is expressed as equivalents


Graph 8.
K
α
A
B
D
Temperature in °C.
0
20
40
60
80
100
Dissociation Constant K x 10³
4·0
3·0
2·0
1·0
Degree of Ionization α
0·8
0·7

of calcium oxide per liter. The specific conductivities were obtained from Series C, Run No.1.

Degree of Ionization, and Dissociation Constants for Saturated Calcium Oxide Solutions at Various Temperatures

$T^{o}C.$	$k \times 10^{2}$	$C \times 10^{2}$	$\Lambda_{c,t}$	$\Lambda_{o,t}$	α	$K \times 10^{3}$
25.0	.850	4.31	197.3	255.5	.772	3.74
37.0	.915	3.88	236.3	308.2	.767	2.91
50.0	.966	3.42	283.0	365.2	.775	2.43
60.0	.982	3.07	319.6	409.0	.781	2.06
70.0	.972	2.73	356.3	453.0	.787	1.70
80.0	.948	2.43	390.	497.0	.785	1.33
90.0	.914	2.21	413.	540.7	.764	.927
100.0	.869	2.06	422.	584.5	.722	.576
Values for C and α at 25° C, calculated from extrapolated value of K						
25.0	.850	4.43	191.8	255.5	.752	3.35

Graph 8 is the plot of both α and K against temperature.

Excepting the 25°C. point(point A in Graph 8) the variation of K with temperature is linear over the whole temperature range. If a value for K at 25°C. is obtained by the extrapolation of this straight line and C and α are calculated from it, the values obtained at the bottom of the above table are obtained. This extrapolation seems justified because the linear relationship holds perfectly over such a large range of temperatures (37°C. to 100°C.). Moreover, if the value of α calculated from C at 25°C. was considered to be correct, then the ionization temperature curve would have to undergo a sudden change in form between 37°C. and 25°C. and pass through point B on the graph. This sudden change is unlikely. It is much more probable that the value of C at 25°C. taken from the solubility curve is in error. If the solubility is calculated from the extrapolation of K a value is obtained which is higher than the value read from the solubility curve at 25°C. If α at 25°C. is calculated from this calculated value for C, the α vs. temperature curve will pass through point D. It seems much more probable that the α vs. temperature curve would have this latter form, and consequently that the value for C, read from the solubility curve, is in error. Moreover, as was previously mentioned, the experimental values for the solubility at these lower temperatures cannot be relied upon in any case.

The accuracy of the values calculated for α and K is limited by the accuracy of the solubility data. From about 40°C. to 100°C. the maximum differences for the solubility determined by different investigators is not more than about 3%. Below and above these temperatures the percentage difference becomes greater. Values for α and K between the temperatures of 37°C. and 100°C., therefore, are accurate to 3% at least. The maximum error involved in the conductivity measurements is less than 1%, consequently errors from this source do not contribute to any large extent to the probable maximum error.

It is evident that the solubilities of calcium hydroxide need to be accurately redetermined, especially at high and low temperatures. When this has been done the values for α and K can be recalculated and given with much greater precision.

The experimental work on the calcium oxide - water system also included the measurement of the vapour pressures of the saturated solutions over a temperature range from 25°C. to 130°C. The data are tabulated in Series C, Run No.1., Table (b). The vapour pressures of the saturated solution are slightly less than those for pure water as would be expected. Since the manometer used in these vapour pressure measurements was designed to measure high pressures, the vapour pressure determinations at low pressures could not be made with as great a percentage accuracy as at high pressures. A preliminary test of the manometer, measuring the vapour pressure of pure water, proved, however, that measurements could be made with a precision of at least 0.1 centimeters for pressures up to one atmosphere. The vapour pressures as measured for the system calcium oxide - water are therefore accurate to at least 0.1 cm. up to atmospheric pressure, and to 0.5% at least, at pressures greater than atmospheric. At high pressures it is probable that much greater accuracy than this was actually attained.

(c) the Three Component System $CaO-SO_2-H_2O$.

(1) The Significance of Graphs 2,3,4,5,6 and 7.

Before any study of the equilibria existing in this three-component system is undertaken, the general form of the curves plotted from the experimental data will be discussed. These curves are divided into three classes, viz., conductivity vs. temperature curves (Graphs 2 and 3), conductivity vs. sulphur dioxide concentration expressed as mols. of sulphur dioxide per mol. of calcium oxide curves (Graphs 5 and 7), and curves of partial sulphur dioxide pressure vs. sulphur dioxide concentration expressed as above (Graphs 4 and 6). Each class of curves will be treated separately.

Conductivity vs. Temperature Curves: The form of these curves is dependent on the mol.-ratio of sulphur dioxide to calcium oxide. There are two distinct types, viz., those in which the conductivity increases to a maximum, then decreases again as the temperature is raised, the whole change taking place in such a way as to give the smooth curves shown in Graphs 2 and 3, and the second type in which the increase and decrease are both linear and the maximum point is the intersection of two straight lines. The first type of curves occur when a solid phase exists in contact with the solution (i.e. at low sulphur dioxide concentrations) and the second type when the sulphur dioxide concentration is high and the solid phase has disappeared. The solid passes completely into solution when the sulphur dioxide concentration reaches a value of about 2.5 mols. of sulphur dioxide per mol. of calcium oxide.

When the sulphur dioxide concentration is less than one mol. of sulphur dioxide per mol. of calcium oxide the maxima in the conductivity-temperature curves occur at about 60°C., the conductivity at which the maxima occur decreasing slightly as the sulphur dioxide concentration increases. The temperature at which these maxima occur coincides with the temperature at which the maximum in the two-component calcium oxide - water system is found (See Graph 2). The calcium oxide concentration affects the form of these curves to a slight extent as would be expected, especially at high temperatures.

With sulphur dioxide concentrations above one mol. per mol. of calcium oxide the temperatures at which the maxima occur progressively decrease as the sulphur dioxide concentration increases. When the sulphur dioxide concentration is sufficiently high all of the solid phase disappears at low temperatures. If this true solution is now heated, the conductivity increases linearly until a temperature is reached at which solid begins to precipitate from the solution. At this point the conductivity begins to decrease. If the heating is continued, solid continues to precipitate and the conductivity falls off in a linear manner. The temperature at which these two linear curves intersect is the temperature at which the precipitate first appears. It is apparent from the G Series of runs that some relation exists between the temperature at which the maximum occurs and the sulphur dioxide concentration, because a line can be drawn through these maxima and this line will be found to pass through the maximum in Series G, Run 5, formed by the intersection of two straight lines (See Graph 3).

The most interesting feature of these conductivity-temperature curves is the appearance of the maximum when the temperature is increased. Undoubtedly there exists two opposing factors, one tending to increase and the other to decrease the conductivity. The factor tending to increase the conductivity as the temperature is increased is the normal increase in mobility of the ions. Roughly this amounts to about 2% per degree C. Opposing this there is the decrease in conductivity accompanying a decrease in concentration of calcium hydroxide or calcium sulphite as the temperature is raised. The solubility of both of these substances decreases with a rise in temperature. When the decrease in conductivity due to this factor more than offsets the rise due to the increased mobility of the ions, the resultant effect will be a decrease in conductivity, and the curve will be inflected downward toward the temperature axis. Any sudden inflection toward lower solubility in the solubility-temperature curves for either of these substances would tend to make the maxima in the conductivity-temperature curves more pronounced.

It will also be observed from Graph 3 that solutions having approximately the same mol.-ratio of sulphur dioxide to calcium oxide, but double the calcium oxide concentration with respect to water, have a considerably greater specific conductivity at any given temperature (cf. Series G, Run 5, and Series F, Run 4). This increased conductivity is, of course, to be expected.

Conductivity vs. Sulphur Dioxide Concentration Curves: These isothermal curves are to be found in Graphs 5 and 7. Graph 5 is for the Series with a 1% calcium oxide addition, and Graph 7 for the 2% addition.

In general the form of these two series of curves is much the same. The most important conclusion derived from a consideration of these curves is that the conductivity of the solution passes through a minimum value at stoichiometric proportions of sulphur dioxide to calcium oxide of approximately one to one. This is true regardless of the temperature of the isothermal considered. The curves of the 1% series fall off gradually until a minimum is reached at approximately the equivalence point. In the 2% series this decrease is not so marked until the concentration of sulphur dioxide is considerably higher than in the 1% series. The decrease in conductivity is due to the disappearance of hydroxyl ion. The ionic equilibria involved will be discussed in a later section.

The sudden increase in conductivity after the equivalence point has been passed is chiefly due to the appearance of hydrogen ion. This mechanism will also be discussed later.

The tendency toward metastability at high sulphur dioxide concentrations and high temperatures makes it almost impossible to determine what form the high temperature isothermals will have at sulphur dioxide concentrations of four or five mols. per mol. of calcium oxide. The isothermals of Graphs 5 and 7 seem to indicate that the isothermal having the greatest conductivity values in this region approximately corresponds with the temperature at which precipitation took place in these 1 and 2% calcium oxide series. The curves flatten out in this region and both the higher and lower temperature isothermals appear to lie below this particular isothermal.

Partial Pressure vs. Sulphur Dioxide Concentration Curves: The isothermal partial pressure curves for the 1% series are given in Graph 4, and those for the 2% series in Graph 6.

The most significant feature of these curves is that up to the sulphur dioxide - calcium oxide equivalence point the partial pressure of the sulphur dioxide is almost negligible, even at high temperatures. It is obvious that the sulphurous acid formed from the sulphur dioxide has combined with the calcium oxide and that neither free sulphur dioxide nor sulphurous acid are present in the liquid phase in quantities sufficient to exert any appreciable partial sulphur dioxide pressure. The absence of sulphur dioxide from the vapour phase, and consequently also from solution, gives excellent confirmation to the shape of the conductivity curves in this region below the equivalence point.

As the sulphur dioxide concentration is increased the partial pressure increases and the rate of increase is greater the higher the temperature. In the 2% calcium oxide series, above a mol.-ratio of about 2 mols. per mol. the high temperature isothermals are almost linear. The 70°C. isothermal is this series up to 3 mols. per mol. conforms with the low temperature isothermals. The break in this curve occurs at the conditions under which precipitation took place in Series G, Run 5. The upper portion of the curve is almost linear and conforms with the 90°C. etc. isothermals. The low temperature isothermals are smooth curves.

In general the slope of the isothermals in the 1% series is not nearly so steep as in the 2% series. Actually for any given mol.-ratio the percentage of sulphur dioxide present in the solution is approximately twice as great in the 2% series. This accounts for the difference in slopes.

If the two series are compared just above the equivalence point the 1% series will be observed to have greater partial pressures than the 2% series, especially at higher temperatures. This may be attributed to the greater calcium oxide concentration in the latter series.

(2) Equilibria Existing up to Equivalent Proportions of Sulphur Dioxide and Calcium Oxide

A semi-quantitative treatment of the equilibria in the three-component system up to and a little past the point at which the amount of sulphur dioxide added to the system is equivalent to the amount of calcium oxide present, will be given below. The mechanism to be described is based entirely on the experimental results obtained for this portion of the system, chiefly as depicted in Graphs 4,5,6 and 7.

The equilibria existing in this portion of the system may be indicated as follows:-

$$\begin{tikzcd}
 & & SO_2 \text{ gas} \arrow[d, shift right] \arrow[d, leftarrow, shift left, "(5)"] & & & \\
Ca(OH)_2\text{solid} \arrow[d, shift right] \arrow[d, leftarrow, shift left, "(7)"] & & SO_2 + H_2O \arrow[d, shift right] \arrow[d, leftarrow, shift left, "(4)"] & CaSO_3\text{solid} \arrow[d, shift right] \arrow[d, leftarrow, shift left, "(8)"] & & \\
Ca(OH)_2 \arrow[d, shift right] \arrow[d, leftarrow, shift left, "(1)"] & + & H_2SO_3 \arrow[d, shift right] \arrow[d, leftarrow, shift left, "(6)"] \arrow[r, shift left, "(2)"] \arrow[r, leftarrow, shift right] & CaSO_3 \arrow[d, shift right] \arrow[d, leftarrow, shift left, "(3)"] & + & 2H_2O \\
Ca^{++} + 2OH^- & & H^+ + HSO_3^- & Ca^{++} + SO_3^{--} & &
\end{tikzcd}$$

Note: For convenience, reaction (2) is represented as taking place between molecules. Actually the reaction proceeds through the ionic state. In spite of this the equilibrium may be represented in this way.

As a beginning, consider the system in which calcium hydroxide, both solid and in solution, is in stoichiometric excess with regard to sulphur dioxide. Solid calcium hydroxide is in equilibrium with dissolved calcium hydroxide which in turn is in equilibrium with its ions as shown in Equilibria (1) and (7). Since the hydroxyl ion is far more mobile than the calcium ion the conductance is chiefly due to this ion.

Now suppose that a small amount of sulphur dioxide gas is introduced into the system. The gas in the gas phase is in equilibrium with the dissolved gas which in turn is in equilibrium with sulphurous acid, and the sulphurous acid is in equilibrium with its ions as shown by reactions (5),(4), and (6). The sulphurous acid formed will, however, react with the calcium hydroxide to form calcium sulphite which in turn is in equilibrium with solid calcium sulphite (provided that enough has been formed to saturate the system) and also with its ions (Reactions (2),(8) and (3)). If reaction (2) goes almost to completion in the direction of the formation of calcium sulphite, then, for a small addition of sulphur dioxide, the sulphurous acid formed is used up and ionization (6) does not take place. More calcium hydroxide will come into solution to replace that used up and equilibrium (1) will be restored. What will be the net effect on the conductivity of the solution? The solution now contains calcium ion, hydroxyl ion and sulphite ion, i.e. there are more ions than were present in the original calcium hydroxide solution and the conductivity would be expected to rise after this first small addition. One factor has been omitted, however. The calcium ions formed from the calcium sulphite will repress ionization (1) and consequently the hydroxyl ion concentration will be lowered. Now the hydroxyl ion is by far the most mobile of these three ions and its diminution would be expected to cause the net conductivity of the solution to fall. As can be seen from Graphs 5 and 7 this actually takes place.

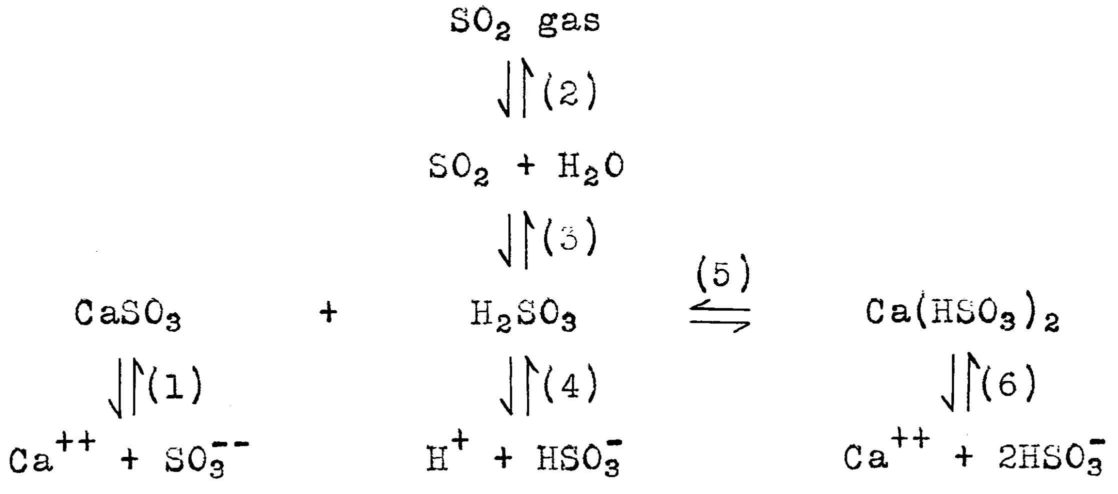
As more sulphur dioxide is added more calcium sulphite is formed and the concentration of the calcium ion from this source increases, causing greater repression of ionization (1) and a consequent fall in the net conductivity of the solution. Finally a point will be reached where practically all the calcium hydroxide will have been used up and no more hydroxyl ions will be formed. This point will occur almost at the point where the quantity of sulphur dioxide added is equivalent to the amount of calcium oxide present. Only calcium and sulphite ions will exist to any appreciable extent at this point and the conductivity at this point will reach a minimum value. This is confirmed by the experimental conductivity values of Graph 5 and 7.

If the concentration of sulphur dioxide is increased beyond this equivalence point free hydrogen ions appear from ionization (6) from the excess of sulphurous acid and a rapid rise in conductivity due to the very high mobility of this ion would be expected to occur. This is also confirmed by the experimental curves. The nature of the equilibria beyond this equivalence point will be treated in the next section.

The behaviour of the partial sulphur dioxide pressures of the system below the equivalence point further prove the validity of the mechanism proposed above. It is evident from the low values of the partial pressures that the concentration of sulphur dioxide existing as such, or as sulphurous acid, is practically nil until the equivalent point has been reached.

(3) Equilibria Existing Above Equivalent Proportions of Sulphur Dioxide and Calcium Oxide

It has been pointed out previously that the equilibria existing in this system are different when the sulphur dioxide concentration exceeds the concentration which is equivalent to the calcium oxide present. Sulphurous acid is present in excess and is therefore capable of combining with the calcium sulphite to form calcium bisulphite. The mechanism given below shows how such a combination can take place.



$$\begin{tikzcd}
 & & SO_2 \text{ gas} \arrow[d, shift right] & & \\
 & & SO_2 + H_2O \arrow[u, shift right, "(2)"'] \arrow[d, shift right] & & \\
CaSO_3 \arrow[d, shift right] & + & H_2SO_3 \arrow[u, shift right, "(3)"'] \arrow[d, shift right] \arrow[r, shift left, "(5)"] & Ca(HSO_3)_2 \arrow[l, shift left] \arrow[d, shift right] \\
Ca^{++} + SO_3^{--} \arrow[u, shift right, "(1)"'] & & H^{+} + HSO_3^{-} \arrow[u, shift right, "(4)"'] & Ca^{++} + 2HSO_3^{-} \arrow[u, shift right, "(6)"']
\end{tikzcd}$$

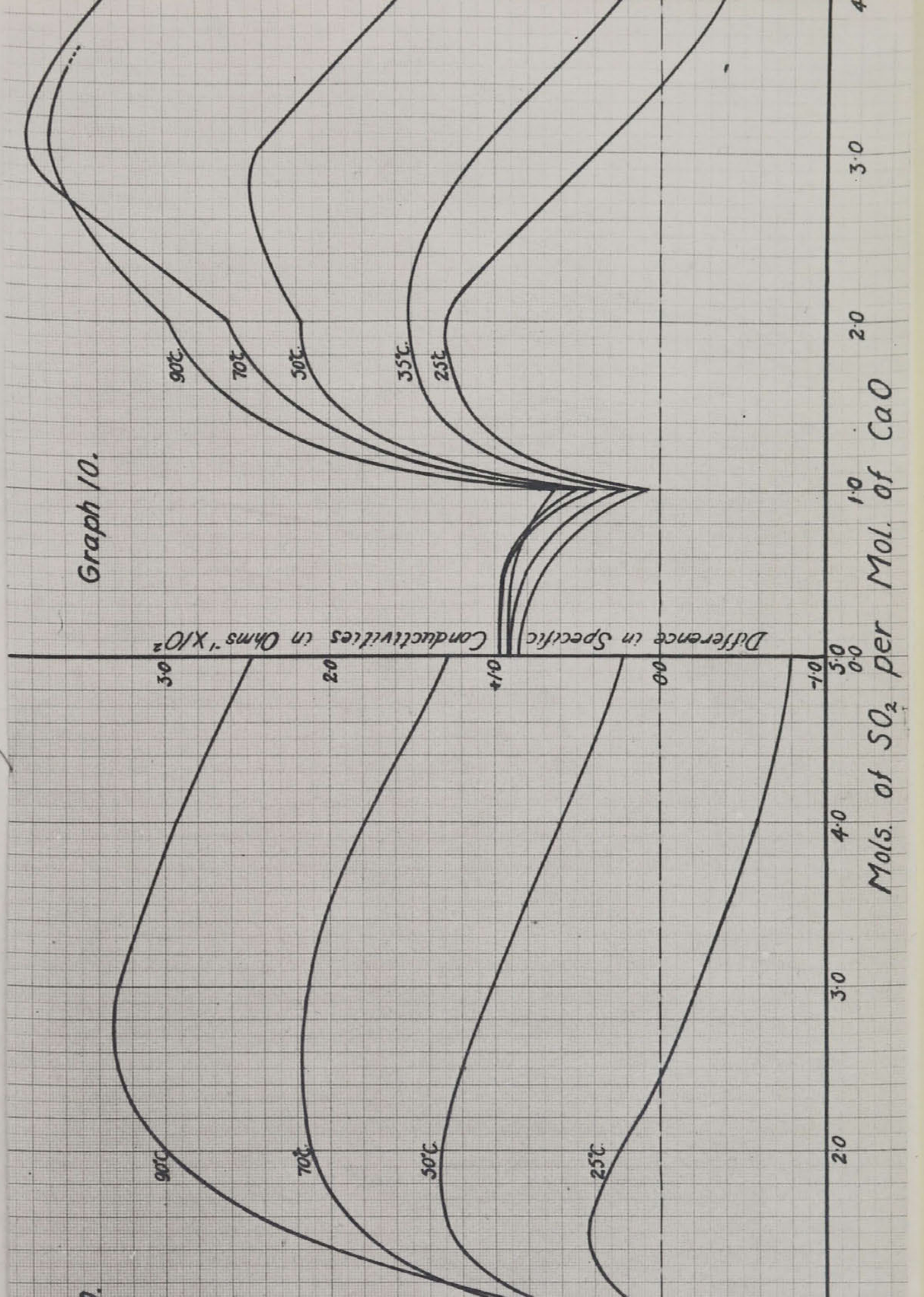
It is apparent that a large number of ions are involved in the conductance process in such a system. Some method of treatment must be found to simplify the analysis.

Equilibria (2),(3) and (4) involve the system sulphur dioxide - water. Campbell and O.Maass[14] have determined what the hydrogen ion and bisulphite ion concentration in this two-component system is for any partial pressure of sulphur dioxide above the solution at a given temperature. Consequently, for any system in which equilibria (2), (3) and (4) occur the hydrogen and bisulphite ion concentration resulting from the dissociation of H_2SO_3 can be estimated if the partial pressure of sulphur dioxide in that system is known. The results of Campbell and O.Maass[14] can be best applied to the three-component system under discussion in a slightly different manner. Suppose that at some given temperature and sulphur dioxide concentration both the partial pressure and the conductivity are read from the isothermal curves of Graphs 4 and 5. This conductivity value is the total of the conductivities of all the ionic species present in the system. Using the above value for the partial pressure of sulphur dioxide, the partial pressure vs. percent sulphur dioxide curves constructad from the data of Campbell and O.Maass[14] can be consulted, and the percentage composition at which the partial pressure in this two-component system is the same as for the three-component system may be determined. The conductivity corresponding to this composition and temperature can then be determined from conductivity-composition isothermal curves plotted from their data. This value for the conductivity is the conductivity due to the hydrogen and bisulphite ions resulting from sulphurous acid. If this value is subtracted from the value read from the conductivity-composition curves for the three-component system, the resulting conductivity value is the sum total of the conductivities of the ions resulting from

$$Ca^{++} + SO_3^{--} \leftrightarrows \sim \leftrightarrows Ca^{++} + 2HSO_3^{-}$$

of the general scheme of equilibria given in the equilibrium chart. In this way the conductance due to the ions formed in equilibrium (4) has been eliminated.

In Graphs 9 and 10 the difference in conductivities for a series of temperatures and sulphur dioxide to calcium oxide mol.-ratios, obtained as indicated above, have been plotted. Graph 9 is for the 1% and Graph 10 for the 2% calcium oxide series. The data are given in the following tables.


Graph 9.
Graph 10.
90°C.
70°C.
50°C.
35°C.
25°C.
0
1·0
2·0
3·0
4·0
5·0
0·0
1·0
2·0
3·0
4·0
3·0
2·0
+1·0
0·0
-1·0
Mols. of SO_2 per Mol. of CaO
Difference in Specific Conductivities in $\text{Ohms}^{-1} \times 10^2$

The 1% Calcium Oxide Series

Mols. SO_2/ Mol. CaO	Sp.Cond. in $ohms^{-1}$	Part. V.P. SO_2	$\%SO_2$ at this p.p. Campbell	Cond.at this $\%SO_2$	Diff.in Spec. Cond.
Temperature 25°C.					
0.0	.00850	0.0	0.0	.0	.0085
0.5	.0068	0.4	0.05	.0012	.0056
1.0	.0029	0.7	0.09	.0022	.0007
1.5	.0144	3.3	0.46	.0100	.0044
2.0	.0195	6.8	0.94	.0170	+.0025
2.5	.0226	11.0	1.53	.0229	-.0003
3.0	.0250	15.5	2.10	.0272	-.0022
3.5	.0270	20.8	2.72	.0312	-.0042
4.0	.0289	26.3	3.33	.0348	-.0059
4.5	.0309	31.9	3.92	.0380	-.0071
5.0	.0329	37.8	4.50	.0409	-.0080
Temperature 50°C.					
0.0	.00966	0.0	0.0	.0	.00966
0.5	.0087	0.4	0.01+	.0002	.0085
1.0	.0048	0.8	0.04	.0009	.0039
1.5	.0212	6.7	0.39	.0085	.0127
2.0	.0287	13.5	0.80	.0154	.0133
2.5	.0327	21.4	1.26	.0207	.0120
3.0	.0351	31.0	1.79	.0249	.0102
3.5	.0367	42.3	2.37	.0285	.0082
4.0	.0381	54.4	2.98	.0320	.0061
4.5	.0393	67.3	3.61	.0354	.0039
5.0	.0405	80.3	4.23	.0383	.0022

Mols. SO_2/ Mol. CaO	Sp.Cond. in ohms^{-1}	Part. V.P. SO_2	%SO_2 at this p.p. Campbell	Cond.at this %SO_2	Diff.in Spec. Cond.
Temperature 70°C.					
0.0	.0097	0.0	0.0	.0	.0097
0.5	.0087	0.3	0.01	.0002	.0085
1.0	.0062	1.5	0.05	.0009	.0053
1.5	.0257	11.8	0.42	.0077	.0180
2.0	.0350	22.9	0.80	.0138	.0212
2.5	.0403	35.0	1.21	.0187	.0216
3.0	.0433	49.0	1.68	.0220	.0213
3.5	.0451	66.0	2.24	.0250	.0201
4.0	.0460	85.4	2.87	.0281	.0179
4.5	.0464	106.5	3.535	.0312	.0152
5.0	.0467	128.0	4.20	.0339	.0128
Temperature 90°C.					
0.0	.00913	0.0	0.0	.0	.00913
0.5	.0080	.4or.5	0.01	.0002	.0078
1.0	.0070	4.2	0.095	.0016	.0054
1.5	.0287	18.5	0.41	.0066	.0221
2.0	.0414	33.5	0.74	.0113	.0301
2.5	.0484	50.0	1.10	.0155	.0329
3.0	.0515	70.4	1.54	.0186	.0329
3.5	.0518	94.5	2.07	.0206	.0312
4.0	.0521	123.2	2.695	.0228	.0293
4.5	.0524	156.	3.41	.0253	.0271
5.0	.0526	191.	4.17	.0279	.0247

The 2% Calcium Oxide Series

Mols. SO_2/ Mol. CaO	Sp.Cond. in $ohms^{-1}$	Part. V.P. SO_2	%SO_2 at this p.p. Campbell	Cond. at this %SO_2	Diff. in Spec. Cond.
		Temperature 25°C.			
0.0	.0085	0.0	0.0	-	.0085
0.5	.0083	0.4	0.05	.0012	.0071
1.0	.0030	0.7	0.09	.0022	.0008
1.5	.0207	3.0	0.41	.009	.0117
2.0	.0318	8.0	1.11	.0189	.0129
2.5	.0378	17.5	2.34	.0289	.0089
3.0	.0408	30.0	3.72	.0369	+.0039
3.5	.0428	43.5	5.04	.0435	-.0007
4.0	.0445	57.0	6.25	.0487	-.0042
		Temperature 35°C.			
0.0	.0091	0.0	0.0	-	.0091
0.5	.0090	0.3	0.03	.0008	.0082
1.0	.0037	0.7	0.06	.0016	".0021
1.5	.0245	5.0	0.48	.0107	.0138
2.0	.0369	13.8	1.34	.0217	.0152
2.5	.0441	26.5	2.44	.0299	.0142
3.0	.0480	42.5	3.70	.0370	.0110
3.5	.0500	61.0	5.03	.0437	.0063
4.0	.0509	80.2	6.33	.0492	.0017
		Temperature 50°C.			
0.0	.0097	0.0	0.0	-	.0097
0.5	.0097	0.3	0.01	.0002	.0095
1.0	.0049	0.8	0.04	.0009	.0040
1.5	.0288	7.3	0.43	.0092	.0196
2.0	.0427	21.9	1.29	.0210	.0217
2.5	.0523	41.0	2.30	.0281	.0242
3.0	.0586	63.0	3.40	.0343	.0243
3.5	.0602	89.7	4.70	.0404	.0198
4.0	.0603	118.0	6.03	.0454	.0149

Mols. SO_2/ Mol. CaO	Sp.Cond. in $ohms^{-1}$	Part. V.P. SO_2	%SO_2 at this p.p. Campbell	Cond.at this %SO_2	Diff.in Spec. Cond.
		Temperature 70°C.			
0.0	.0097	0.0	0.0	-	.0097
0.5	.0097	0.3	0.01	.0002	.0095
1.0	.0061	1.5	0.05	.0010	.0051
1.5	.0338	19.0	0.66	.0117	.0221
2.0	.0475	45.7	1.57	.0213	.0262
2.5	.0588	72.5	2.45	.0260	.0328
3.0	.0682	99.2	3.31	.0302	.0380
3.5	.0717	138.5	4.52	.0351	.0366
4.0	.0725	187.8	5.98	.0399	.0326
		Temperature 90°C.			
0.0	.0091	0.0	0.0	-	.0091
0.5	.0091	0.4	0.01	.0002	.0089
1.0	.0072	2.0	0.05	.0008	.0064
1.5	.0357	29.2	0.65	.0100	.0257
2.0	.0487	74.2	1.63	.0190	.0297
2.5	.0574	128.0	2.80	.0232	.0342
3.0	.0639	181.2	3.96	.0272	.0367
3.5	.0668	235.0	5.12	.0312	.0356

Consider the general form of the curves in Graphs 9 and 10. That portion of the curves in both Graphs up to the sulphur dioxide concentration of one mol. per mol. of calcium oxide needs no further elucidation. The amount subtracted from the conductivity as measured for the three-component system in this region is small since the partial pressures are practically nil. Consequently the shape of the curves in this region will be only very slightly modified by the subtraction, and will be almost identical with the curves of Graphs 5 and 7. This point, however, will be referred to later (page 127). In the region of sulphur dioxide concentrations greater than one mol. per mol. of calcium oxide all of the curves pass through a maximum. In some cases the curves pass below the zero value of conductivity, and it is evident from the shape of the curves that all of them would, if high enough sulphur dioxide concentrations could be attained.

The presence of the maximum indicates the existence of two opposing tendencies. An increase in the sulphur dioxide content will increase the bisulphite ion concentration which will tend to cause an increase in the conductivity. However, the equilibria which have been subtracted also have bisulphite ions in them and the bisulphite ions from this source will repress the equilibrium

$$CaSO_3 + H_2SO_3 \leftrightarrows \sim \leftrightarrows Ca(HSO_3)_2$$

(where $\sim$ represents the subtracted equilibria), and tend to cause a decrease in conductivity. At higher sulphur dioxide to calcium oxide ratios further addition of sulphur dioxide will cause the second effect to become increasingly predominant with the result that the conductivities are bound to become less. This retroactive effect of the bisulphite ions from the calcium bisulphite on the

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

equilibrium, which has not been taken into account in the subtraction and which will result in a subtraction of conductivity greater than is warranted, will eventually account for the curves actually passing on to values below the zero value of conductivity.

The results, when considered from the point of view of the effect of an increase in temperature, give excellent confirmation to the conclusion drawn by Campbell and O.Maass[14] that at higher temperatures the amount of sulphurous acid, and therefore of its resulting ions, is greatly decreased. With an increase in temperature the maxima rise continually and they also occur at higher sulphur dioxide concentrations. The bisulphite ion concentration in the subtracted equilibria becomes less with a rise in temperature and hence its effectiveness in repressing the bisulphite ion formed from the calcium bisulphite will be less at higher temperatures, and also at higher sulphur dioxide concentrations. It must be remembered, however, that Graphs 9 and 10 differ by nearly 100% in the total concentration of ions on the basis of the amount of water, and therefore in the more highly concentrated solutions, as given in Graph 10, the bisulphite ion concentration resulting from the calcium bisulphite can be expected to show less dissociation. The calcium bisulphite dissociation, if it really exists, can therefore be expected to be shown by an inflection in the isothermals of Graph 10, either revealed as a maximum or a discontinuity in these curves. Beyond the possibility of experimental error, all the isothermals of Graph 10 show inflections at the two to one ratio of sulphur dioxide to calcium oxide. The most important conclusion to be drawn from the above analysis is that the existence of a bisulphite ion, resulting from the presence of calcium bisulphite, has been established for the first time beyond any doubt.

It is possible to calculate the hydrogen ion concentration in the three-component system over the temperature and concentration range covered, with a fair degree of accuracy using the data for the three-component system together with that of Campbell and O.Maass[14]. Knowing the partial pressure of sulphur dioxide in the three-component system at a definite temperature, the concentration of sulphur dioxide in the liquid phase of the sulphur dioxide - water system at the same temperature and pressure may be determined from their data. The hydrogen ion concentration corresponding to this sulphur dioxide concentration is also given in their results. Values of the hydrogen ion concentration calculated in this way may be given for the three-component system provided the retroactive effect of bisulphite ion from the calcium bisulphite is small. This condition is realized when the mol.-ratio of sulphur dioxide to calcium oxide is high.

Reference has been made (page 124) to the difference between the curves of Graphs 9 and 10 and those of Graphs 5 and 7 in the region where the ratio of sulphur dioxide to calcium oxide is less than one to one. In the discussion of the equilibria in this thesis these differences are too small to be of much significance but they will be of great importance in the complete quantitative elucidation of the system. In the analogous two-component sulphur dioxide - water system the data of Morgan and O.Maass[15], obtained at low temperatures, made possible an exact quantitative elucidation of those of Campbell and O.Maass[14], obtained at high temperatures. The writer's research covered the range of temperature and pressure comparable to the latter. The apparatus required for the determination of the high pressures developed at these high temperatures did not permit the making of as accurate measurements at low temperatures as one designed especially for low temperature work. An investigation by another worker, A.D.Grieve, was started simultaneously with that of the writer to carry out work in this field, analogous to that of Morgan and O.Maass[15]. The completion of this work, now in progress, will make data available which will allow an exact quantitative elucidation of such parts of the system as the one mentioned above.

Practical Significance of Results

Some of the results obtained in the investigation of the three-component system will undoubtedly prove to be of considerable practical value to the pulp and paper making industry. While the measurements have been made on a system in which no wood was present, the results will be applicable to the commercial cook, allowance being made for changes in the concentration of the solution due to the presence of the wood.

One of the difficulties encountered in the industrial process is the "Liming-Up" of the digester. The term applies to the formation of a precipitate in the digester occurring when the temperature is raised during the cook. Saunderson[18] has shown that this precipitate forms on the surface of the wood, hindering the penetration of the cooking liquor into the wood. The writer's work has shown that this precipitate forms at temperatures much lower than has been commonly supposed. From the following table it may be seen that precipitation takes place at temperatures as low as 65°C.

Series and run	Approx. % CaO	Approx. total % SO_2	Mols.SO_2/ Mol. CaO	Pptn. Temp.
F - 4	1.0%	3.3%	2.98	95°C.
G - 5	2.0%	6.6%	2.99	65°C.

Moreover for a constant ratio of sulphur dioxide to calcium oxide the precipitation temperature decreases markedly with an increase in the lime concentration. Results of this nature are of great use to the industry inasmuch as they define the limits of precipitation in the digester.

The work of Campbell and O.Maass[14] on the vapour pressure of aqueous solutions of sulphur dioxide has proved of considerable value in the design of apparatus used in connection with sulphite cooking and acid making. In the investigation reported in this thesis the vapour pressures of solutions containing the third component have been determined. These solutions more nearly approach those found in the digester and the vapour pressure data are therefore more closely applicable.

The variations in conductivity, with temperature and concentration, of these solutions suggests the possible use of such measurements in the industrial process as a method of control. Such an application would require extensive investigation of the conductivities of the liquor during a cook. These variations are especially large in the region in which precipitation occurs (page 75). The conductivity drops suddenly as the precipitate forms and this may furnish a means of determining when precipitation actually begins to take place in the digester.

This thesis describes the equilibria existing in an ideal three-component system. These equilibria will be modified by the presence of wood, but the apparatus and technique developed, and the results obtained in this research will be applicable to the system complicated in this way. The completion of such an investigation will add considerably more to our knowledge of the changes which take place in the cooking process.

SUMMARY

The results, with particular reference to claims for original work and contributions to knowledge, are summarized below.

(1). Vapour pressures and conductivities of saturated solutions of calcium oxide in water have been measured over the range of temperature from 25°C. to 135°C. From these data the degree of ionization and the dissociation constants of these solutions have been calculated. This work has been done over a greater temperature range, and with more experimental precautions as to the purity of calcium oxide and the absence of gases other than water vapour above the solutions, than ever before. Previous data consist of vapour pressure measurements at a few scattered points.

(2). Vapour pressures and conductivities of the three-component system calcium oxide - sulphur dioxide - water over the temperature range from 25°C. to 130°C. have been measured at calcium oxide concentrations of approximately 1 and 2% and sulphur dioxide concentrations up to 5 mols. of sulphur dioxide per mol. of calcium oxide. This is the first time that such measurements have been made over any considerable range of temperatures and concentrations. Moreover, the investigation was original in that special precautions were taken to ensure the purity of the components, and the accurate determination of their concentrations.

(3). Information has been obtained for the first time regarding the equilibria which exist in this three-component system. While an exact quantitative treatment of the equilibria cannot yet be made, a general analysis of the data has proved that certain equilibria occur which were previously only assumed to exist. For instance this is true of the equilibria involved in the formation of calcium bisulphite.

(4). Determinations of the temperatures at which the formation of a precipitate in this three-component system takes place have been made for the first time by means of conductivity measurements. It has been suggested that this type of measurement might be used as a method of control in the sulphite cooking process.

(5). A technique has been developed for making accurate vapour pressure and conductivity measurements over a large range of temperatures on a three-component system in which one of the components is a solid, the second a gas, and the third is a liquid (at room temperature). The apparatus and technique were developed in this research and were used for the study of the calcium oxide - sulphur dioxide - water system. Both can, however, be used in the study of any similar three-component system.

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