THE SYSTEM CALCIUM OXIDE-SULPHUR DIOXIDE - WATER

STUDIES IN THE SYSTEM
CALCIUM OXIDE - SULPHUR DIOXIDE - WATER.

Thesis

Submitted to the Faculty of Graduate Studies
and
Research of McGill University
in Partial Fulfilment of the Requirements
for the Degree of
Doctor of Philosophy.

by

PAUL ERNEST GISHLER M.Sc.

McGill University.　　April, 1935.

The writer wishes to express to

Dr. O. Maass

his sincere gratitude for advice and direction received during the course of this investigation.

Acknowledgement is made to the National Research Council of Canada for a Bursary and a Studentship, the tenure of which has made this work possible.

TABLE OF CONTENTS

2. Introduction

3. Experimental

4. Results

5. Discussion of Results

NATURE OF THE PROBLEM.

The work to be described in this thesis is a continuation of a general investigation of the system sulphur dioxide-calcium oxide-water, which was started in this laboratory several years ago. Up to that time there was little available data on equilibria existing in aqueous solutions of sulphurous acid and its calcium salts, and much information was lacking in accuracy as well as in scope.

A completed study of the equilibria existing between sulphur dioxide and water carried out by Campbell and Maass (1) formed the starting point of the work to be described below. Specifically this deals with the influence of calcium oxide addition on these equilibria. It is known that calcium sulphite exists, and it has been assumed that calcium bisulphite forms under certain conditions of temperature and concentration, but nothing quantitative is known in regard to the conditions governing their relative concentrations.

The temperature range, and range of concentration of sulphur dioxide and calcium oxide to be covered in order to permit complete elucidation of the equilibria is so large that several investigators were needed to complete it. Initial measurements at 1 and 2 per cent calcium oxide concentration have already been made by Gurd (2) in this laboratory. The writer has investigated the systems containing 1.2 and 2.3 per cent calcium oxide. In both investigations the temperature range of 25 to 130°C. and sulphur dioxide concentrations of 0-7 per cent were covered. As a result, vapour pressures and conductivities of the system are fully known for the first time.

Apart from this, two other interesting and closely related problems were investigated. One was a study of the solubility of varying concentrations of the salts formed, and a study of the influence of temperature and supersaturation on this. The other was a study of the influence of the presence of wood and cellulose on the vapour pressure of the system calcium oxide, sulphur dioxide and water.

The results of each of these problems can best be treated under a separate section, but the experimental technique can, to some extent, be treated as a whole. Before doing this, however, a more detailed account will be given of the previous work and the scope and purpose of each of the investigations.

NOTE:-

A fourth investigation was completed. It is, however, not at all connected with the above work, but will be included in this thesis in order to give a complete record of the work done while a member of the Graduate School of McGill. A description of this, "The development of a new means of measuring pulp consistency", is presented in the form of an appendix.

INTRODUCTION.

Before it was possible to study the system calcium oxide-sulphur dioxide-water, it was necessary to know the properties of each of the components, and also to study the two systems: sulphur dioxide-water and calcium oxide-water. A brief review of what is known of the equilibria of interest will be given below.

a. System Sulphur Dioxide-Water.

The first system to be studied in this laboratory was that of sulphur dioxide-water, which may be expressed as:

$$[SO_2] \text{ (soln)} = h \, [SO_2] \text{ (gas)} = hp \quad (1)$$

Where h is Henry's constant, and p is the partial pressure of sulphur dioxide. Maass and Maass (3) measured vapour pressures and conductivities of aqueous solutions of sulphur dioxide at temperatures below 27° C. Campbell and Maass (1) measured densities, conductivities and vapour pressures of sulphur dioxide solutions within the temperature range, 23° - 110° C. Morgan and Maass (4) have made very careful measurements of conductivities and vapour pressures of sulphur dioxide solutions within the temperature range 0° - 25° C., and to pressures of approximately one atmosphere.

Mention will be made of a few who investigated this system, but whose data have been superceded by the above on account of greater accuracy. Hudson (5) determined the solubility of sulphur dioxide in water at approximately atmospheric pressures, and at temperatures up to 90° C. Linder (6) made vapour pressure determinations at 25° and 50° C. with a concentration range of 0.05-3.8% sulphur dioxide.

Equation (1) gives the equilibrium existing between gaseous sulphur dioxide and sulphur dioxide in solution in the water. Part of the sulphur dioxide in solution forms H_2SO_3 according to the equation:

$$[H_2O] + [SO_2] \leftrightarrows [H_2SO_3] \qquad (2)$$

applying the mass law

$$[H_2O]\,[SO_2] = K_1 [H_2SO_3] \; (3)$$

The H_2SO_3 in solution is in equilibrium with its ions

$$H^+ + HSO_3^- \leftrightarrows H_2SO_3 \qquad (4)$$

and, assuming that the Ostwald dilution law holds

$$[H^+]\;[HSO_3^-] = K_2\;[H_2SO_3] \; (5)$$

Further ionization

$$H^+ + HSO_3^- \leftrightarrows 2H^+ + SO_3^= \quad (6)$$

may be considered to be negligible. These three equilibrium constants have been determined by Maass and Maass (3). It was found that K_1 increased rapidly with increase in temperature and, therefore, that the amount of dissolved SO_2 in the form of H_2SO_3 diminished rapidly with increase in temperature. The value for K_2 was found to be approximately 0.02 and it was found that changes in temperature did not vary this value appreciably.

Campbell and Maass (1) working in higher temperature and pressure ranges also determined these constants. Both Maass (C) and Campbell worked within a narrow concentration range, and this increased the difficulty of arriving at true equilibrium values. Morgan and Maass (4) working in the temperature range 0-25°C. and, using concentrations up to 14% sulphur dioxide, were able to arrive at more accurate values.

The most important inference drawn from the results of these workers was that on account of the decrease in the formation of sulphurous acid, with rise in temperature as indicated by equation (2), the hydrogen ion concentration markedly decreased with rise in temperature. Estimates of the hydrogen ion concentration for varying concentrations and temperatures were made by Campbell and Maass (1).

b. Calcium Oxide-Water.

Although the system calcium oxide-water has been studied by a number of workers, a large part of the data furnished is of little value. This is due to the fact that it is difficult to avoid impurities in the system, especially carbon dioxide. The lack of agreement among various workers is an indication of the unreliability of the published results. Ostwald (7) measured the conductivity of calcium hydroxide solutions. He casts doubt on the accuracy of his results by stating that carbon dioxide was probably present. Measurements have also been made by Maben (8), Lamy (9), Hertzfeldt

(10), Guthrie (11), Moody (12), Haslam, Calingaert and Taylor (13), and Miller and Witt (14). It was found that above 30° C. the results of the above workers agreed much better than below that temperature. Grieve (15) working in this laboratory made conductivity measurements of the system calcium oxide-water within the temperature range 0 to 25° C. Probably the best determinations of solubility of calcium oxide up to 30° C. were made by Larocque (16), using a conductivity method.

c. Calcium Oxide-Sulphur Dioxide-Water.

Little accurate data are available regarding the system calcium oxide-sulphur dioxide-water. This is probably due to the fact that those who have investigated this field have been more interested in the industrial application of their results than in the possible theoretical value of the work, and, therefore, have not taken the extreme care necessary to obtain accurate results. Schwartz and Müller-Clemm (17) have studied the ratio of the free to combined sulphur-dioxide in solutions ranging from 3 to 10 per cent concentration and within the temperature range 2°- 35° C. Smith and Parkhurst (18) measured the solubility of sulphur dioxide in solutions of calcium hydroxide. Farnell (19) has measured the pH of certain solutions of calcium sulphite and bisulphite. A recent investigation of some equilibrium relations in the system calcium oxide-sulphur dioxide-water in the acid region, and at pressures below atmospheric has been made by Conrad and Beuschlein (20).

A comprehensive study of the system calcium oxide-sulphur dioxide-water was undertaken in this laboratory by Gurd (2) and by Grieve (15). Grieve confined his investigation to a temperature range below 25° C. Gurd worked between the temperatures of 25° and 130° C., and at concentrations of approximately 1% and 2% calcium oxide. For each of these calcium oxide concentrations, the sulphur dioxide concentration was varied from approximately 0.5 to 7%. Conductivities and vapour pressures were determined. Gurd took every precaution to insure against the possibility of impurities entering into the system, and used methods of introducing the reagents into the reaction cell, which permitted a high degree of accuracy in the measurement of their concentrations.

The data of Campbell and Maass (1) may be considered as part of the three component system, in which the concentration of calcium oxide is zero. Vapour pressures and conductivities were, therefore, known at the start of the writer's investigation at 0, 1 and 2 per cent calcium oxide concentrations. There were two reasons why further measurements were necessary. In the first place, it was important to check the accuracy of the data obtained by Gurd by an independent investigation. In the second place, it was not known whether interpolation and extrapolation were justified on the basis of such few calcium oxide concentrations. Hence, for economy of effort, two calcium oxide concentrations at

1.2 and 2.3 per cent were chosen close enough to the previous concentrations, to act both as a check on the former work, and at the same time helping to fill in existing gaps. A 1.2 per cent calcium oxide concentration is of particular interest, as it is the concentration of lime most generally used in the sulphite cooking of wood.

d. Solubility Experiments.

For each concentration of calcium oxide and sulphur dioxide, there is a temperature at which a precipitate is formed. This precipitation is phenomenal in as much as apparently a copeous precipitation takes place, and also because there is an unusual tendency towards "supersaturation". The nature of the precipitate has been determined by Saunderson (21) and found to be calcium sulphite.

No exact measurements of these precipitation temperatures have previously been made. The nature of the precipitation is similar to that which occurs in the system $Na_2SO_4 \cdot 10H_2O$ at 33°C. (22), and $CaSO_4 \cdot 2H_2O$ at 63.5°C. (23) only that it is more complicated by the fact that it is a three component system, and the sulphur dioxide, as well as the calcium oxide concentration, determine the precipitation temperature.

Three concentrations of calcium oxide were studied; namely, 0.6, 1.2, and 2 per cent. For each of these calcium oxide concentrations the influence of six different sulphur dioxide concentrations was investigated.

e. Influence of Cellulose and Wood on the System Calcium Oxide-Sulphur Dioxide-Water.

The above heading might almost be called the mechanism of the sulphite cooking of wood. The data to be determined, as mentioned above, are of great importance in this connection. In the first place, the pressure of the system at the start would then be accurately known for the first time, in terms of the composition of any sulphite liquor. The temperature at which that bugbear in sulphite cooking, known as the liming up of the digester, can take place, could then also be predetermined by the composition of the sulphite liquor.

The object of this section of the investigation was to go beyond this, namely, to see whether the changes that take place during the actual cooking could be followed by vapour pressure changes. This is obviously an extensive investigation, and it was realized in the time available that only a start could be made. All that could be hoped for was to show that the technique developed could be used as a weapon for elucidating what actually goes on during a "Sulphite Cooking" operation.

With this in mind, a review will first of all be given of some of the ideas which have been advanced in this connection. While accurate information regarding the system sulphur dioxide-calcium oxide-water was practically non-existant, the literature regarding "sulphite cooking" of wood is so extensive that only a small part of this can be selected for presentation here.

Wood has a cell structure. Each cell is surrounded by a resinous material. The interior of each cell consists of bundles of cellulose fibres cemented together by a material called lignin. Before the cellulose fibres can be used for paper making, it is necessary to free them of this binding material. One procedure is to heat with what is known in mill practice as sulphite liquor. This consists of aqueous solutions containing varying amounts of calcium oxide and sulphur dioxide. The concentrations used vary from mill to mill, but usually 1.2 per cent calcium oxide and 5 per cent total sulphur dioxide are used. Before the effect of sulphite liquor on wood can be studied, it is necessary to know something of the properties of lignin.

H. Wislicenus (24) has defined lignin as the sum of all the high molecular dissolved colloids which have been precipitated from the cambial sap by adsorption on the surface of the cellulose fibre. He believed that pentosans, which can produce high molecular gels, were the main contributing factors in the formation of lignin. Kurschner (25) believed coniferin to be the main source of lignin. This he thought was polymerized during the life of the plant. Jonas (26) agreed in part with the theory of Wislicenus.

Pauly (27) made a study of the action of acids on wood, and found that a fairly strong mineral acid was required to remove the lignin, as it appeared firmly attached to the fibres. He found that it was possible to dissolve away the incrustations in wood with a 5% sulphurous acid solution at 90°C., but that a bisulphite solution was more efficient.

In mill practice wood chips about ½" long are used. Before the sulphite liquor can react with the wood, it must be able to penetrate to the interior of the chip. Before the reaction can be studied, it is necessary to know the rate of penetration. That is, whether sulphurous acid or dissolved calcium bisulphite penetrate faster, and to know the effect of an excess or deficiency of either.

Considerable work has been done in this laboratory by Saunderson, Johnston, and Maass (28), and also by Montigny and Maass (29). Saunderson has found that the penetration of free sulphur dioxide into the wood takes place more rapidly than that of calcium bisulphite. In the absence of the base, it was found that above 110° C. it will cause lignin to polymerize to a brown insoluble substance which deposits out on the cellulose fibres. For a time, the wood is exposed to an excess of acid solution causing it to turn brown. This is called "Burning". Burning may also take place at the end of a cook. It was claimed by Montigny and Maass (29) that this was due to a depletion of base.

Several investigations have been made on the amount of free sulphur dioxide used up during a cook. Mitcherlick and Frank (30) found that 75% of the sulphurous acid present at the beginning of a cook is used up in reducing the lignin, whereas, only 23% of the lime disappears. The evidence of Hägglund and Carrick (31), however, is quite contradictory. They claimed that there were three sources of sulphur:

(1) H_2SO_4 which is formed from H_2SO_3 in the presence of air in the digestors; (2) loosely bound sulphur in the form of sulphurous acid and (3) firmly bound sulphur as $CaSO_3$. This third form of sulphur really does not exist during cooking, as calcium is actually present as calcium ~~bi~~sulphite, but it is merely a convenient way of expressing and estimating the amount of calcium salt. They found that the concentration of sulphurous acid depends on the concentration of sulphur dioxide. This in turn is dependent on the pressure and temperature at which the cook is being carried on. It was found that 20-30 per cent of the sulphur consumed during cooking was supplied by the sulphurous acid and 50-60 per cent by the calcium salt. The percentage of firmly bound sulphur used was found independent of the amount of free sulphur present, and dependent on the amount of base, up to a limiting concentration.

Miller and Swanson (32), who have done a vast amount of work of a technical nature, stated that the amount of lignin removed depended on the amount of ionized sulphurous acid present, which in turn was governed by the presence of any other acid. This was contradicted by Campbell and Maass (1), who have found that at cooking temperature, the extent of ionization of sulphurous acid was negligible.

The effect of the presence of calcium oxide has been carefully studied, and especially the rate at which it is used up during the cooking reaction. Montigny and

Maass (29) have found that below a definite minimum, which was found to be 0.5 per cent, satisfactory cooking, could not take place. Above this concentration, apparently the amount of calcium oxide present did not appreciably effect the yield of pulp. Hagglund (33) has modified the above finding by stating that there was a definite, though small, increase of cellulose yield, with increased concentration of calcium oxide, even up to and above 1 per cent. Similar results were obtained by Nepenin and Sapraigina (34).

Eliashberg and Martuinov (35) have made a thorough study of the changes in the calcium oxide concentration of the cellulose, and of the lignin and liquor during cooking by means of ash determinations. They found that the ash content of the cellulose rose at the beginning of a cook, then remained constant until near the end, when it fell off. Corresponding to this, the calcium oxide in the liquor declined at the start of a cook and then increased near the end. They examined the undissolved residue, and found that the sulphur and lime content increased near the start of a cook, then remained constant, and eventually fell near the end. The per cent lignin in the wood did not change till a temperature of 130° C. was reached, when it rapidly decreased. During cooking the sulphur content in the undissolved residue was found to increase continuously in relation to the lignin content. These results are of especial interest and will be referred to later in a discussion on the work described in this thesis.

During cooking a certain amount of sulphuric acid is formed, and the reasons given for this formation vary as widely as do the estimations of the amounts formed. Klasen (36) claimed that sulphur dioxide decomposed, to some extent, and sulphur and sulphuric acid resulted. The mechanism of the reaction may be represented as:-

$$4SO_2 \rightarrow S_2O_3 + S_2O_5 \quad \text{(di-thionic acid)}$$
$$2S_2O_3 \rightarrow S_2O_2 + 2SO_2$$
$$S_2O_5 \rightarrow SO_3 + SO_2$$
$$S_2O_2 \rightarrow S + SO_2$$

Hagglund (31) claimed that the sulphuric acid was due to the presence of air in the digester. Miller and Swanson (32) have made determinations of the amount of sulphuric acid formed during cooking and found that the percentage was very small - amounting, usually, to less than 0.1% of the sulphur present and never exceeding .3%, even after 15 hours cooking. Hagglund and Carrick (31), on the other hand, claimed that 20% of the sulphur went to form sulphuric acid.

Evidence has been brought forth to show that lignin is not the only substance in wood that is attacked by sulphite liquor. Hagglund (37) has found that the formation of sugar parallels the accumulation of sulphuric acid.

Eliashberg & Martuinov (35) have found that sugars were formed during the first part of the cook from hemicelluloses. Resins and fats were reduced by 60% during cooking. Kurschner (25) has made a list of compounds formed during cooking. They included calcium salts of lignosulphonic acid, sugars, formic acid, acetic acid, methyl alcohol, ethyl alcohol, acetone, acetaldehyde, furfural, cymal, resins, nitrogen compounds, carbon dioxide, and a number of others. It is of interest to note that the lignin sulphonic acid molecule seems to be much smaller than the original lignin molecule.

The above pages indicate that the delignification of wood involves an unknown number of complicated reactions. Several attempts have been made to describe the general trend of the reaction. Penetration of the wood by the liquor has already been described.

Klasen (36) assumed the lignin molecule to contain three ethylene bonds, two of which united with two sulphurous acid molecules to form the stable lignin sulphonic acid, as $\overset{\cdot}{\underset{\cdot}{C}}:\overset{\cdot}{\underset{\cdot}{C}}-\overset{\cdot}{\underset{\cdot}{C}}H \cdot CSO_3H$. The third bond held a sulphurous acid molecule much less firmly, while a fourth bond, believed to be in a carbonyl group, bound the molecule so weakly that it could break up even at room temperature.

Michel and Jaffard (38) suggested that the lignin of the wood first formed a solid compound with the sulphur dioxide of the cooking liquor. This compound then passed into solution by some process, which was mainly hydrolytic, and in which the base in the liquor played a part. The relative rates of these reactions are not known.

According to Hagglund (37) the reaction takes place in three steps:-

(a) A sulphite addition to the lignin carbohydrate compound in the solid phase.

(b). Hydrolysis of the lignin sulphonic carbohydrate in the solid phase.

(c). Hydrolysis of the liberated carbohydrate. Kunschner (25) did not agree with the idea that direct sulphonation completely accounted for the decomposition of the solid lignin. He believed that it is not only sulphurous acid, but also the products formed by the simultaneously resulting decompesition of the cellulose, etc., which functioned jointly in making the lignin soluble in the cooking liquor. This was based on the fact that cellulose, when placed with lignin in sulphite liquor, aids the lignin to go into solution. He added: "Without a doubt, a number of reactions take place jointly and successively with osmotic reactions playing a part". There is evidence to support the above explanation, for, during cooking, not only lignin compounds are brought into solution, but pentosans and hexosans are partly decomposed. During the average cook, about 13% of the original cellulose is lost. A given number of products are formed, which, under favorable pressure and temperature conditions, react with one another in many different ways. Kunschner was forced to come to the conclusion that very little was known even about the main reactions taking place.

The above review indicates the importance of having a clear understanding of the equilibria existing in sulphite liquor, in order to be in a position to theorize regarding the delignification of wood by sulphite liquor. It is apparent, from what was outlined above, that in most of the speculations there was no background of information on the system: calcium oxide-sulphur dioxide-water. In this sense, the above review may be looked upon as giving additional emphasis to the importance of this work from a practical point of view. Apart from this, the review serves as a special introduction to Part III of this thesis.

Part III is a study of the influence of cellulose and wood on the system; calcium oxide-sulphur dioxide-water. A reaction temperature of 130° C. was chosen as most suitable, and changes in equilibria were followed by means of vapour pressure determinations. It was necessary that as little chemical action as possible take place before this temperature was reached. This required rapid heating of the liquor and wood to 130° C. Wood meal was used rather than chips, as it permitted rapid heating without burning.

EXPERIMENTAL SECTION.

GENERAL.

The first three problems to be investigated were closely related, and, therefore, to some extent the same apparatus could be used for all. For instance, sulphur dioxide was purified and measured by the same method in the three investigations. One description of this part of the apparatus and procedure should, therefore, suffice. On the other hand, the method of making "runs" was quite different in each case, and will therefore have to be dealt with separately.

The following method was adopted as the most convenient means of describing the experimental work. A detailed description will first be given in Part I of the apparatus and prodedure used in the determination of the vapour pressures and conductivities.of the system calcium oxide-sulphur dioxide-water. In it will be described how each of the components was purified and accurately measured. The procedure used in making the vapour pressure and conductivity measurements will be described in detail.

Part II is an investigation of the precipitation temperatures of varying concentrations of the above systems. The apparatus and procedure were both less complicated as neither vapour pressure nor conductivity measurements were made. The procedure involved the filling of bombs with the desired solutions and determining at what temperature precipitation occurred.

In the cooking experiments (part III), it was necessary to use an apparatus capable of measuring vapour pressures. The technique of filling the reaction cell with the four substances, wood, sulphur dioxide, calcium oxide, and water, was quite involved as all impurities had to be excluded.

PART I.

Vapour Pressure and Conductivity of the System Calcium Oxide - Sulphur Dioxide - Water.

Description of Apparatus.

The apparatus may be conveniently divided into three sections: (1) Gas supply and purification system, (2) Gas measuring and introduction system, (3) Reaction cell with attached manometer system.

Gas was supplied from a high pressure cylinder. It had to be dried and then purified by redistilling several times, with rejection in each case of the top and bottom fraction. Carbon dioxide was used as a condensing medium. The sulphur dioxide was measured in two bulbs of carefully determined volume. These were attached to a two-armed manometer, one arm of which could be evacuated. The pressure was carefully determined before and after introducing the gas into the cell and the amount of gas introduced was determined by difference. The gas was introduced into the cell by first condensing it from the measuring bulbs into a tiny bulb which was connected to the cell through a mercury seal. The temperature of the cell was regulated by means of a bath containing the necessary heaters and stirrer. The manometer was of the closed end type with a special arrangement whereby pressures up to 100 pounds per square inch could be obtained.

Pure calcium oxide was obtained by heating choice crystals of Iceland Spar in a current of air. A special method for degasing the water without loss of water vapour was employed. A detailed description follows:

I. Detailed description of apparatus.
    (a) Gas purification system.
    (b) Gas measuring and introduction system.
    (c) The reaction cell.
    (d) The manometer system.
    (e) The heating bath.
II. Conductivity measurements.
III. Preparation of pure calcium oxide.
IV. Procedure for the preparation of solutions.
V. Procedure in making a"run".
VI. The calculation of results.

I. Detailed Description of Apparatus.

(a) Gas purification system.

A detailed diagram of the entire apparatus can be seen in Plate A. ~~This-will-be-referred-to-frequently.~~ This will be referred to frequently. This system was made of soft glass, a seal being made to the high pressure sulphur dioxide cylinder by means of DeKhotinsky cement. The apparatus was evacuated and then flushed several times with sulphur dioxide to remove the last traces of air. Bulb B_1 was then surrounded with a freezing mixture of carbon dioxide in acetone. The needle valve on the cylinder was opened and sulphur dioxide was slowly bled into B_1 where it condensed. The bulb was allowed to warm up and the lighter fraction was allowed to evaporate through the exhaust. The middle fraction was allowed to evaporate into B_2 where it was condensed. This was then redistilled into B_3 with rejection of the light and heavy fractions. A similar redistillation into B_4 yielded pure sulphur dioxide. B_4 acted as the storage bulb.

(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 and S_3 and a fixed level of 2 cm. on the right hand side of the manometer M. The left hand side was completely evacuated and S_2 closed. The mercury was raised or lowered in the two arms of the manometer by applying air or vacuum above the mercury in the mercury well. In all measurements the level of mercury in the right hand arm was adjusted to 2 cm. The difference of the two levels was read off on a calibrated glass scale, and the necessary glass scale temperature corrections were applied.

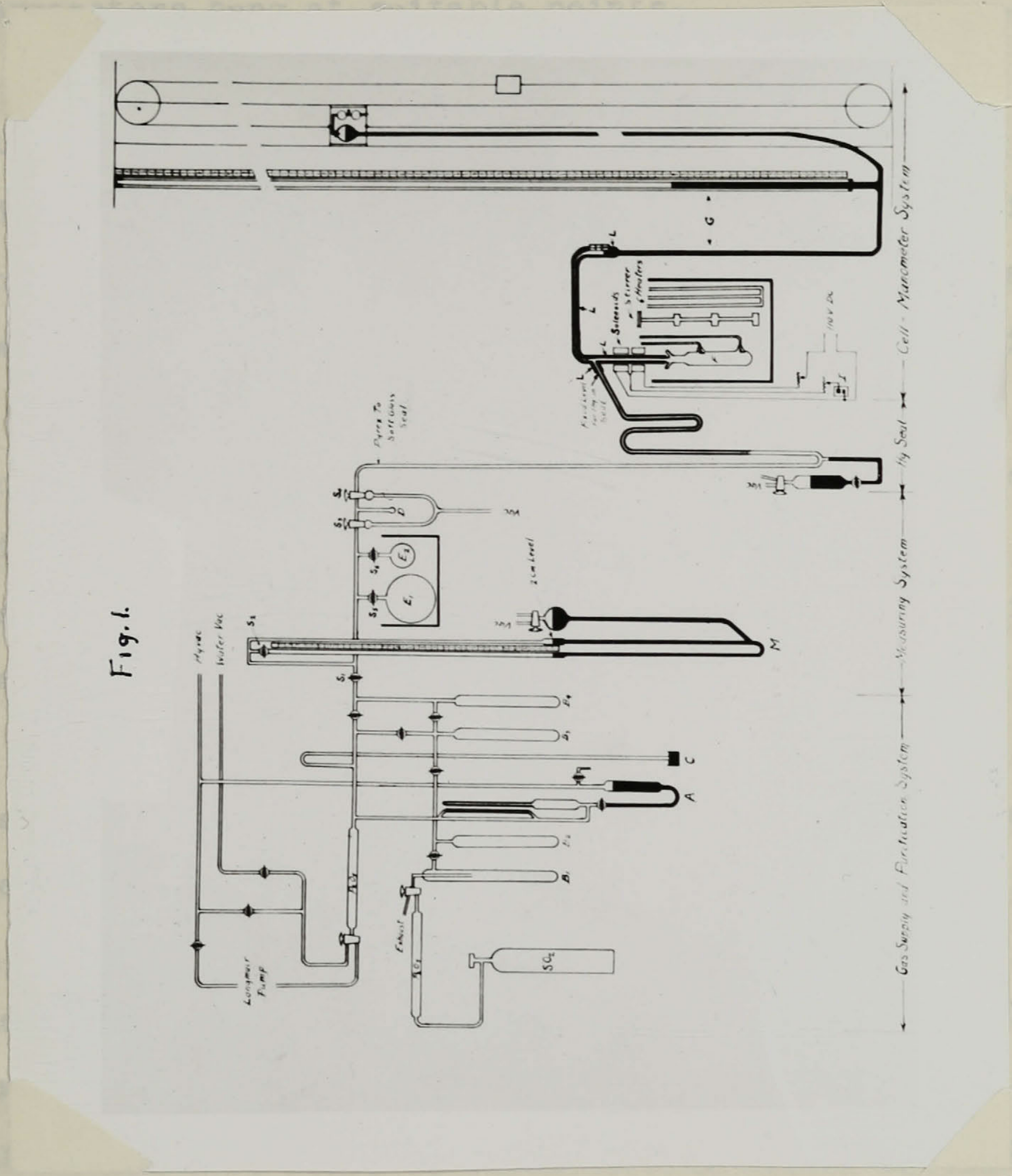

Gas Supply and Purification System
Measuring System
Hg Seal
Cell - Manometer System
Longmuir Pump
Hyvac
Water Vac
Exhaust
SO_2
P_2O_5
B_1
B_2
B_3
B_4
A
C
S_1
S_2
S_3
S_4
S_5
S_6
E_1
E_2
D
M
2 cm Level
Pyrex To Soft Glass Seal
Kovar Level
Solenoids
Stirrer
Heaters
110 V DC
L
G

Fig. 1.

The temperature of the two bulbs E_1 and E_2 was kept equal by immersing both in the same water bath. The temperature of the connecting tubing was determined by means of two thermometers hung at suitable points.

The volumes of the two bulbs E_1 and E_2 were carefully determined by weighing full of water, and again empty and applying the necessary corrections. The volume of the connecting tubing was determined by the use of the gas laws. The two bulbs and the connecting tubing were filled to a certain pressure with dry air. Temperatures and pressures were carefully observed. S_5 and S_6 were then closed off and the connecting tubing evacuated. The air was allowed to expand from the bulbs into the connecting tubing and the pressure observed.

Let p_1 be the pressure at the beginning and v_1 the combined volume of E_1 and E_2. Let p_2 be the final pressure.

$$\text{Then,}\quad P_1V_1=P_2(V_1+X)$$

where X is the volume of the connecting tubing. If the temperature changed during the measurement, the necessary correction had to be made. The accuracy of the measuring system was checked by condensing a determined volume in a bulb and weighing.

Volume	E_1	587.82 cc.
	E_2	126.80 cc.
	X	75.96 cc.

The procedure followed in measuring out the desired amount of sulphur dioxide and introducing it into the cell was as follows. After the measuring system was thoroughly evacuated, pure SO_2 was allowed to evaporate from the bulb B_4 until the desired pressure had been built up. The system was given a few minutes to reach temperature equilibrium, the mercury was adjusted to 2 cm. in the right hand arm of the manometer and the pressure and temperatures read. A freezing mixture was then placed around D and the desired amount of SO_2 allowed to condense into that tiny bulb. S_3 was then closed and S_4 opened and the gas allowed to pass into the reaction cell through the capillary tubing which later went to form the mercury seal. After the gas had expanded into the cell, mercury was run into the seal and it was frozen with a carbon dioxide-acetone mixture. The amount of gas left in the apparatus between S_4 and the mercury seal was then condensed back into the bulb D from whence it was allowed to expand into the measuring system. The small amount remaining beyond S_4 could be calculated. The gas laws were used in calculating the amount of SO_2 introduced into the cell. A graduated soft to hard glass seal connected the soft glass of the measuring system to the hard glass of the cell manometer system. Some auxiliary apparatus necessary for the proper functioning of the system as a whole needs mentioning. To insure proper purification and accurate measurement of the gas, two things were necessary, namely, an efficient evacuation system and a pressure gauge suitable for measuring low pressures. Figure I illustrates the arrangement of the apparatus. A water pump was used to evacuate down to about 2 cm. pressure. For low pressures, the apparatus to be evacuated was connected to a Langmuir pump backed by a Cenco Hyvac. The McLeod gauge (A) was used to test the efficiency of the evacuating system, and to test for slow leaks.

(c) The Reaction Cell.

The reaction cell is shown in detail in Fig. 2. It was made of one inch pyrex tubing with a quarter inch stem into which the stirrer stem fitted. Two side arms (A) and (B) were sealed into the top of the cell and served for the introduction of water and calcium oxide respectively. Stirring was effected by means of an all glass magnetic stirrer with an iron core sealed into the stem of the stirrer. A double solenoid was placed over the tubing and fixed firmly in a position suitable for effective stirring. The lower half of the solenoid was so wired that a constant current was delivered to it. This solenoid served to hold the bottom of the stirrer about a quarter of an inch above the bottom of the cell. The upper solenoid was connected to a make and break device which was simply an arm attached to the rim of a wheel driven by a motor. The speed of the stirrer could be governed by varying the rate of the motor, and the amplitude of the stroke was adjusted by adjusting the current through the top solenoid. The solenoid was kept from over heating by means of a water cooled copper coil.

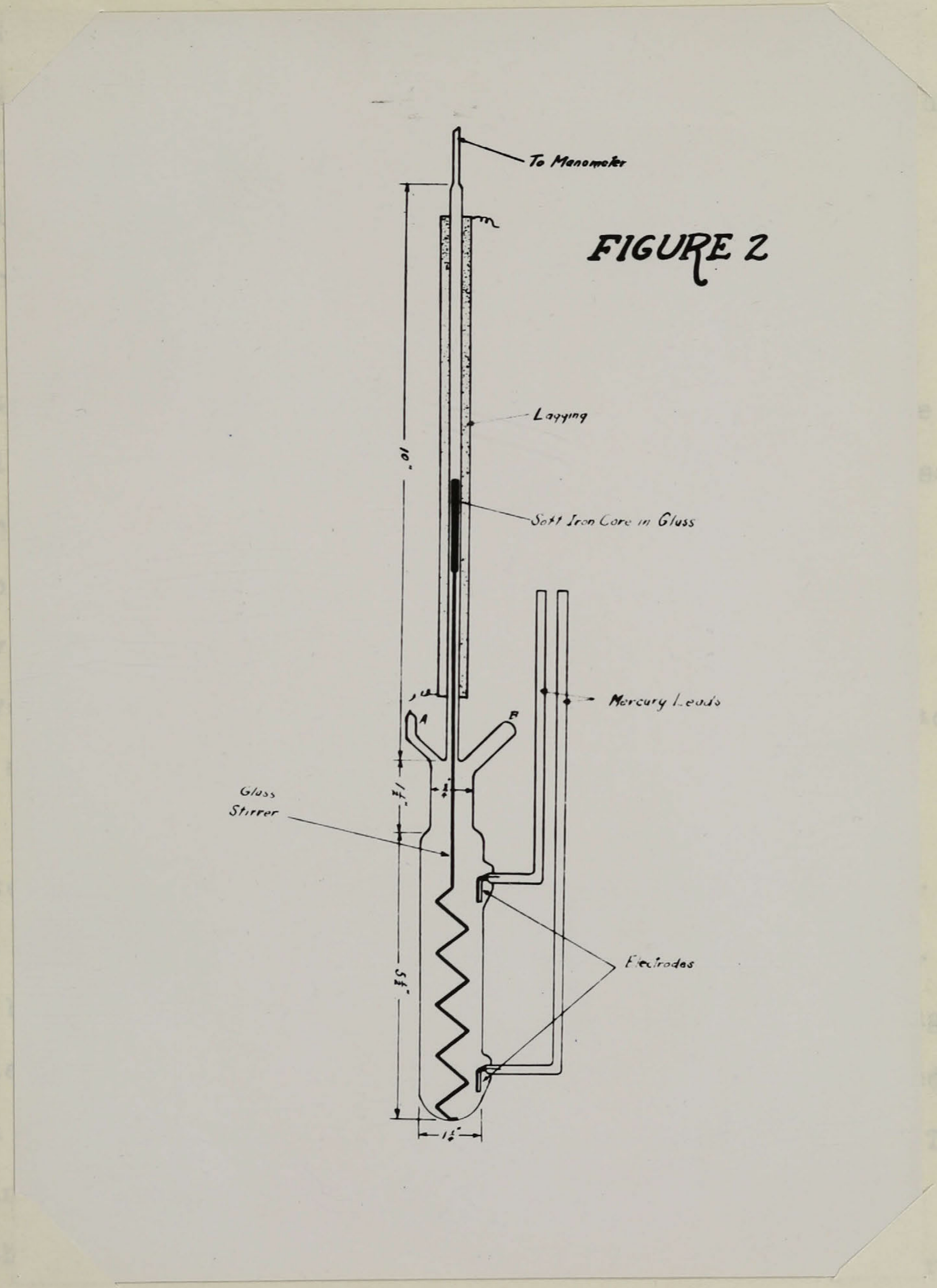


FIGURE 2

To Manometer
Lagging
10"
Soft Iron Core in Glass
Mercury Leads
A
B
1¼"
¼"
Glass Stirrer
Electrodes
5½"
1½"

The stirring was so adjusted that the stirrer barely "clicked" the bottom of the cell on the down stroke. Stirring was quite vigorous. To prevent condensation in the stem above the cell, a heating coil was wound around this part and covered with asbestos lagging. The stem was kept about 20 C. above the temperature of the cell. This temperature was determined by thermometers placed at suitable points.

Conductivity measurements were made by means of two platinum electrodes, sealed into the side of the cell according to the method of Housekeeper (39). These electrodes were placed in a vertical position in order to prevent calcium sulphite from depositing on them. They were sealed into bay windows which kept them a convenient distance from the stirrer. Electrical contact was made by means of a column of mercury.

The cell was connected to the gas measuring system by means of a capillary tube bent in the form of a U. Mercury could be forced into this from a stationary bulb. In order to seal the cell from the measuring system, mercury was run into the U and it was surrounded with a freezing mixture of carbon dioxide in acetone. The advantage of this was that succeeding concentrations of sulphur dioxide could be introduced into the cell without changing the water and CaO used in preceding runs.

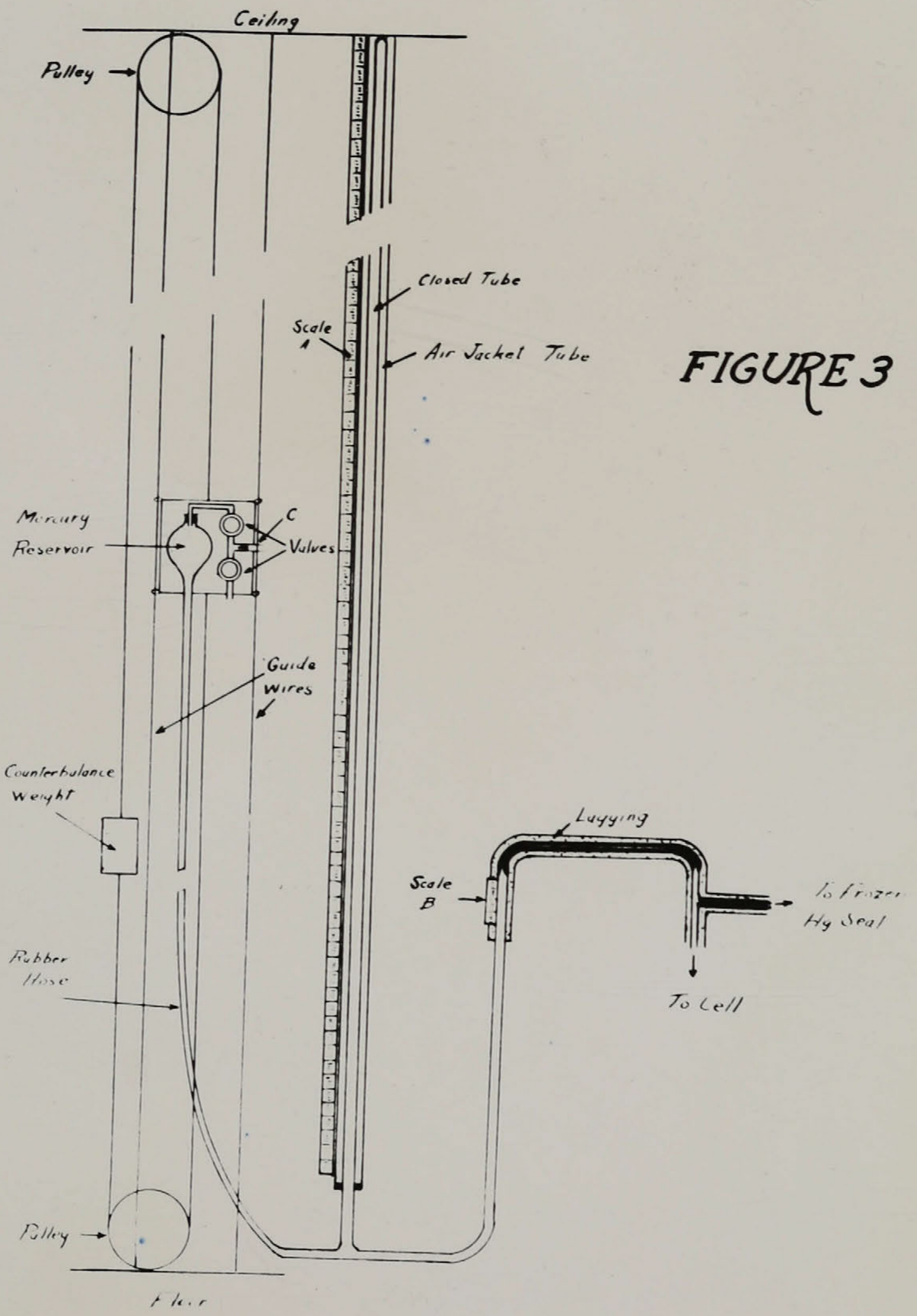

Ceiling
Pulley
Closed Tube
Scale A
Air Jacket Tube
Mercury Reservoir
C
Valves
Guide Wires
Counterbalance Weight
Lagging
Scale B
To Frozen Hg Seal
To Cell
Rubber Hose
Pulley
Floor

FIGURE 3

(d). The Manometer System.

For this work, a manometer capable of measuring up to at least 7 atmospheres pressure was necessary. The manometer used in this work was the one built and calibrated by Gurd. (Please see Fig. 3).

The manometer was connected to the cell by means of a capillary tube which was sealed onto the 1 cm. pyrex tubing of the manometer. Just below this seal, was a glass scale (B) about 6 cm. long. During an experiment, this length of tubing was wound with resistance wire which was well lagged. The purpose of this was to keep all the connecting tubing above the temperature of the cell, thus preventing condensation of liquid from the cell. Two thermometers, one placed in the lagging behind scale B, and a second near the "T" opposite B gave its temperature.

During an experiment, the mercury level was kept at zero on scale B, therefore, making the cell reaction system one of constant volume.

The closed end manometer tubing extending from the floor to the ceiling was connected to a high pressure rubber tube. This was attached to a one litre bulb which served as the mercury reservoir which was fastened to a board. The board could be raised and lowered by means of a pulley device. Thus, as the pressure increased or decreased, the height of the bulb could be altered in order to keep the mercury level at zero on scale B. However, a mercury column, nine feet high, did not give sufficient pressure for the experiments to be carried out. Extra pressure was obtained by pumping air above the mercury in the reservoir.

The necessary valve arrangement is shown in Figure 3. A copper tube was passed through a rubber stopper which was firmly held in the mercury reservoir. Two needle valves were attached, in series, to the other end of the tubing. A bicycle valve stem was soldered between the two needle valves. Excess pressure was obtained by pumping air into the reservoir with a small bicycle pump. The double valve system served to release pressure uniformly during the cooling of the cell.

As the manometer was of the closed end variety, it was necessary to know the volume of the tubing accurately. A wood scale was firmly attached behind the manometer tube. This scale was carefully calibrated. The volume of the tube was determined by weighing in mercury and noting the height to which the mercury rose. In order to prevent sudden temperature changes, a larger glass tube 2.5 cm. in diameter was placed around the manometer tube. Three calibrated thermometers were placed against this tube. One near the top, one at the centre, and one at the base of the tube.

Clean dry mercury was used. Before experiments were made, the constant of the manometer had to be determined. In order to calculate this, the capillary tubing leading to the cell was left open to the air. The mercury was raised to zero on scale B. This was found to correspond to 291.92 cm. on the large scale. The level of mercury in the manometer tube was read and scale corrections made, and the relation PV=KT was applied. The volume was calculated from the table of volumes. The pressure was that of atmosphere, plus or minus the level of mercury, which was either above or below 291.92 cm. on the scale.

A part of these values will be given below, Table I. The complete values can be found in the thesis of Gurd.

Table I

SCALE READING	CORRECTED SCALE	CORRECTED VOL.
20.00	20.00	15.46
50.00	50.03	38.36
100.00	100.25	77.35
101.00	101.35	78.20
180.50	180.85	139.96
200.00	200.45	155.09
201.00	201.65	156.01
260.00	260.63	201.08
299.00	299.62	231.90
301.00	301.89	233.71
360.90	361.79	281.58
370.49	371.38	289.35

(e). Heating Bath.

The reaction cell was immersed in a di-butyl phthalate bath to a point where the side arms A and B were covered. A pyrex jar 8.5 inches in diameter and 18 inches deep served to contain the bath oil which was agitated by means of a three paddle stirrer. Two sets of bare nichrome coils served to heat the bath. An arrangement of rheostats, convenient for the purpose, made it possible to regulate the temperature to within 0.05°C. The temperature was kept constant at any desired value, by means of an all mercury thermo-regulator. When necessary, the bath could be cooled by means of a water cooled copper coil.

Because of the fact that pressure tubing was not used in this work, there was the possibility of an explosion. The bath was therefore enclosed in a box-like protective arrangement, containing the necessary shatter proof windows.

II. Conductivity Measurements.

A cell suitable for both vapour pressure and conductivity determinations was constructed. It has been described above. The apparatus necessary for the measurement of conductivity included, (1) A Leeds and Northrup Kohlrausch slide wire bridge, (2) A Curtiss-wound non inductive resistance box (0 to 100,000 ohms in 1 ohm steps), (3) A pair of good quality high resistance ear phones and (4) A Vreeland oscillator with a frequency of 1000 cycles per second. The ordinary type of bridge hook-up was used.

Before determining the cell constant, it was necessary to know the resistance of the lead wire and the platinum foil leading through the glass seal to the electrodes. This was done by filling the cell with mercury and measuring the resistance of the circuit. The electrodes were carefully platinized and the cell constant determined with both 1/50 N. and 1/10 N. potassium chloride solutions. The specific conductivities of Kohlrausch, Holborn and Dusselhorst (40) were used.

III. Preparation of pure Calcium Oxide.

It was found that C.P. calcium oxide contained too high a percentage of carbonate to be of any value in this work. Calcium oxide was therefore prepared from clear, select, natural crystals of Iceland Spar obtained from the Eimer and Amend Company. This was ground up finely, and placed in a platinum boat. The carbonate was heated in a quartz tube which had a furnace built around it. A current of dry, carbon dioxide free, air was passed over the salt. The furnace was held at about 1000 C. for a week..

The oxide formed was tested for carbonate by placing some of the oxide in a test tube with carbon dioxide free water. HCl was added, and CO_2 free air was sucked through a solution of barium hydroxide. CaO was also determined by titration methods. An excess of 1/10 N HCl was added, and titrated back with 1/10 N. NaOH using methyl orange as indicator. These tests showed the CaO to be pure.

The CaO was stored in a vacuum dessicator containing phosphorus pentoxide and sodium hydroxide.

IV. Procedure for the Preparation of Solutions.

The cell was carefully cleaned and dried. The solenoid was slipped over the stem and both were clamped in position, after which the stem was sealed to the tube leading from the manometer system. The resistance wire was wound around the ~~expand~~ stem and lagging placed thereon. Side arm B was left about three inches long. Side arm A was left long enough to extend out in front of the bath. To this, a 500 cc. distillation bulb was attached. The entire apparatus was now evacuated, and left to stand, in order to test for leaks. It was then ready for filling.

Dry carbon dioxide free air was allowed into the apparatus and side arm B was broken open. The desired amount of calcium oxide was weighed out, and poured into the cell through B, using a glazed paper funnel. The side arm B was then sealed off. The top stem of the distillation bulb was broken off, and the desired amount of distilled water introduced into it with a weight pipette, care being taken not to wet the upper walls of the flask. This stem was sealed off and the water in the flask was rapidly frozen, using a mixture of carbon dioxide in acetone.

The apparatus was then thoroughly evacuated and the mercury was raised part way up to the mercury seal between the cell and the gas, measuring system. The object of this, was to isolate the cell system from the rest of the apparatus. The following procedure was for the purpose of removing any traces of dissolved gases from the water.

The freezing mixture was removed from around the flask and the ice allowed to slowly melt. As it did, bubbles of gas came out of solution. As soon as the ice had all melted, it was again rapidly frozen. Any water that had escaped into the vapour phase was recondensed, whereas, very little gas that had been removed from the water would re-dissolve when present in such small quantities. After the water was again completely frozen, the mercury shut-off was lowered and the cell system evacuated. Three such freezings and thawings were found sufficient to remove dissolved gases. The water was then slowly distilled into the cell. To facilitate distillation, the cell was surrounded with the bath oil which was kept at as low a temperature as possible by means of the copper cooling coil.

The final step involved the introduction of sulphur dioxide into the calcium oxide-water system. The method of purification and measurement of the gas has already been described. In order to increase the rate at which sulphur dioxide went into solution, the temperature of the bath was lowered by means of the cooling coil. The stirrer was set in vigorous motion. After the pressure and temperature of the gas in the two measuring bulbs E_1 and E_2 were determined, the desired amount of gas was condensed in D. Stopcock S_3 was closed and S_4 opened and the gas allowed to rush into the cell. After the gas had all evaporated from D, mercury was run into the mercury seal and frozen. The gas between S_4 and the mercury seal was condensed back into D from which it was allowed to evaporate into the measuring system. The pressure and temperatures of the gas remaining in the measuring system were read. The amount of gas introduced into the cell could be calculated by difference. An example is given below in section VI.

V. Procedure in Making a "Run".

The stirrer, and thermometer, and thermo-regulator were fixed in place. With low sulphur dioxide concentrations, it it was found that equilibrium was reached very slowly, expecially in some cases where the solid tended to cake at the bottom of the cell. To make sure that equilibrium was reached at the beginning of an experiment, the solution was stirred for at least 24 hours, and in some cases for 3 days. At higher concentrations of sulphur dioxide, this was not necessary as all the calcium oxide went into solution as the bisulphite at the beginning of a run. The temperature was held constant until equilibrium was reached. This required several hours at the lower temperatures. One very convenient method for speeding up the attainment of equilibrium was to heat up the solution 1 degree above the desired point, hold it there for twenty minutes, then cool down to the point where readings were to be made. The best method for determining when equilibrium was reached was by following conductivities. Conductivity readings were made every 15 minutes. After the values remained constant for half an hour, readings were made of (1) The temperature of the bath, (2) The temperature of the connecting tubing, (3) The three temperatures on the manometer tube. The height of the mercury on the scale was kept at 0, and the height of the mercury in the manometer was read. The first few runs were checked by repeating the experiment after equilibrium had again been reached at room temperature. The results could be duplicated.

VI. Calculation of Results.

A vast amount of time was required in the calculation of results. It will be possible to give only a brief review of the procedure adopted. In order to leave no doubt as to this procedure, type calculations will be included where necessary.

Corrections in weighing out the calcium oxide and water were small. As the water was distilled from the 500 cc. distillation flask, a volume of water vapour was left in the flask for which correction had to be made. The calculation of the weight of sulphur dioxide required the correction of the mercury heights read on the glass scale to 0°C. An example will be given below.

Two corrections were necessary to the column of mercury in the large manometer. Most of the column was at room temperature, and its height had to be corrected to 0°C. A few centimeters in scale B which was heated avove the temperature of the bath had also to be corrected to 0°C.

The quantity of sulphur dioxide and water in the gaseous phase above the solution had to be calculated. As the temperature increased, the volume of the solution increased, thus diminishing the gaseous volume.

The volume of gas above the solution had to be divided into two parts. That in the cell was at bath temperature, while that in the connecting tubing was at a temperature recorded by two thermometers placed inside the lagging, one at scale B and the other above the reaction cell.

Type Calculation. D_3.

1. Wt. Sulphur Dioxide.

	Man. L. R.	Tubing. Temp.	Bath. Temp.	Corrected pressure.
Before introducing	73.80-20	23.5	21.3	71.55
After introducing	21.65-20	24.4	21.5	19.57

$$\text{Wt. } SO_2 = \left[\frac{71.55 \times 714.6 \times 65.10}{76 \times .08209 \times 294.4} + \frac{71.55 \times 75.96 \times 65.08}{76 \times .08209 \times 295.6}\right]\frac{1}{1000}$$

$$- \left[\frac{19.57 \times 714.6 \times 64.32}{76 \times .08209 \times 294.6} + \frac{19.57 \times 75.96 \times 64.30}{76 \times .08209 \times 297.5}\right]\frac{1}{1000}$$

$$= 1.4631 \text{ gm.}$$

Correction for SO_2 trapped in tubing .0009 gm.

Wt. SO_2 = 1.4622 gm.

Type Calculation.

Vapour Pressure.

Scale reading	313.5
Correction	0.89
Corrected reading	314.39 cm.

To find vol. in manometer

$$\begin{array}{r} 314.39 \\ \underline{302.14} \\ 12.25 \end{array} = \begin{array}{r} 233.91 \\ \underline{9.80} \\ 243.71 \text{ cc.} \end{array}$$

Volume of air above mercury 243.71 cc.

Temperature	Top	Middle	Bottom
	29.3	26.7	21.6
Corrected	29.1	26.7	21.4

$$\begin{array}{rl} 12\times29.1 &= 349.2 \\ 16\times26.7 &= 427.2 \\ \underline{3}\times\underline{23.6} &= \underline{70.8} \\ 31 \quad \rightarrow & \ \ 847.7 \end{array}$$

Average temperature 27.3°C. 300.4 A.

P. Due to enclosed air $= \frac{KT}{V} = \frac{57.22\times300.4}{243.71}$

$P = 70.53$

Reading on Scale B -0.1

$$\begin{array}{lr} \text{True scale reading} & 314.39 \\ \text{Zero value} & \underline{291.92} \\ & 22.47 \\ \text{Scale+Temp. correction} & \underline{.30} \\ & \underline{22.17} \\ & 70.53 \\ \text{VP} & \underline{22.17} \\ & 48.36 \text{ cm.} \end{array}$$

The specific conductivities were calculated in the usual manner:

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

where K the specific conductivity in ohms-1.
C the cell constant.
R total resistance of the system, as measured by the bridge.
r the lead resistance.

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

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

where A the bridge reading.
B the reading of the resistance box in the bridge circuit.

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

PART II.

Solubility Studies.

Description of Apparatus.

The apparatus may be conveniently divided into three sections. (see Fig. 4 & 5.)

I. Gas purification and measuring system.
2. System for making up solutions.
3. Apparatus for determining precipitation temperatures.

I. Gas Purification and Measuring System.

The apparatus used in purifying and measuring the gas was the same as that used in Part I of this thesis. It has been carefully described before and, therefore, further description is unnecessary.

II. System for making up Solutions.

In the work on vapour pressures and conductivities, a specially constructed reaction cell was used. This included a magnetic stirrer and sealed-in platinum electrodes. An elaborate cell such as this, was not required for the solubility work. It was decided to use one inch pyrex tubing made in the form of bombs, as shown in figure 4. A stem of

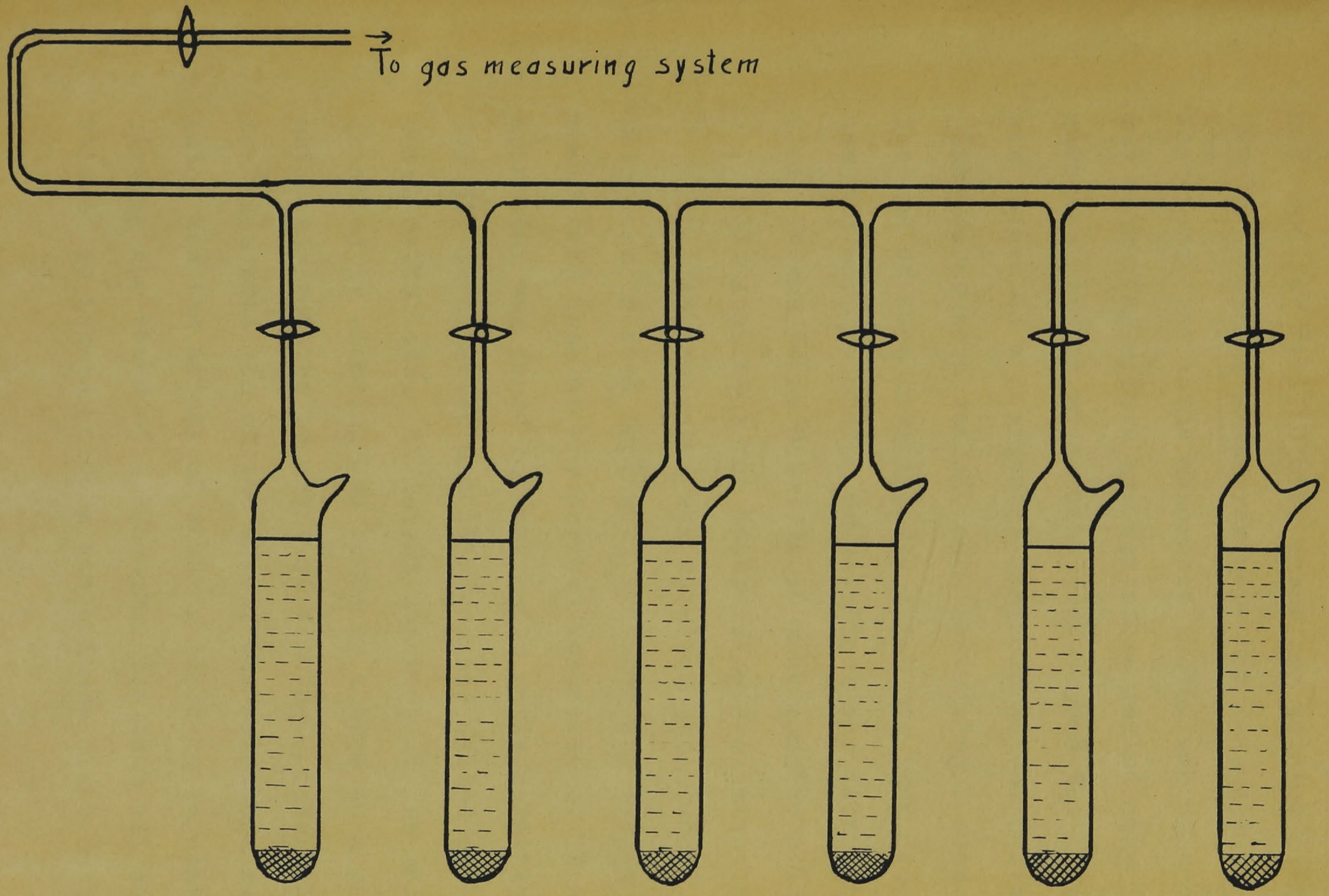


Figure 4

quarter inch pyrex was sealed onto one end, and this stem was sealed onto an arm of the manifold M, which was used for filling with gas. (Fig. 4.) Each bomb had a side arm which was used for filling with water and calcium oxide.

Vapour pressures were not measured in this work therefore, the large manometer system was unnecessary. The gas measuring system was therefore sealed away from the cell manometer system at a point just beyond S_4. (Fig. I.) S_4 was joined to a horizontal manifold to which five vertical glass tubes were sealed, each containing a stopcock. To the end of each stem a bomb, which has been described above, was sealed. By making up solutions for five bombs at a time, it was found possible to save considerable time.

III. Apparatus for Determining Precipitation Temperatures.

An apparatus was required which would keep the solutions in each bomb well agitated and at the same time would hold them at any desired temperature. The following apparatus was found to work quite satisfactorily. A pyrex jar $8\frac{1}{2}$" in diameter and 18" deep was filled with fresh di-butyl phthallate. Efficient stirring of the solutions was obtained by clamping two bombs at a time to a vertical wheel which was rotated by means of a motor. (see Fig. 5.) Thus for each rotation of the wheel, the solutions ware shaken twice and the amount of shaking could be regulated by regulating the speed of the motor. The bath oil was kept well stirred to insure uniform temperature distribution by means

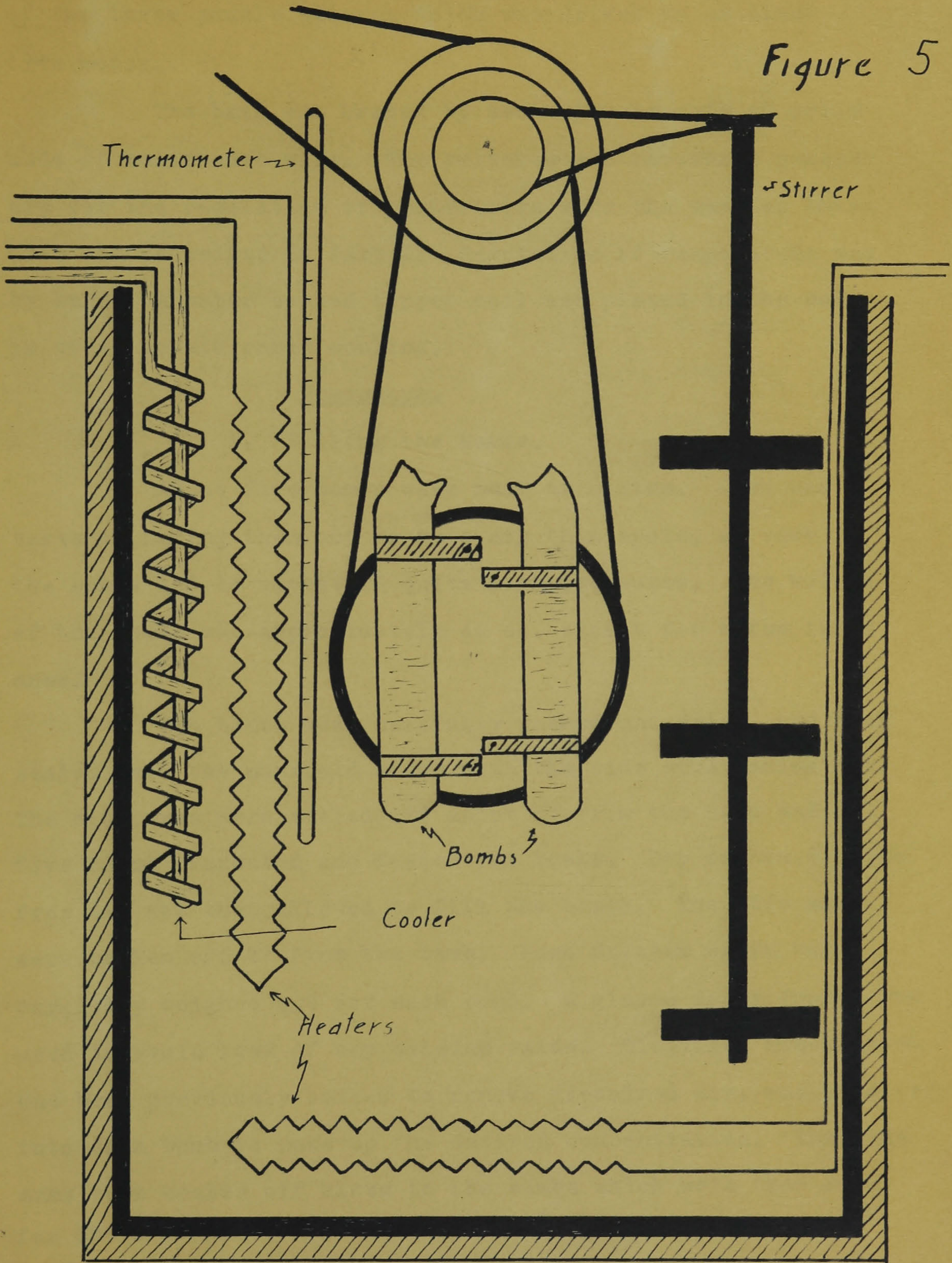


Figure 5
Thermometer
Stirrer
Bombs
Cooler
Heaters

of the three paddle stirrer which was driven by an electric motor.

The bath was heated by two separate sets of coils made of resistance wire. The switches and rheostats necessary for the regulation of temperature were the same as those used and described in Part I. Regulation of temperature was by hand. A water cooled copper coil was placed in the bath in order to aid rapid cooling.

Procedure.

I. Filling the Bombs.

About five bombs were made at a time. Care was taken in making them not to have any thin spots, as some of the bombs had to withstand quite high pressures. The volume of the bombs was approximately 40 cc. except for a few large ones.

The bombs were carefully washed and dried, and then sealed onto the manifold stems with the side arms facing out. The side arms were sealed off about 3" from the bomb and all five bombs evacuated and tested for leaks. Dry carbon dioxide free air was then allowed to fill the bombs. The side arms were broken off 2" from the bomb. Pure Calcium oxide was carefully weighed out for each bomb. A glazed paper funnel was used to avoid loss of any calcium oxide. Distilled water which had been previously boiled to remove dissolved air, was pipetted into each bomb to make up the desired concentration. The side arms were sealed off close to the bombs which were then ready for the removal of the last traces of air.

The stopcocks above the bombs were closed and the manifold evacuated. The air above the water in each bomb was removed by quickly turning each stopcock several times. As soon as the pressure in each bomb was reduced to the vapour pressure of water at that temperature, bubbles of dissolved gases were seen to rise from the water. As soon as this bubbling had ceased, the pressure was again reduced by turning the stopcock. Several repetitions of this procedure insured complete removal of dissolved gases. The solutions were then ready for the introduction of sulphur dioxide.

The purification and measurement of sulphur dioxide has been described in Part I of this thesis. The procedure used in filling the bombs, however, had to be somewhat modified. During the work on vapour pressures and conductivities, the sulphur dioxide to be introduced into the cell was measured, then condensed in a tiny bulb D (Fig. I) from which it was allowed to evaporate rapidly into the cell. Rapid filling in that case was possible, because the solution could be thoroughly stirred. However, in filling the bombs there was no means of stirring, therefore, the gas went into solution quite slowly. The gas could not be first condensed into a tiny bulb, as rapid evaporation from this would have built up much higher pressures than the stopcocks on the manifold would withstand.

A quantity of sulphur dioxide was evaporated from its storage bulb until the pressure in the measuring bulbs was about atmospheric. The pressure and temperature were measured and the gas was allowed to pass directly over to the bomb where it went slowly into solution. The pressure decrease was followed, and when the calculated amount of sulphur dioxide had gone into solution, the bomb was sealed away from its manifold stem. The gas remaining in the manifold and connecting tubing was condensed and allowed to pass back into the measuring system, where the amount remaining was determined. The difference represented the sulphur dioxide in the bomb. Corrections were made for the small amount of gas remaining in the manifold after the bulk had been condensed back into the measuring system. Since the solubility of sulphur dioxide increases rapidly with decrease in temperature, the bombs were kept in an ice mixture during filling. Each bomb had to be filled separately. After the bomb was sealed off, it was thoroughly shaken by hand till the salt went into solution. In this solubility work it was necessary always to introduce enough gas to dissolve all the calcium oxide present. Some solutions that had just enough sulphur dioxide to form a clear solution required lengthy cooling and shaking to get all the salt in solution. The bombs were now ready to be put in the bath for determining precipitation temperatures.

Two bombs were clamped onto the wheel (Fig.5) The precipitation temperature of each bomb had to be determined separately, but by using pairs of bombs, two purposes were served. In the first place, the extra bomb served as a counterpoise, insuring more even rotation of the agitation wheel. In the second place, the apparatus had to be torn down only half as often when bombs were replaced. A third advantage also became evident, but this will be described later.

After the two bombs were clamped onto the rotating wheel, the wheel was firmly fixed into place. The necessary pulleys and belts were attached and the bath filled with oil. It was found that there was a strong tendency towards supersaturation. In some cases, the solution could be rapidly heated to more than 15° C. above the actual precipitation temperature.

The solutions were shaken simply by rotating the wheel to which the bombs were clamped, thus causing the solution to splash continually from one end of the bomb to the other. First a trial attempt of the precipitation temperature was made. The bath was heated up rapidly until precipitation took place. Precipitation was always rapid and voluminous, indicating that at that point a large part of the dissolved calcium bisulphite rapidly changed over to the less soluble calcium sulphite. Previous experience and data derived from conductivity readings had shown that unless the solution was heated up very slowly, precipitation took place from 10 to 15 degrees above the true precipitation temperature. In order to save time, the bath temperature was allowed to continue increasing until the second bomb on the wheel showed a precipitate. The bath was rapidly cooled in order to bring the salt of both bombs into solution.

The object of the remaining determinations was to find the lowest possible temperature at which precipitation would take place. The bath was again heated up to within 10° of the previous precipitation temperature. It was held there for an hour. If precipitation took place, the bath was cooled down until solution was effected. If precipitation did not take place, the bath was slowly heated up at a rate of about 2 degrees per hour until precipitation took place. This was not considered as the true precipitation temperature, but as a reasonable approach to it. Several more similar attempts were then made to lower this temperature. Eventually a temperature was obtained below which precipitation would not take place. This was considered as the precipitation temperature.

It is admitted that this is not the ideal way to study solubility. Just below the precipitation temperature, it should have been possible to bring the precipitate into solution. A great deal of time was spent in the attempt to dissolve the precipitate at a few degrees below the apparent precipitation temperature. There was one insurmountable obstacle and that was the time factor. It was found that 15 degrees below an apparent precipitation temperature, it was possible, within a reasonable time (3-4 hours), to bring the precipitate into solution, but at 10 degrees below that temperature , the time required increased tremendously.

PART III

C

COOKING EXPERIMENTS

Description of Apparatus.

The ratio of woodmeal or cellulose to cooking liquor varied from experiment to experiment, but in all cases, the consistency of the "mash" formed was too great to permit the use of a magnetic stirrer. In fact, it was impossible to find any means of stirring the contents of the reaction cell. The method used in Part I of this thesis for introducing the reagents could, therefore, not be used. It was found necessary to prepare the sulphite liquor in a separate piece of apparatus and then to introduce it into the reaction cell containing the woodmeal. It was also necessary that no foreign substances be present in the cell during the experimental work, and, furthermore, a procedure had to be adopted which would permit the introduction of a known quantity of an accurately known concentration of liquor. On the other hand, vapour pressures could be determined with the manometer system that was used in Part I.

A detailed description of the apparatus and experimental procedure is given below:

Detailed Description of Apparatus.

The apparatus may be divided into three parts:-

1. Gas purification and measuring system.
2. Apparatus for preparing solutions.
3. Cell-Manometer system.

1. Gas purification and measuring system.

Part I of this thesis gives a detailed description of the apparatus used in purifying and accurately measuring the sulphur dioxide. This apparatus was also used in the purification and measurement of the sulphur dioxide used to make up sulphite liquor for the cooking experiments.

2. Apparatus for Preparing Solutions.

Calcium oxide when placed in water settled to the bottom where it formed a compact mass. If sulphur dioxide is added without stirring, sulphurous acid is formed. This attacks the calcium oxide extremely slowly. The means adopted to bring the calcium oxide into solution was to measure the reagents into a filler tube, which could be sealed away from the gas measuring system and shaken.

The filler tube (see Fig.6) was made of three quarter inch pyrex tubing. It had two side arms A & B.

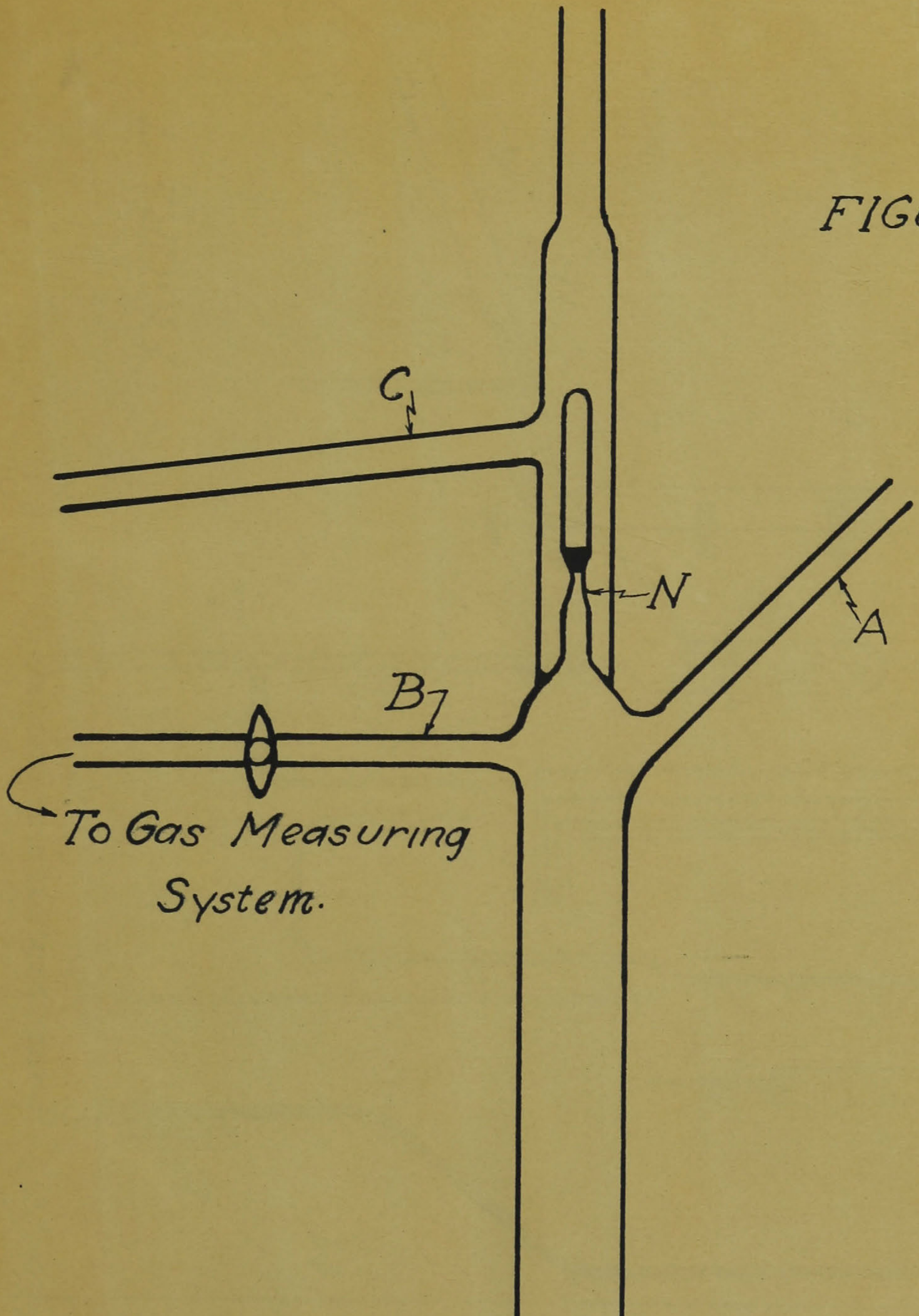
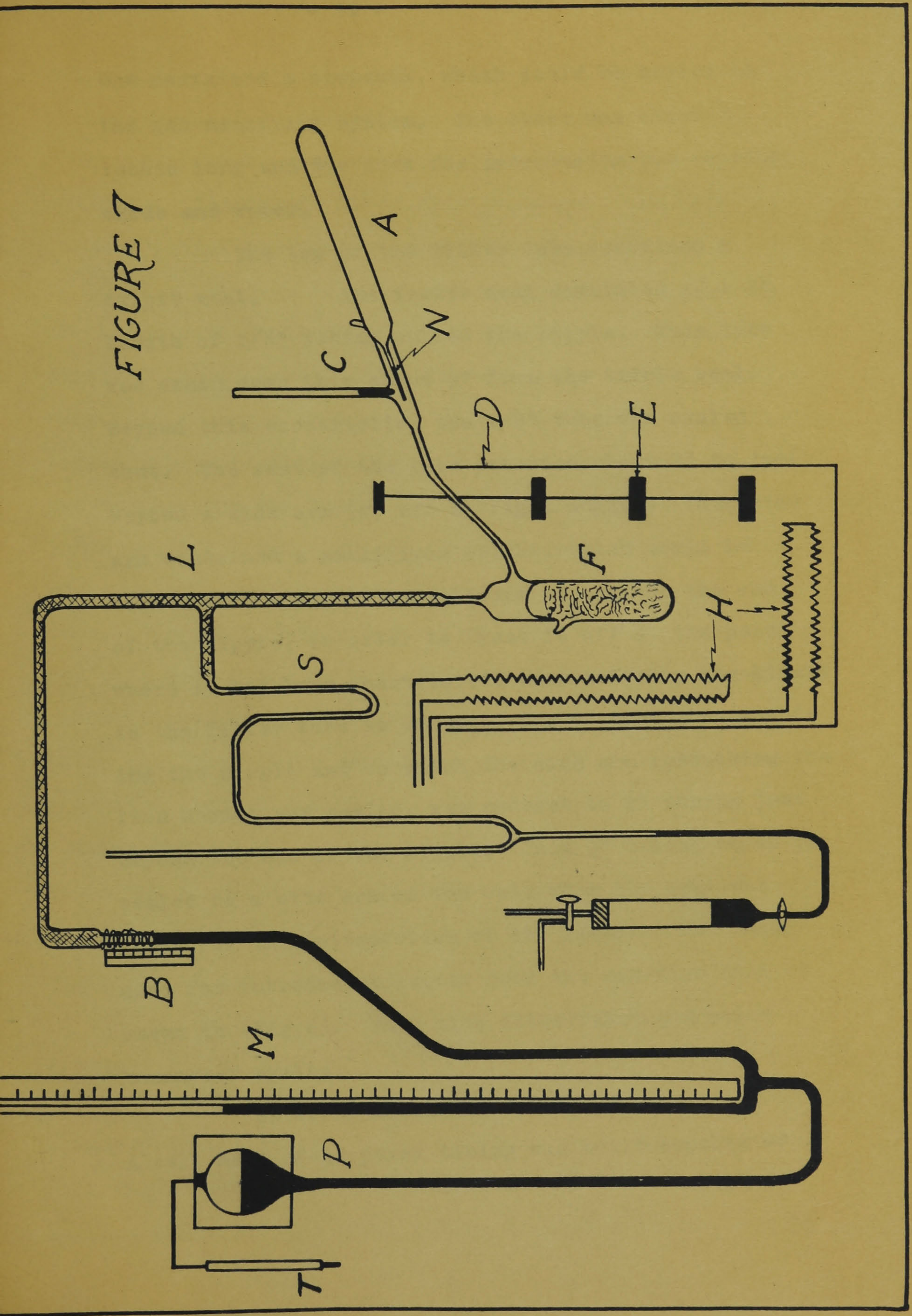


FIGURE 6

FIGURE 7



One contained a stopcock, which could be sealed to the gas measuring system. The other was about 3 inches long and was used for introducing the calcium oxide and water.

The top of the filler tube contained a triple seal. The inside seal consisted of a 3" length of 1/8" tubing called the nipple. This tube was drawn down thin about ½" from the triple seal. Beyond this constriction the 1/8" tube was sealed shut. The rest of the tube extended about 2" to just beyond a side arm (c) set at right angles. This side arm contained a small iron weight, which could be raised with a magnet and allowed to drop on the end of the nipple, in order to break it off at the point where it had been constricted, thus allowing any liquid in the filler tube to escape. The ½" tubing surrounding the nipple and to which the side arm containing the iron hammer was sealed, was reduced to ¼" tubing just beyond the end of the nipple. This ¼" tubing could be sealed to a side arm of the cell when the cell was ready for the introduction of the liquor. The setup used for introducing liquor into the reaction cell is shown in (Fig.6). This also illustrates the cell-manometer system.

3. Cell- Manometer System.

A cell made of 1" pyrex tubing was built capable of withstanding over 500 cm. Hg. pressure. (see Fig. 7). The first cell constructed had a volume of 100 cc. The reaction products were analyzed for sulphur dioxide, lignin, and pulp. Therefore, after each experiment the cell was sealed away from the manometer system, and it was necessary to build a new cell for the next experiment. The volume of the cells varied slightly. It was found that during an experiment the woodmeal tended to "shove up" in the reaction tube, and in order to prevent any wood from getting into the lagged tubing leading to the manometer, a cap was set about two inches from the top of the cell. A tube was selected which would fit snuggly into the cell, and a large number of very small perforations were blown into the end of this tube. The perforated end was then cut off short. This cap was slid into place in the cell and held there by means of several glass notches placed conveniently just above and below it. The bottom end of the cell was then sealed shut. A $\frac{1}{4}$" side arm was sealed onto the cell just below the perforated cap. This was for filling the cell with woodmeal. There was a second side arm near the top of the cell to which the filler tube could be sealed when the cell was to be filled with cooking liquors.

The stem of the cell was sealed to the manometer system. A"T"on this stem led to the evacuating system through a mercury seal. This was necessary to remove the air from the woodmeal in the cell. During an experiment, mercury was run into the mercury seal, and kept frozen in a carbon dioxide acetone mixture. The glass tubing leading from the cell to the manometer and also to the mercury seal was wrapped with resistance wire, in order to hold the vapour phase contained in it well over 130° C., thus preventing condensation of water.

The large closed end manometer, as described in Part I, was used to measure vapour pressures.

The bath consisted of an $8\frac{1}{2}$ x 18" pyrex jar full of di-butyl phthalate. The heating coils were similar to these~~nes~~ used in the solubility experiments, except that an extra heater was added, making it possible to heat the bath from 25° to 130° C. in 45 minutes. The temperature could be regulated to within 1/10 degrees.

Experimental Procedure:

Solutions of varying concentrations of calcium oxide, sulphur dioxide and water were prepared and mixed with woodmeal. The vapour pressures of this system were then determined at 130° C. for a period of 8 to 31 hours. A detailed description of the experimental procedure involved is given below. It may be divided into 5 parts:

1. Purification and Introduction of Calcium Oxide and Water.
2. Purification, Measurement and Introduction of Sulphur Dioxide.
3. Preparation of woodmeal and cellulose.
4. Introduction of Liquor into the Reaction Cell.
5. Procedure in Conducting an Experiment.

1. Purification and Introduction of calcium oxide and water.

Clear select crystals of Iceland Spar (calcium carbonate) were ground up finely in an agate mortar and heated for four days in a platinum boat at 1000° C. A current of dry carbon dioxide free air was continuously passed over the boat. All the necessary precautions were taken to keep the calcium oxide formed in the pure condition by storing in a vacuum dessicator containing phosphorus pentoxide and sodium hydroxide.

A reaction cell and filler tube, as described above, were made. They were carefully cleaned and dried. The filler tube was sealed to a glass tube connecting it to the gas measuring and evacuation system. The side arm A (see Fig.6) was sealed shut, leaving about 3 inches of tubing. The filler tube was then evacuated, in order to dry it and test for leaks. If the apparatus held, it was ready for the introduction of calcium oxide and water.

Dry carbon dioxide free air was allowed to fill the filler tube. The end of the side arm (A) was then nipped off. The desired amount of pure calcium oxide was then weighed out and poured into the filler tube, using a glazed paper funnel.

Distilled water, which had been boiled for an hour and rapidly cooled, was introduced, using a weight pipette. The side arm was then sealed off close to the filler tube.

It was now necessary to remove the air above the water and also to remove any small amount of air that had dissolved in the water. The stopcock S_1 was closed until the connecting tubing was evacuated. S_1 was rapidly opened and closed several times to remove the air above the water. Any gas dissolved in the water began to bubble out. This removal of gas was continued for an hour, in which time the stopcock S_1 was rapidly opened and closed about half a dozen times. The filler tube was then ready for the introduction of sulphur dioxide.

2. Purification Measurement and Introduction of Sulphur Dioxide.

The procedure was similar to that used in filling the bombs for the solubility experiments and, therefore, only a brief description will be given here.

The purification apparatus was evacuated and the required amount of sulphur dioxide condensed from the pressure cylinder. This sulphur dioxide was redistilled 3 times with the rejection of the top and bottom fractions. The pure gas was stored in a bulb which was surrounded with carbon dioxide in acetone.

The measuring system was thoroughly evacuated and sulphur dioxide allowed to evaporate into it, until approximately atmospheric pressure was reached. The pressure of the gas and its temperature were thus observed and the gas allowed to pass over to the filler tube. As no stirring was possible, solution took place slowly. Solution was aided somewhat by surrounding the filler tube with an ice bath. In this work, two fillings were required to get the desired amount of sulphur dioxide into solution. After the first filling, S_1 was closed and the gas left in the connecting tube was condensed back and evaporated into the gas measuring system in the usual manner. The pressure and temperature were read and the small amount of gas left in the connecting tubing accounted for. The measuring system was then evacuated and a fresh supply of gas evaporated into it. It was measured and introduced in the same way. The rate at which the sulphur dioxide went into solution could be followed by means of the manometer on the gas measuring system. When the desired amount had passed into solution, the filler tube was sealed off by sealing off the side arm (B). The sulphur dioxide remaining in the connecting tube was returned to the measuring system and the pressure and temperature determined.

The filler tube was then shaken until all solids had gone into solution and was allowed to stand until the rest of the apparatus was set up.

3. Preparation of Woodmeal and Cellulose.

Two different grades of spruce woodmeal were used. That used in experiments 1 and 2 passed 100 mesh. The second passed 40 mesh, but was retained by a 60 mesh screen. It was thoroughly washed with a solution of 50% alcohol and 50% benzene to remove resinous materials. These solutions were thoroughly removed by heating to 100° C. and evacuating. As dry woodmeal is exceedingly hygroscopic, it was necessary to leave it in contact with the air, in order to pick up moistures before weighing. The moisture contained at the time of weighing was carefully determined and the weight corrected for bone dry wood.

The cellulose was purified in the following manner: Absorbent hospital cotton was placed in a flask and enough 1% NaOH was added to just cover it. It was refluxed at 100° for 12 hours. It was then washed free of alkali and acidified with 1% acetic and then washed free of acid. Refluxing and washing was repeated seven times. The purified cotton was then air dried on a rack and finally oven dried for 2 days at 100° C. and stored in a bottle. At the time the experiment was made, it contained 5% moisture.

The weighed amount of woodmeal or cellulose was placed in the clean dry cell and the cell sealed onto the manometer system. The side arm, through which the wood had been introduced, was sealed off.

4. Introduction of Liquor into the Cell.

The iron weight was carefully slipped into its containing side arm (c) on the filler tube and allowed to rest on the end.of the nipple. The filler tube was then sealed to the upper side arm of the reaction cell, as shown in Figure 7. The open end of the side arm was then sealed off.

Oil was poured into the bath and heated to 70° C. The cell was evacuated for 4 hours at this temperature, in order to remove air absorbed on the woodmeal. Mercury was run into the mercury seal and frozen. The cell was ready for the introduction of the liquor.

The iron hammer was raised in its side arm by means of a small electro magnet and the hammer allowed to drop on the nipple, which broke at the constriction near the triple seal. The liquor drained into the cell. Time was given for it to drain completely, and the filler tube with connecting tube was sealed away from the cell, leaving the upper side arm of the cell about an inch long.

The lagged tubing between the cell and the manometer was heated well above room temperature to prevent condensation of liquid and the system allowed to stand over night, in order to give it time to reach equilibrium

5. Procedure in Conducting an Experiment.

After sufficient time had been given for the vapour pressure to become constant, it was determined at 25° C. The bath was then rapidly heated to 130° C., where it was held constant throughout the duration of an experiment. Vapour pressure readings were made in a manner similar to that used in Part I. The time of cooking varied from 8 to 31 hours and in some experiments the bath was cooled down and the vapour pressure determined at room temperature. This was done in order to check vapour pressure rises during cooking.

After an experiment, the cell was sealed away from the connecting tubing and the contents analyzed for pulp,lignin and sulphur content .

RESULTS.

Part I.

Vapour pressures and conductivities of the system calcium oxide-sulphur dioxide-water.

In the study of the vapour pressures and conductivities of the system calcium oxide-sulphur dioxide-water, the data of nine different concentrations are given. These may be divided into two parts. In one series four different concentrations of sulphur dioxide were studied in which the quantity of calcium oxide remained constant, with approximately 1.2 % present. This work is classified as series B. In a second series, five different concentrations of sulphur dioxide were studied, with the calcium oxide concentration approximately 2.3%. This is classified as Series D. Two other series were completed, but in each case, experimental difficulties arose which cast doubt on the accuracy of the data obtained. These results are, therefore, not included in the thesis. The data of the nine successful runs are given below. (Tables II-X). It is quite impossible to include all the readings of these runs. Some idea of all of the readings required may be obtained from a study of the section "Calculation of Results". Instead, only the calculated results are given below.

The percentage of each component is calculated on the basis of the total sulphur dioxide (in the liquid phase) plus calcium oxide plus water.

Each series includes:
I. Weight of water.
II. Weight of calcium oxide.
III. Total weight of sulphur dioxide.
IV. Weight sulphur dioxide in solution.
V. % sulphur dioxide in solution.

VI. Ratio SO_2/CaO in mols.
VII. Temperature.
VIII. Total V.P.
IX. Partial V.P. of sulphur dioxide.
X. Specific conductivity.

Specific conductivity measurements are included for series B only.

Tables II to X include the results of the individual experiments performed by the writer. This investigation, however, was a completion of the work started in this laboratory by Campbell and by Gurd, and its main object was to sum up the results of all three workers. This information is contained on Table XI for vapour pressures and on Table XII for specific conductivities. Vapour pressure values are given for temperatures of 25, 50, 70, 90, 110 and 130°C. and conducdivities for temperatures of 25, 50, 70 and 90°C. For each of these temperatures, the vapour pressures and conductivities for concentrations of 1, 2, 3, 4, 5, and 6 percent sulphur dioxide, and concentrations of 0, 0.5, 1.0, 1.5, 2.0 and 2.5 percent calcium oxide are given. The method of presenting these data requires a more detailed explanation.

A study of Table XI reveals that the first horizontal line of figures gives the vapour pressures of a 1 percent sulphur dioxide solution containing zero percent calcium oxide at each of the temperatures stated above. The second line of figures gives the vapour pressures for a one percent sulphur dioxide solution containing 0.5 percent calcium oxide at each of the temperatures stated above. It can be seen that entire sulphur dioxide and calcium oxide concentration ranges have been dealt with in a similar manner. Obviously, this required considerable calculation and correlation of data. However, an attempt was being made to determine equilibria in the system calcium oxide-sulphur dioxide-water and, therefore, all these data were required. Sufficient data had also been obtained on the specific conductivities of this system to permit the drawing up of a composite table covering similar temperature and concentration ranges. The results are found in Table XII. In this table, however, the data for temperatures of 110 and 130°C. are omitted.

It is impossible to include the tables and graphs that had to be prepared in order to obtain the data found in Tables XI and XII. Instead, the method used in arriving at the data given, will be described below. The data of tables II to X will be dealt with first.

Series B consists of four experiments. The calcium oxide concentration was kept constant, but the sulphur dioxide concentration was varied for each. Four sets of vapour pressure and conductivity values were obtained covering a temperature range of 25 to 130°C. A curve was drawn with vapour pressure as ordinate and temperature as abscissa. For instance, the first curve drawn represented experiment B_1 in which the initial concentration of the calcium oxide was 1.14% calculated as $CaO/CaO+SO_2+H_2O$, and the concentration of the sulphur dioxide in solution was 1.420. It must be mentioned here that as the partial pressure of the sulphur dioxide increased its concentration in the liquid phase diminished. This is shown below in the tables referring to series B.

Experiment B_2 yielded a similar curve with higher vapour pressures due to the fact that the solution contained a higher concentration of sulphur dioxide. Series B when completed would, therefore, yield four curves, each with the same calcium oxide content, but with different sulphur dioxide concentrations.

Isotherms were next drawn by picking the values from the above set of curves. Vapour pressures were plotted against percent concentration of sulphur dioxide. At 25°C. vapour pressures were known for four sulphur dioxide concentrations. These were plotted. Similar curves for 50, 70, 90, 110 and 130°C. were drawn. This included the completed graphical representation for the results at one calcium oxide concentration. A similar series of curves had to be drawn for series D.

The ultimate object of all this work was to determine the change in vapour pressure with change in both calcium oxide and sulphur dioxide concentration. The above describes the method used in vapour pressure values for any concentration of sulphur dioxide up to 6%, for any temperature value between 25 and 130°C, but for only 2 calcium oxide concentrations. There are four variables:(I.)vapour pressure, (II) temperature, (3) sulphur dioxide concentration, and (4) calcium oxide concentration, therefore, in any graphical representation, two of these must be fixed. In the first set of curves, calcium oxide and sulphur dioxide concentration were fixed. In the second set, calcium oxide concentration and temperature were fixed, therefore, in order to cover the whole temperature range, six isotherms had to be drawn.

The object of the next step was to make it possible to study vapour pressure changes with gradual change in calcium oxide concentration. The writer had data for only two calcium oxide concentrations, and these were not sufficient for interpolation and extrapolation. Gurd had conducted similar experiments with this system at two calcium oxide concentrations, which differed from those used by the writer. Later, it was found that except for one or two points, the two sets of data were in excellent agreement. In order to get Gurd's results in comparable form, it was necessary to make up two complete series of groups of curves.

To complete the necessary data, vapour pressure values for zero calcium oxide concentrations were necessary. These values were contained in the results of Campbell. (41). This gave sufficient data to permit plotting vapour pressures against calcium oxide concentration. The first curve was drawn, with vapour pressure as ~~co~~-ordinate, and percentage calcium oxide as abscissa. It gave the vapour pressure of a one percent sulphur dioxide solution at 25°C. Campbell's vapour pressure value at 25°C. for a one percent sulphur dioxide and a zero percent calcium oxide solution was plotted. Similarly, Gurd's two values at one and two percent calcium oxide and the writers values at approximately 1.2 and 2.3 % calcium oxide were plotted. These five points were found to fall on a smooth vurve. The remaining curves at 25°C. for 2, 3, 4, 5 and 6% sulphur dioxide were plotted in a similar manner. The same lengthy procedure was required to plot each of the values at 50, 70, 90, 110 and 130°C.

The final step in this work was to convert the last set of curves, (36 in number), to curves of constant calcium oxide concentration. These graphs (#3to #8) are shown below. Vapour pressures have been plotted against percent sulphur dioxide for values of 0, 0.5, 1.0, 1.5, 2.0 and 2.5% calcium oxide.

The conductivity studies were of a similar nature. This work, however, has been dealt with in detail only up to 90°C. There are two reasons for this. In the first place, Campbell's data was not complete for higher temperatures. In the second place, sharp breaks in the conductivity curves due to precipitation of calcium sulphate make interpolation and extrapolation extremely difficult. Graph #9 gives the change of conductivity with temperature of the experiments of series B. Graph #10 shows the same values, but representing changes of conductivity due to variation in the sulphur dioxide concentration. In the four succeeding graphs (11 to 14) are represented the combined results of Campbell, Gurd, and the writer.

	B	Wt. H_2O gms.	Wt. CaO gms.	Wt. SO_2 gms.	Temp. Deg. Cent.	Wt. SO_2 in Soln gms.	SO_2 in Soln mols	SO_2/CaO SO_2 H_2O %	SO_2/CaO mols	Total VP cm	PP SO_2 cm	SP. Cond. X10^2
TABLE II	1	84.257	.9887	1.4241	30.1	1.420	.02216	1.642	1.257	6.0	2.8	1.502
	2				50.0	1.419	.02214	1.640	1.256	13.5	4.2	2.091
	3				70.0	1.416	.02210	1.637	1.254	29.9	6.5	2.721
	4				90.1	1.413	.02205	1.633	1.251	62.4	9.8	3.229
	5				109.5	1.406	.02195	1.624	1.245	125.1	18.1	3.088
	6				120.0	1.397	.02181	1.616	1.237	177.3	29.2	2.858
	7				130.1	1.392	.02173	1.610	1.232	238.9	35.2	2.688
TABLE III	1	84.257	.9887	2.7157	25.0	2.704	.04220	3.083	2.393	10.9	8.5	2.412
	2				30.0	2.701	.04216	3.080	2.391	13.5	10.3	2.624
	3				50.0	2.692	.04202	3.065	2.383	27.6	18.3	3.509
	4				70.0	2.681	.04185	3.058	2.373	52.6	29.2	4.454
	5				90.1	2.670	.04167	3.042	2.363	94.7	41.9	4.886
	6				100.1	2.660	.04152	3.032	2.355	126.3	50.0	5.778
	7				109.5	2,639	.04119	3.005	2.336	112.2	77.2	4.741
	8				120.0	2.620	.04089	2.984	2.319	249.3	100.3	4.138
TABLE IV	1	84.257	.9887	3.9073	25.0	3.870	.06040	4.345	3.426	27.7	25.3	2.889
	2				50.0	3.840	.05993	4.313	3.399	60.1	50.8	3.871
	3				70.0	3.810	.05947	4.280	3.372	103.4	80.0	4.871
	4				80.1	3.796	.05925	4.261	3.360	132.2	96.5	5.067
	5				90.1	3.781	.05901	4.250	3.347	166.9	114.1	5.449
	6				100.1	3.766	.05878	4.230	3.334	209.3	133.0	5.857
	7				114.5	3.740	.05847	4.215	3.316	287.9	163.0	6.389
	8				120.0	3.740	.05838	4.200	3.310	321.3	172.2	6.583

		Wt. H_2O gms.	Wt. CaO. gms.	Wt. SO_2 gms.	Temp. Deg. Cent.	Wt. SO_2 in Soln gms.	SO_2 in soln mols	SO_2/CaO SO_2 H_2O %	SO_2/CaO Mols	Total VP cm	PP SO_2 cm	Sp. Cond$_2$ X10
TABLE V	1	84.257	.9887	4.9977	25.0	4.943	.07715	5.50	4.375	40.6	38.2	3.304
	2				40.0	4.919	.07678	5.47	4.354	63.8	58.3	3.955
	3				60.0	4.876	.07611	5.42	4.316	115.0	91.1	4.856
	4				80.0	4.833	.07544	5.38	4.278	183.4	147.9	5,200
	5				100.1	4.788	.07473	5.315	4.238	276.3	200.0	5.687
	6				109.5	4.763	.07434	5.30	4.216	338.2	234.2	6.235
	7				114.7	4.742	.07401	5.27	4.197	375.1	250.1	6.396
	8				125.1	4.722	.07370	5.24	4.180	475.0	282.2	6.749

		Wt. H_2O gms.	Wt. CaO gms.	Wt. SO_2 gms.	Temp. Deg. Cent.	Wt. SO_2 in Soln gms.	SO_2 in Soln mols.	% SO_2	SO_2/CaO Mols	Total VP cm.	PP SO_2 cm.
TABLE VI	1	88.294	2.0613	1.4091	24.9	1.409	.02199	1.535	0.598	2.8	0.2
	2				40.0					6.0	0.5
	3				60.0					15.1	0.2
	4				80.0					35.9	0.4
	5				100.1					76.1	0.0
	6				115.3					128.6	0.6
	7				130.1					204.8	1.0
TABLE VII	1	88.294	2.0613	2.4333	25.5	2.431	.03794	2.622	1.032	4.3	1.9
	2				40.0	2.430	.03793	2.62	1.032	8.5	3.0
	3				60.0	2.426	.03786	2.62	1,030	20.9	6.0
	4				80.0	2.418	.03774	2.61	1.027	41.0	12.5
	5				100.1	2.409	.03760	2.60	1.023	98.2	22.0
	6				113.0	2.402	.03749	2.59	1.020	147.0	29.0
	7				130.1	2.394	.03756	2.58	1.016	243.6	40.1

		Wt. H_2O gms.	Wt. CaO gms.	Wt. SO_2 gms.	Wt., SO_2.	Wt. SO_2 in Soln gms.	SO_2 in Soln mols	% SO_2	SO_2/CaO Mols	Total VP cm.	PP SO_2 cm.
TABLE VIII	1	88.294	2.0613	3.8954	25.0	3.887	.06067	4.133	1.650	8.9	6.5
	2				40.0	3.882	.06059	4.13	1.648	16.2	10.7
	3				60.0	3.865	.06033	4.12	1.641	41.5	26.6
	4				80.0	3.821	.05964	4.10	1.622	85.4	49.9
	5				100.1	3.799	.05930	4.08	1.613	157.3	81.0
	6				114.7	3.782	.05903	4.06	1.606	232.4	107.4
	7				128.1	3.763	.05873	4.05	1.598	321.0	133.0
TABLE IX	1	88.294	2.0613	5.3281	25.0	5.313	.08293	5.563	2.256	14.6	12.2
	2				40.0	5.306	.08282	5.56	2.253	24.6	19.1
	3				60.0	5.279	.08240	5.53	2.241	61.0	46.1
	4				80.1	5.243	.08183	5.49	2.226	120.4	84.8
	5				100.1	5.201	.08118	5.45	2.208	211.5	135.2
	6				114.7	5.173	.08074	5.42	2.196	303.5	178.5
	7				130.0	5.147	.08034	5.40	2.185	425.7	222.7
TABLE X	1	88.294	2.0613	6.8449	25.5	6.808	.1063	7.042	2.890	30.8	28.4
	2				40.0	6.786	.1059	7.02	2.881	54.1	48.6
	3				60.0	6.760	.1055	7.00	2.870	90.4	75.9
	4				80.0	6.700	.1046	6.94	2.844	178.1	142.6
	5				100.1	6.644	.1037	6.89	2.821	291.3	215.0
	6				114.7	6.595	.1029	6.84	2.800	411.8	216.8

TABLE XI

VAPOUR PRESSURE OF THE SYSTEM CaO - SO_2 - H_2O

Temperature		25	50	70	90	110	130
SO_2	CaO	V.P.	V.P.	V.P.	V.P.	V.P.	V.P.
%	%	cm	cm	cm	cm	cm	cm
1	0.0	9	26	52	96	166	275
1	0.5	6	17	40	72	129	235
1	1.0	4	12	30	57	115	212
1	1.5	3	9	22	52	108	203
1	2.0	3	9	22	52	107	202
1	2.5	3	9	22	52	107	202
2	0.0	17	44	82	142	230	353
2	0.5	11	30	62	101	174	303
2	1.0	7	19	42	76	146	263
2	1.5	5	12	25	63	125	240
2	2.0	3	9	22	56	116	220
2	2.5	3	9	22	52	108	210
3	0.0	26	64	104	190	290	431
3	0.5	19	47	88	140	234	375
3	1.0	12	32	62	106	193	325
3	1.5	8	20	43	87	162	295
3	2.0	6	13	35	74	140	275
3	2.5	4	11	31	66	127	256
4	0.0	36	85	148	237	355	518
4	0.5	29	68	119	190	295	462
4	1.0	23	52	91	152	250	409
4	1.5	17	36	67	123	218	372
4	2.0	11	22	53	102	190	340
4	2.5	6	13	36	88	170	314
5	0.0	46	107	180	283	420	610
5	0.5	41	87	155	244	374	560
5	1.0	35	76	130	210	332	516
5	1.5	29	57	102	180	293	467
5	2.0	18	37	80	152	256	420
5	2.5	8	18	63	130	226	377
6	0.0	57	128	223	330	484	709
6	0.5	54	117	198	302	452	675
6	1.0	49	102	175	275	414	635
6	1.5	42	79	140	242	375	580
6	2.0	27	55	110	210	331	516
6	2.5	13	32	86	180	290	450

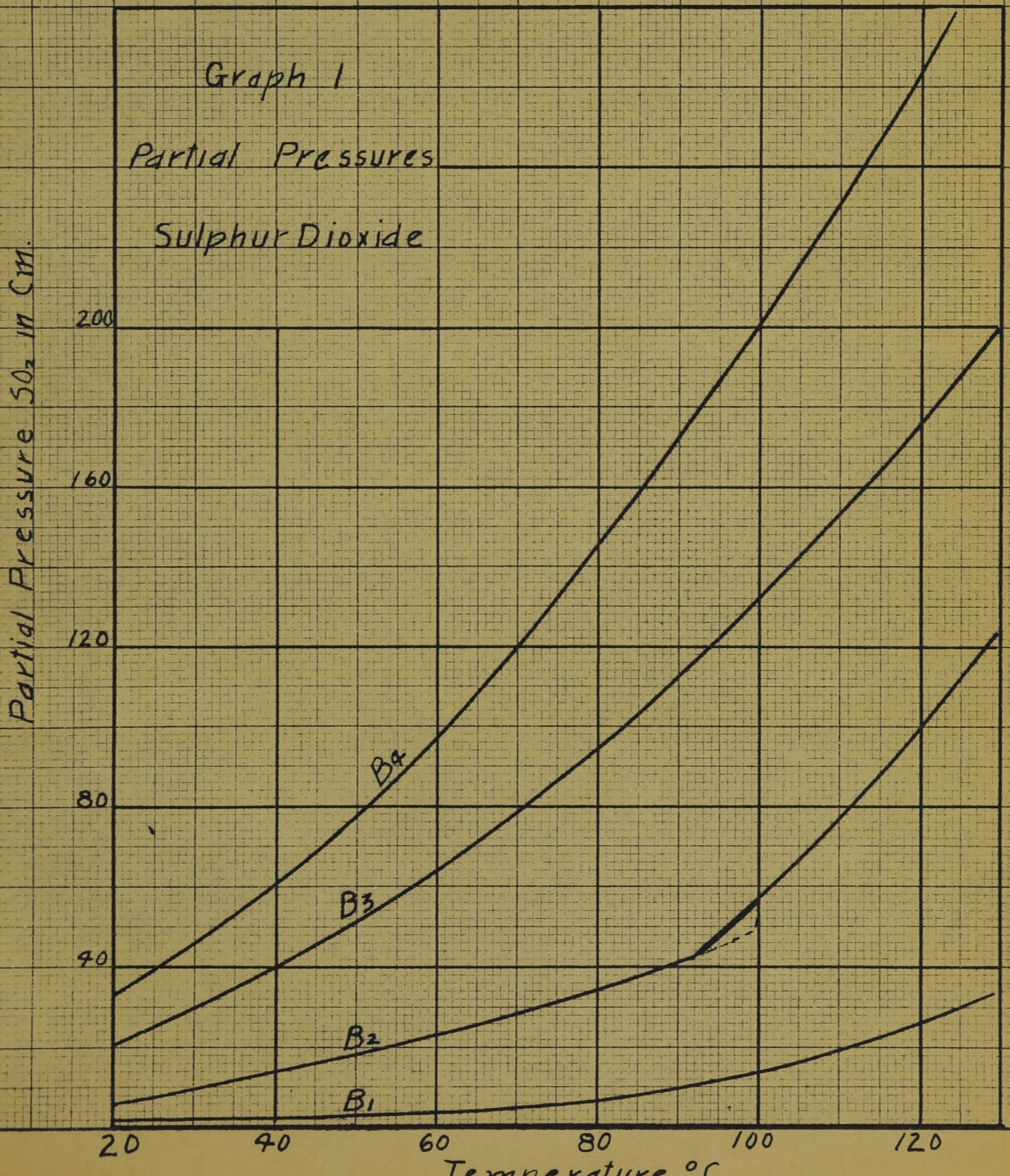
- **TABLE XI** -

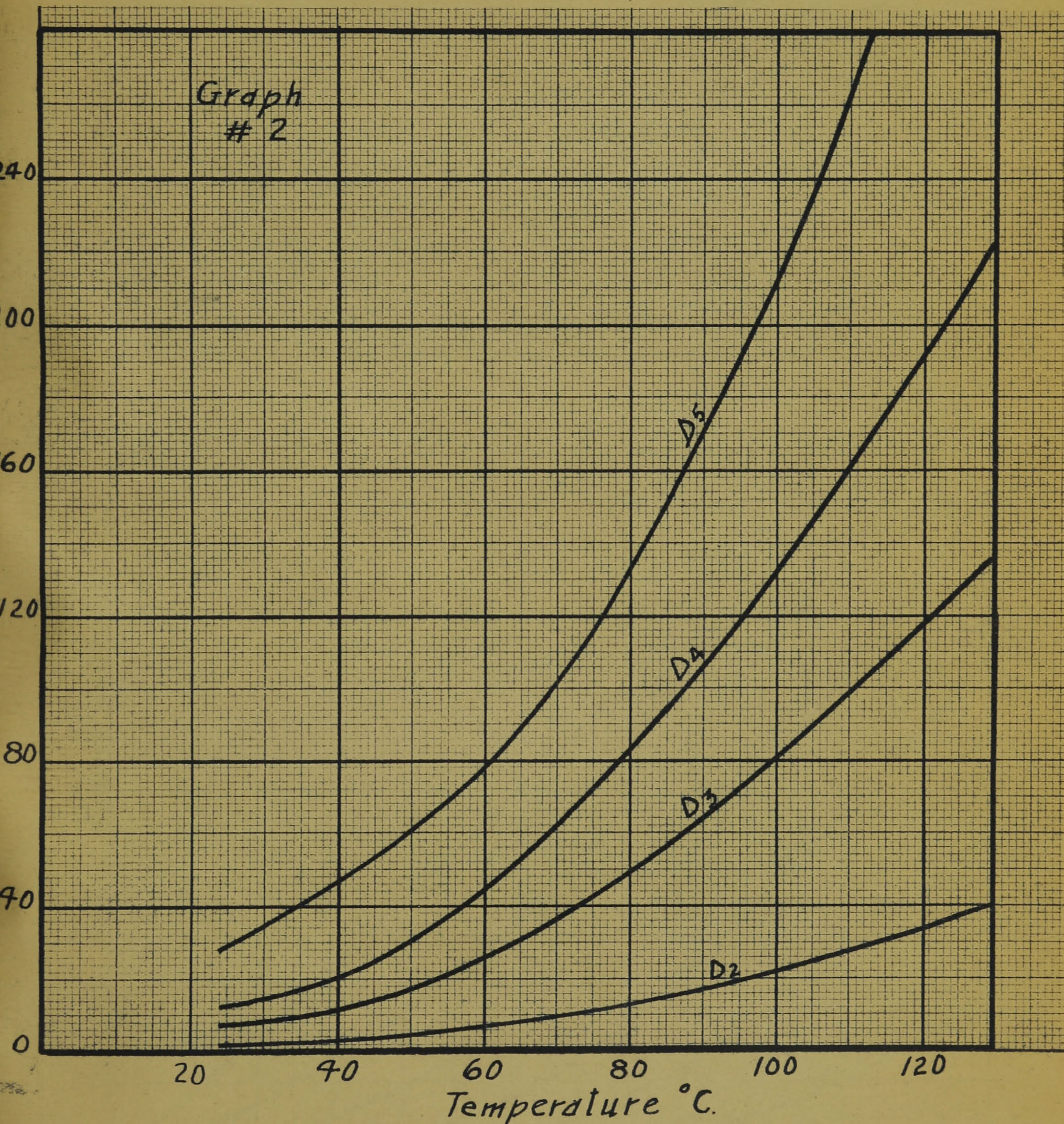
TABLE XII

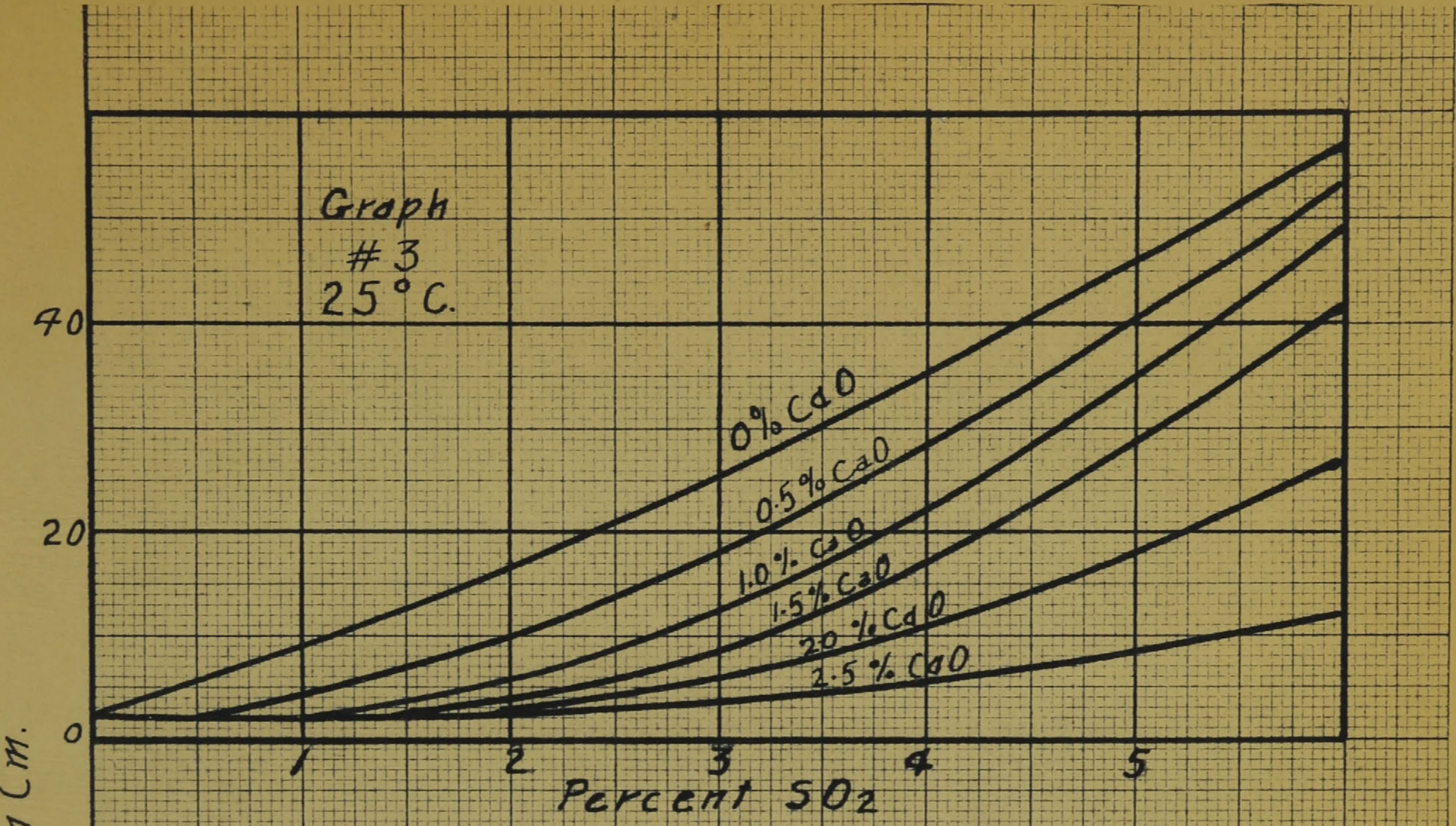
CONDUCTIVITIES OF THE SYSTEM CaO - SO_2 - H_2O -

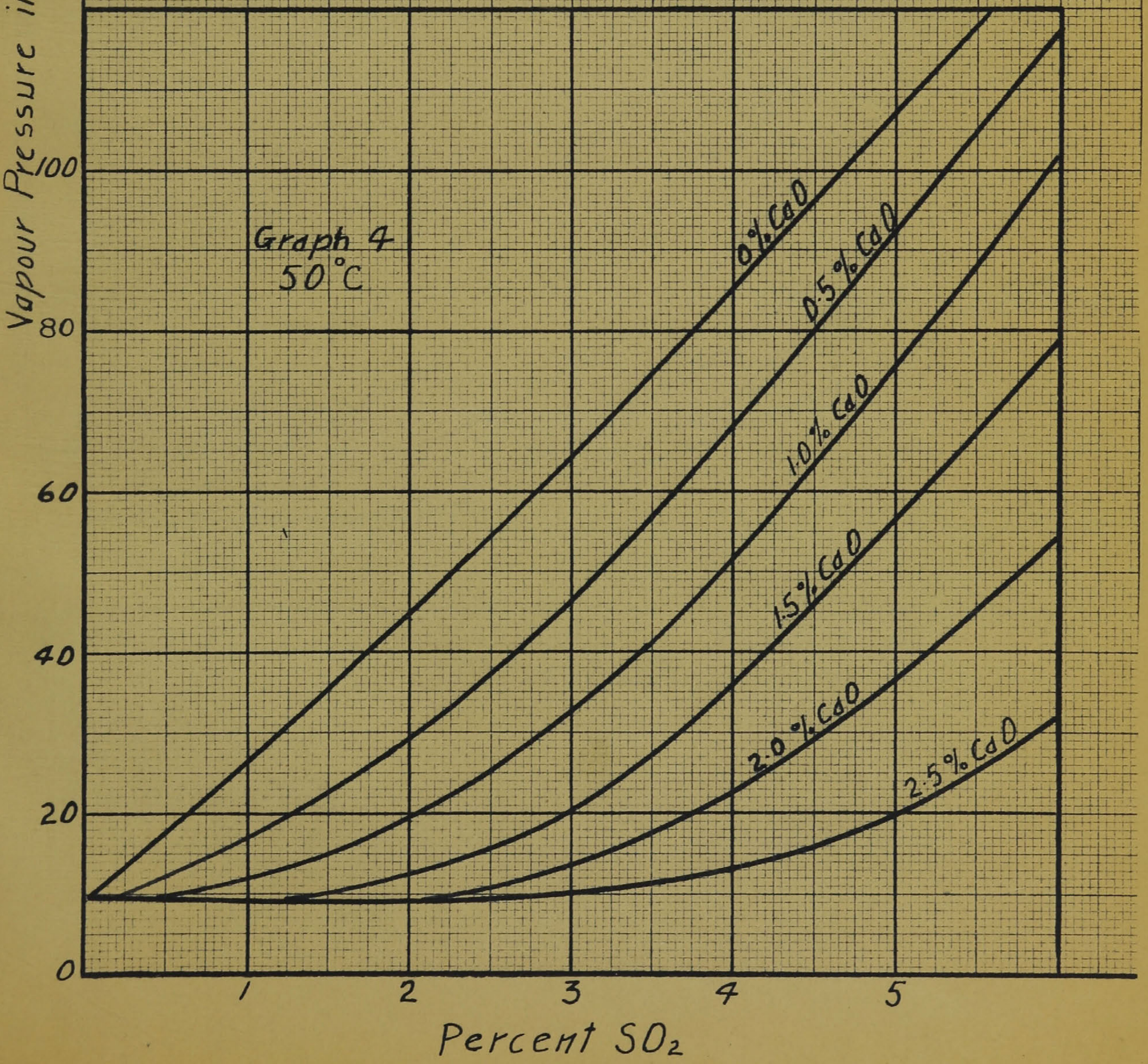
	Temperatures	25	50	70	90
SO_2 %	CaO %	Sp.Cond. $Ohms^{-1}$	Sp.Cond. $Ohms^{-1}$	Sp.Cond. $Ohms^{-1}$	Sp.Cond. $Ohms^{-1}$
1	0.0	.0190	.0188	.0175	.0150
1	0.5	.0150	.0137	.0150	.0128
1	1.0	.0090	.0057	.0061	.0054
1	1.5	.0065	.0070	.0070	.0090
1	2.0	.0065	.0075	.0082	.0095
1	2.5	.0065	.0075	.0082	.0095
2	0.0	.0265	.0254	.0240	.0208
2	0.5	.0237	.0264	.0304	.0351
2	1.0	.0180	.0260	.0329	.0390
2	1.5	.0118	.0216	.0278	.0346
2	2.0	.0055	.0093	.0108	.0126
2	2.5	-	-	-	-
3	0.0	.0330	.0327	.0285	.0245
3	0.5	.0272	.0335	.0370	.0421
3	1.0	.0239	.0330	.0423	.0500
3	1.5	.0212	.0300	.0410	.0477
3	2.0	.0195	.0235	.0300	.0321
3	2.5	.0180	.0157	-	-
4	0.0	.0383	.0376	.0330	.0280
4	0.5	.0313	.0380	.0406	.0443
4	1.0	.0277	.0380	.0456	.0530
4	1.5	.0265	.0377	.0451	.0523
4	2.0	.0267	.0367	.0418	.0455
4	2.5	.0284	.0354	.0327	.0316
5	0.0	.0435	.0415	.0370	.0310
5	0.5	.0348	.0398	.0423	.0450
5	1.0	.0317	.0400	.0468	.0535
5	1.5	.0321	.0420	.0500	.0553
5	2.0	.0342	.0457	.0520	.0532
5	2.5	.0375	.0510	.0535	.0497
6	0.0	.0475	.0455	.0400	.0335
6	0.5	.0372	.0415	.0432	.0455
6	1.0	.0342	.0412	.0474	.0535
6	1.5	.0352	.0452	.0528	.0575
6	2.0	.0381	.0530	.0598	.0588
6	2.5	.0424	.0635	.0677	.0593

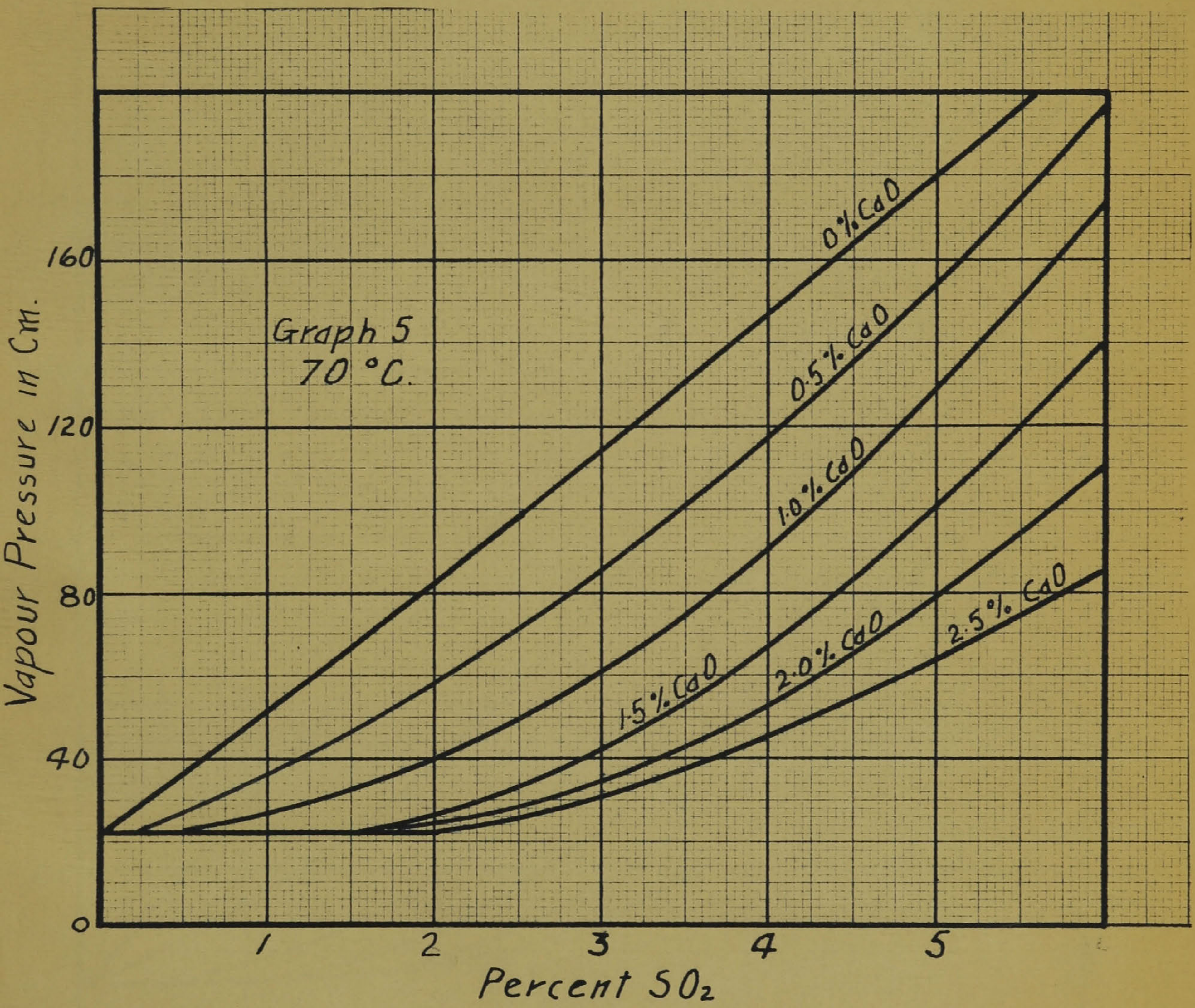
- TABLE XII -

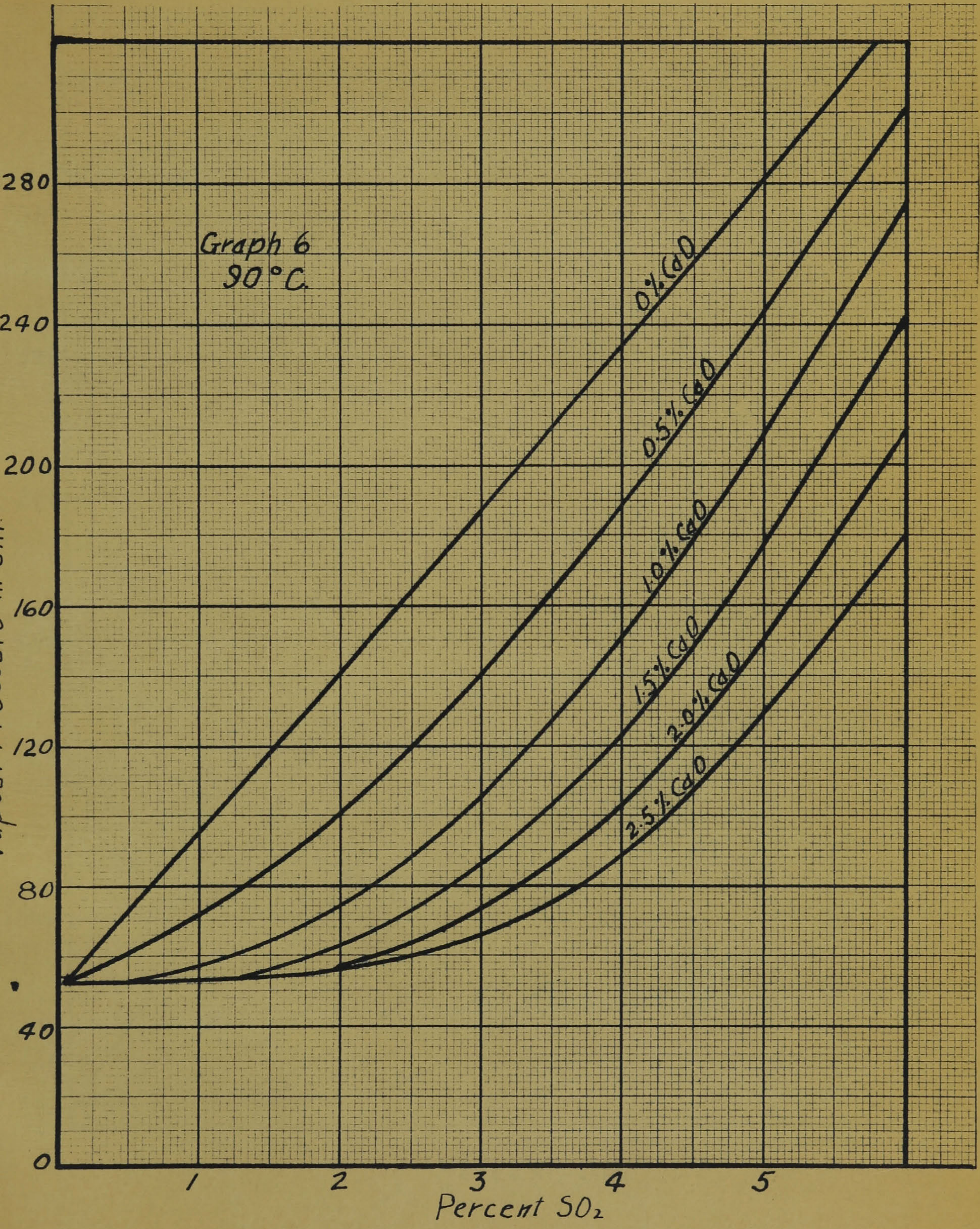

Graph 1
Partial Pressures
Sulphur Dioxide
Partial Pressure SO_2 in Cm.
200
160
120
80
40
B4
B3
B2
B1
20
40
60
80
100
120
Temperature °C

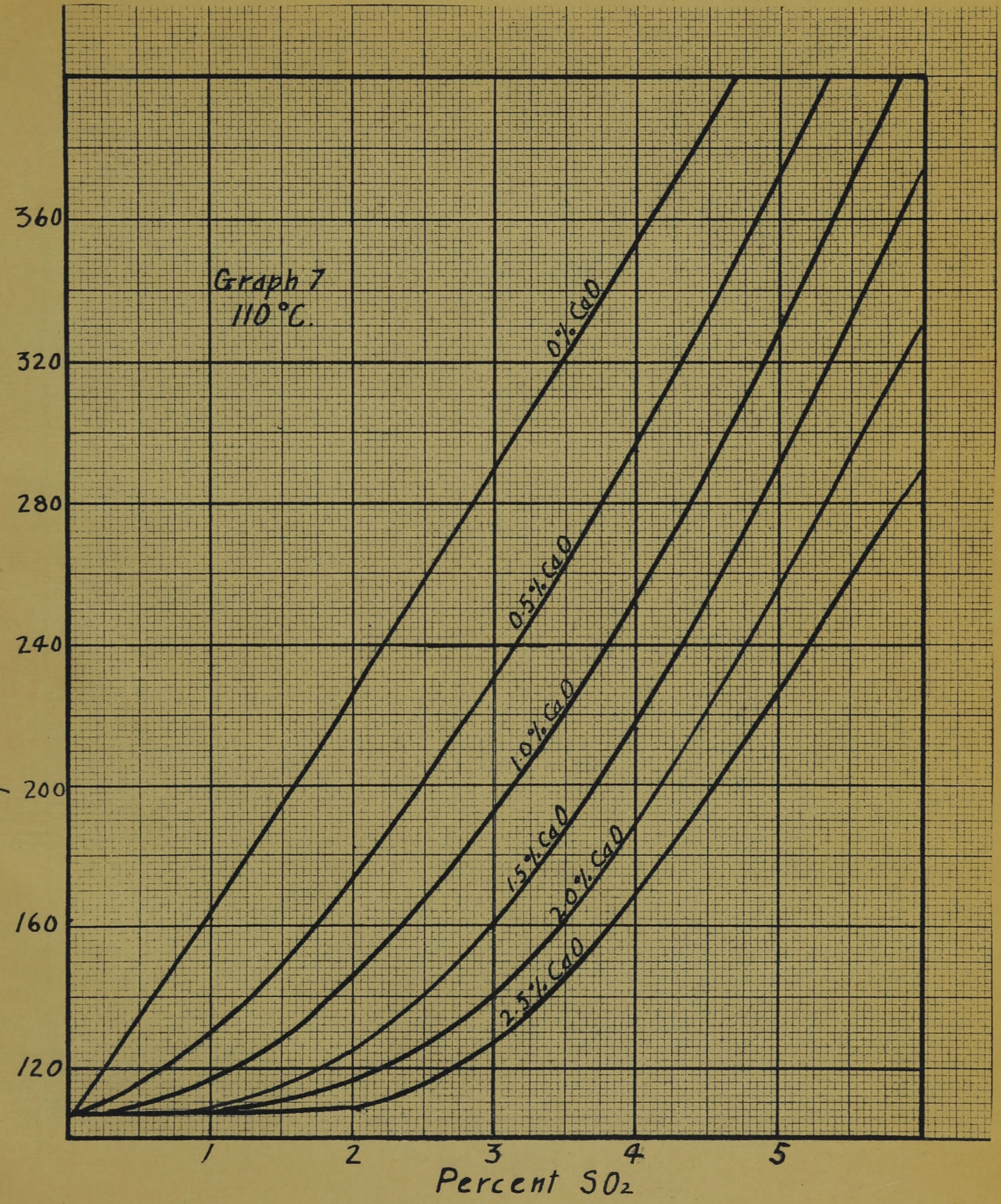

Graph
2
240
00
60
120
80
40
0
20
40
60
80
100
120
Temperature °C.
D5
D4
D3
D2

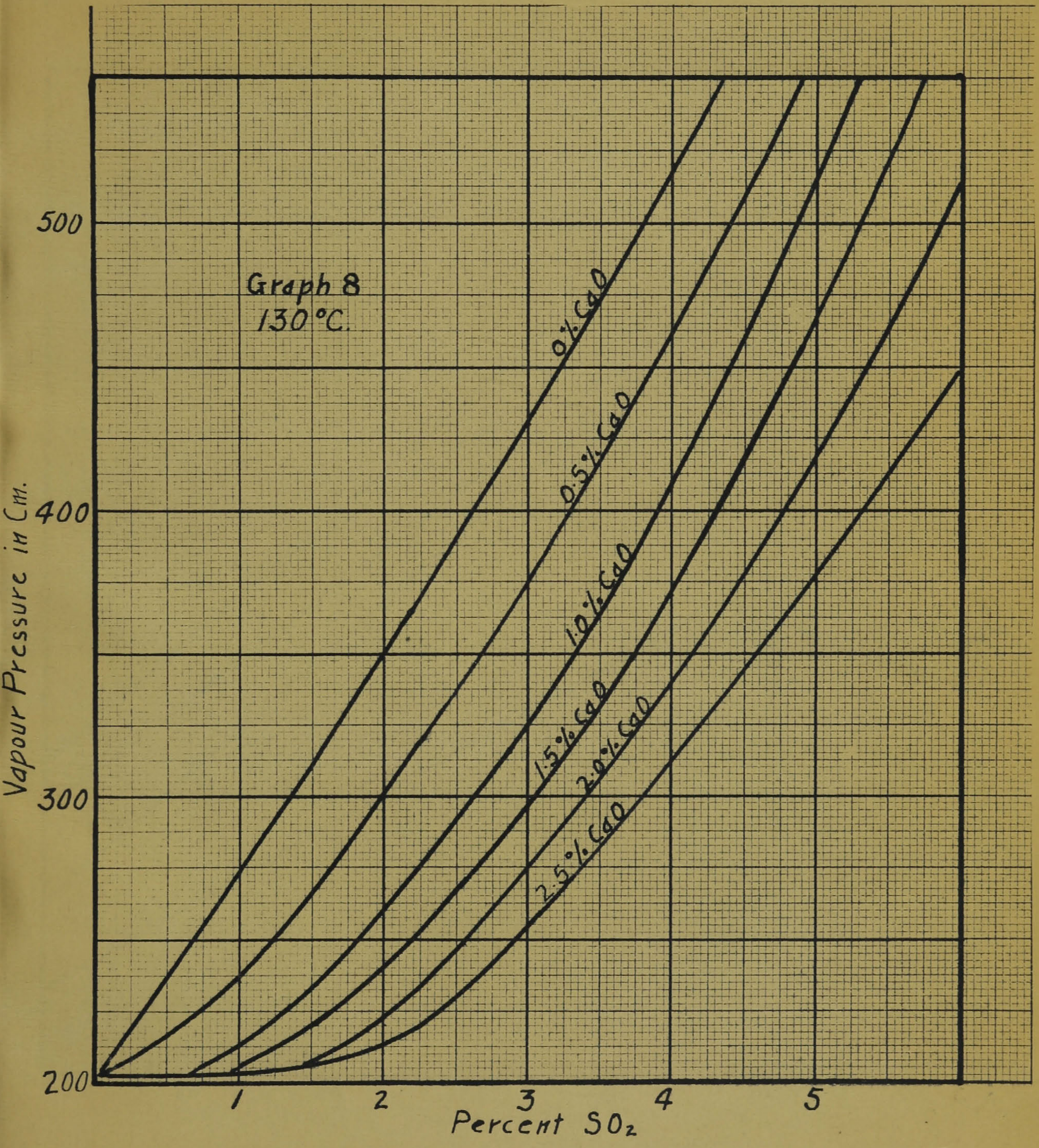

Graph
#3
25°C.
40
20
0
1
2
3
4
5
Percent SO_2
0% CaO
0.5% CaO
1.0% CaO
1.5% CaO
2.0% CaO
2.5% CaO

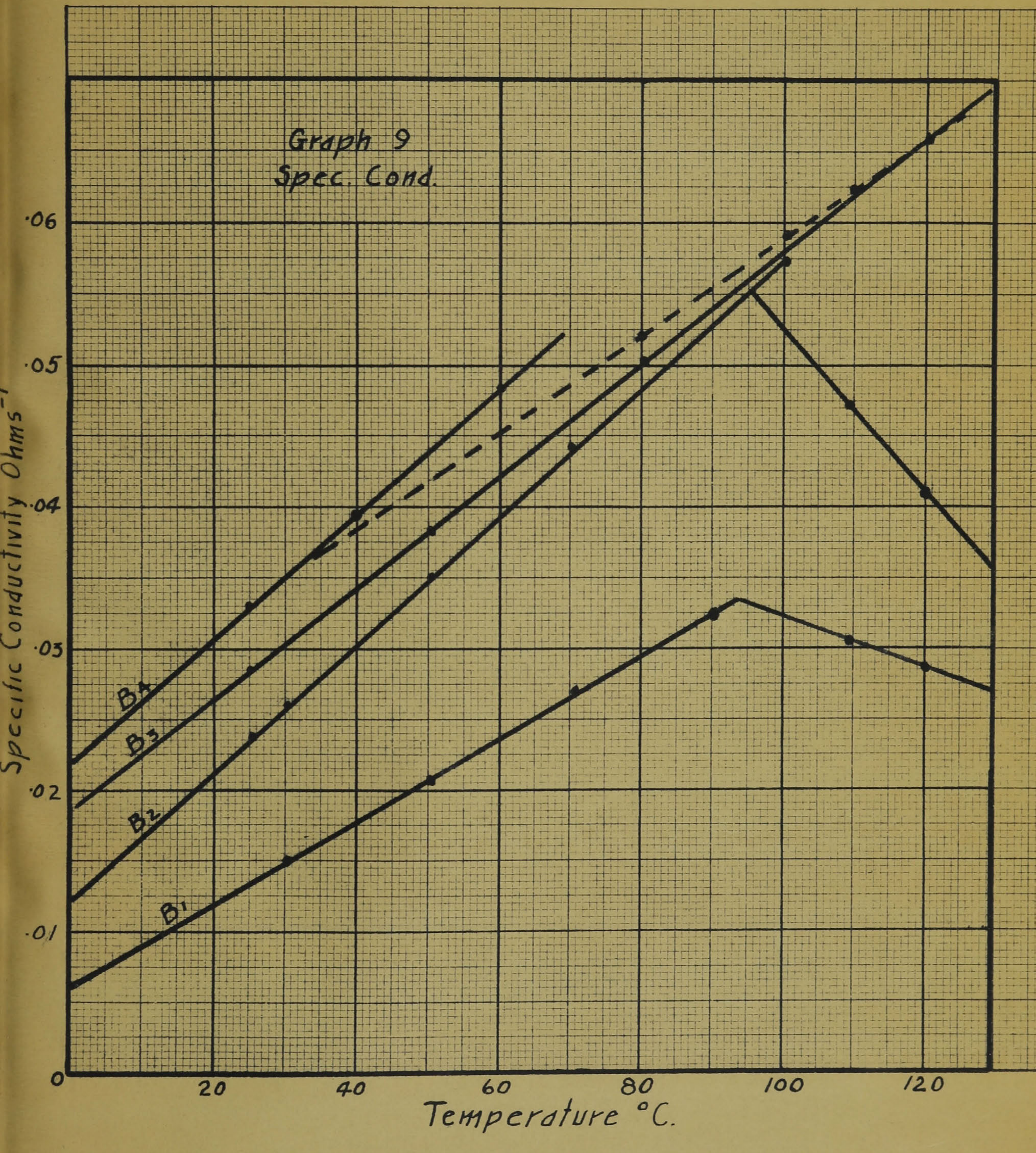

Vapour Pressure in Cm.
Graph 4
50°C
100
80
60
40
20
0
1
2
3
4
5
Percent SO_2
0% CaO
0.5% CaO
1.0% CaO
1.5% CaO
2.0% CaO
2.5% CaO

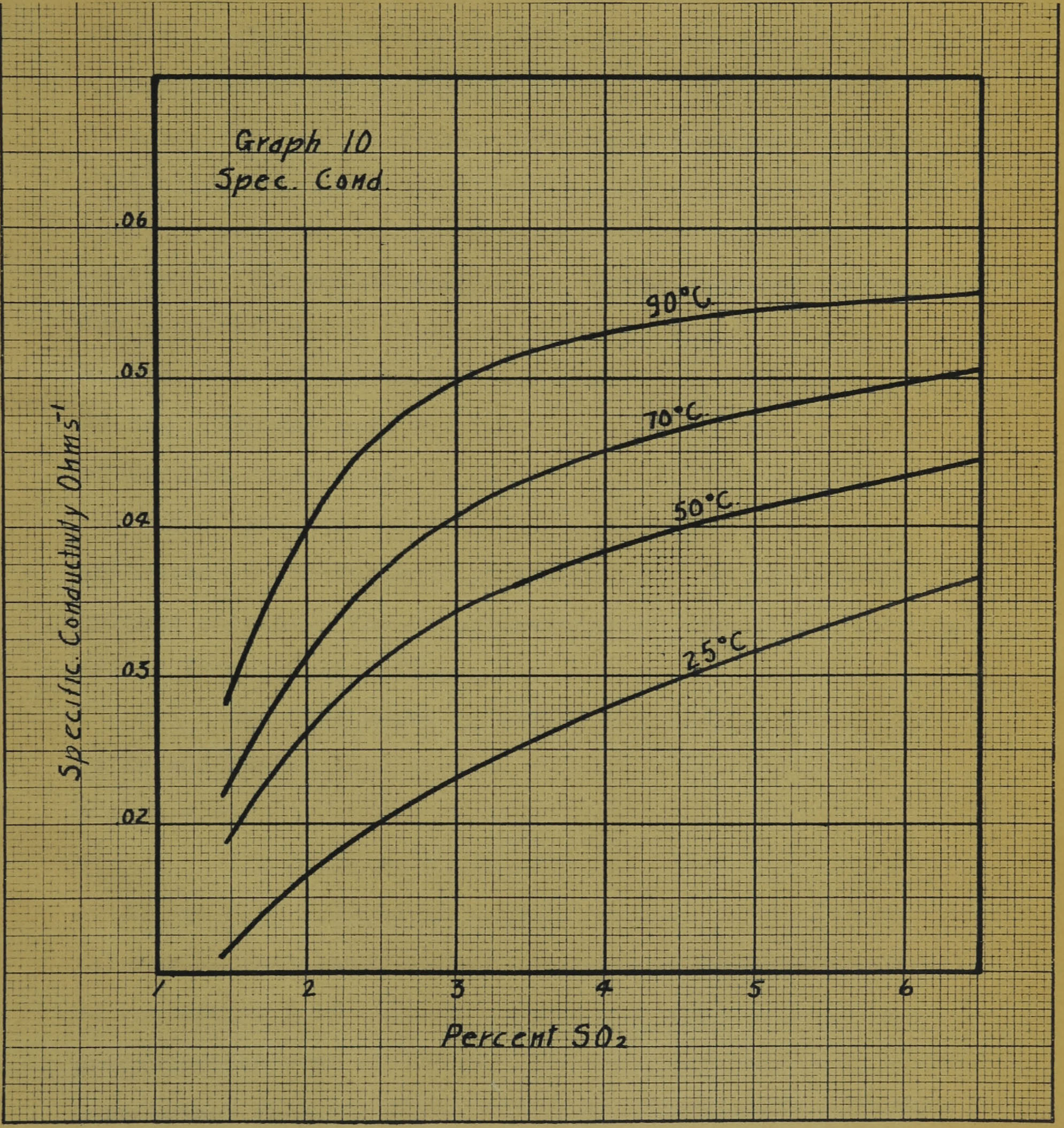

Graph 5
70 °C.
Vapour Pressure in Cm.
0
40
80
120
160
1
2
3
4
5
Percent SO_2
0% CaO
0.5% CaO
1.0% CaO
1.5% CaO
2.0% CaO
2.5% CaO


Graph 6
90°C.
0% CaO
0.5% CaO
1.0% CaO
1.5% CaO
2.0% CaO
2.5% CaO
280
240
200
160
120
80
40
0
1
2
3
4
5
Percent SO_2


Graph 7
110°C.
360
320
280
240
200
160
120
0% CaO
0.5% CaO
1.0% CaO
1.5% CaO
2.0% CaO
2.5% CaO
1
2
3
4
5
Percent SO2


Graph 8
130°C.
Vapour Pressure in Cm.
500
400
300
200
Percent SO₂
1
2
3
4
5
0% CaO
0.5% CaO
1.0% CaO
1.5% CaO
2.0% CaO
2.5% CaO


Graph 9
Spec. Cond.
Specific Conductivity Ohms⁻¹
·06
·05
·04
·03
·02
·01
0
20
40
60
80
100
120
Temperature °C.
B4
B3
B2
B1


Graph 10
Spec. Cond.
.06
.05
.04
.03
.02
Specific Conductivity Ohms^{-1}
90°C
70°C
50°C
25°C
1
2
3
4
5
6
Percent SO_2

RESULTS.

Part II. Solubility Studies

Seventeen different concentrations were studied. These were divided into four series. Series A consisted of six different concentrations of sulphur dioxide. In each of these, there were 1.2 grams of calcium oxide per 100 grams of water. It was very necessary that the calcium content of each of these solutions be constant. The method adopted to obtain this was to pipette the required amount of water into each bomb. In this series, some of the bombs contained 50 cc. water and some 25 cc. Extreme care was taken to add to each a quantity of calcium oxide equal to 1.2% of the weight of water. On the other hand, the percent of sulphur dioxide added was estimated on the basis of the water plus calcium oxide plus sulphur dioxide. The concentrations of the sulphur dioxide varied from 1.9 to 6.7%.

The five bombs in series B contained 2% calcium oxide and the sulphur dioxide concentration varied from 3.6 to 6.6%.

Six bombs were prepared containing 0.6% calcium oxide and from 1.22 to 5% sulphur dioxide. Bomb #3 containing 1.48% sulphur dioxide precipitated at 130°C. Bomb #4 containing 2.9% sulphur dioxide could not be made to precipitation even at 152°C. The apparatus built for these experiments were designed to work at temperatures no higher than 130°C. It was, therefore, considered inadvisable to push the temperature above 152°C., and this showed that it would be useless to study the two remaining bombs which had a higher sulphur dioxide concentration. Series D is a repetition of series B, except that two different commercial peptizing agents were added to study their effect on the precipitation temperature. (ID was Gardinal (CA), and 2D was Brilliant Avirol (L-142)).

The results are shown in the following table (Table XIII), and graph (Graph 15). In this graph, temperature was plotted against the sulphur dioxide concentration and curves were drawn for constant calcium oxide content. The points all fall on a smooth curve, except for 3A, which is a very good example of persistant supersaturation.

The best method for illustrating this supersaturation, is to include an experiment as made in the laboratory: "#2A and 3A were put on the wheel and heated up rapidly till a precipitate began to form at 109°C. in #2A, the temperature was held there, and soon a heavy precipitate was formed consisting of large white flakes. The bath was heated up to 127°C., but #3A did not precipitate out.

The bath was cooled down until the precipitate in #2A dissolved. It was then heated up slowly, and at 102°C., a precipitate was formed. It was cooled down and at 74°C., the precipitate was all dissolved. The bath was heated to 95°C., and then very slowly to

97°C., where a faint precipitate formed. It was then cooled down and heated up to 90°C. It was heated from there at the rate of one degree per hour and held at 93°C. for an hour with no precipitation. No precipitation took place till 97°C. was reached. Slightly above this temperature a copeous precipitate was formed."

A similar procedure with #3A yielded the following series of precipitation temperatures: 135°C., 123°C., 118.5°C, and 117°C. After precipitation, #3A was held at 105°C. for three hours, and it could be noticed that only a small amount of the precipitate had gone into solution.

At the bottom of the table, three precipitation temperatures are added which had been obtained in part I of this thesis. The first one with a calcium content of 1.19% should fall just above the middle curve in Graph (15), which it does, therefore, indicating the close relation between this work and the work in Section I. The two solutions with a calcium content of 2.3% appear to have precipitation temperatures much lower than would be expected when compared with the curves for 1.2 and 2% calcium oxide. However, this is of special interest when compared with the relation between the curves of 1.2 and 0.6% calcium oxide. Further discussion must be reserved for a later section.

Precipitation Temperatures.

TABLE XIII

	Vol.	Wt.	Wt.	%	Ratio	Prec.
A	H_2O	CaD	SO_2	SO_2	SO_2/CaO	Temp.
1	50	0.600	0.9658	1.87	1.41	50.5
2	25	0.300	0.814	3.29	2.44	97.0
3	50	0.600	2.282	4.32	3.33	117.0
4	50	0.600	2.531	4.76	3.69	117.0
5	25	0.300	1.558	5.78	4.50	135.0
6	25	0.300	1.822	6.72	5.27	137.0
B						
1	25	0.500	0.9649	3.64	1.69	45.0
2	25	0.500	1.091	4.09	1.91	75.7
3	25	0.500	1.411	5.25	2.47	93.0
4	25	0.499	1.644	6.07	2.88	103.5
5	25	0.495	1.802	6.60	3.18	107.5
C						
1	25	0.1505	0.3114	1.22	1.82	100.0
2	25	0.150	0.3523	1.38	2.06	116.0
3	25	0.150	0.3772	1.48	2.20	130.0
4	25	0.150	0.7496	2.89	4.38	7152.0
D						
1	25	0.501	1.330	4.96	2.32	117.8
2	25	0.498	1.192	4.45	2.10	95.5

Precipitation Results from Part I.

84.26	.987	2.70	3.08	2.38	95
88.29	2.06	5.30	5.56	2.25	57
88.29	2.06	6.80	7.00	2.88	65

The graph representing these results will be found in the section on the discussion of results where it will be referred to frequently.

RESULTS.

Part III. COOKING EXPERIMENTS

Six cooking experiments were made. The temperature was maintained at 130°C. in each. For each experiment, a different concentration of calcium oxide and sulphur dioxide was used, but the range of concentration was kept narrow in order to make comparison possible. Aside from knowing accurately the vapour pressure changes during each experiment, it was found of interest to compare the pressures obtained with the pressures, the same system would have in the absence of wood. This was made possible by using the data obtained in Part I of this thesis. The results of the six experiments are given in two forms. Tables 14 and 15 give the change of vapour pressure with time, whereas, the tables following these deal with each experiment separately.

The quantity of water, calcium oxide and sulphur dioxide is statedtogether with the maximum vapour pressure at 25°C., before and after each cook. Experiments I and 2 were made using spruce woodmeal that would pass a 100 mesh screen. Experiments 5 and 6 were made with a coarser spruce woodmeal. The results of these four experiments are shown in Graph 18. The final pressures in each are indicated. #1 was held at 130 C. for eight hours and it can be seen that the pressure increases steadily. #2 was a much longer experiment, and it contains a definite maximum. This maximum appears still sharper in #6, whereas, the pressure in #5 appears to be reaching a maximum towards the end of the cook.

TABLE XIV

Pure cellulose was used in experiment #3, whereas, #4 contained only the sulphite liquor and was made for two purposes. In the first place, it acted as a check on the accuracy of the method of filling the cell, and secondly, it indicated the time required to reach equilibrium.

The results shown bring out many points of interest, but a detailed discussion of these will be left for a later section.

	E 1	E 2	E 3	E 3A
	Total V.P.	V.P.	V.P.	V.P.
Initial P.	26.5	30.2	28.1	31.5
0	412.1	347.8	395.1	401.4
0.5	412.8	349.9		
1	414.2		406.1	402.6
1.5	418.4	352.5	407.7	
2	419.1	354.8	411.1	409.6
2.5	422.1	357.5		
3	424.3	359.4	415.1	412.2
3.5	427.4	362.1		
4	429.8		419.0	416.0
4.5	432.5	365.8	419.0	
5	435.6	369.0		417.6
5.5	440.2	371.3		
6	444.1		419.2	
6.5	446.5	375.2		
7	451.1	378.2	420.2	
7.5	455.0	339.0	420.2	
8	456.9		420.2	
8.5		385.0	420.2	
9.		386.0	420.2	
9.5		388.0		
10		390.0		
10.5		391.8	422.5	
11		392.5		
11.5		389.0		
12.		386.7		
12.5		384.9		
13		383.1		
Final P.	48.5	63.1	31.5	33.4

TABLE XV

Time	E 4	E 5	E 6	E 6A
	V.P.cm.	V.P.cm.	V.P.cm.	V.P.cm.
Initial P.	25.9	24.3	31.5	61.0
0	389.6	370.9	437.9	409.0
.5	416.4		438.2	423.6
1	417.7	378.1	440.4	426.7
1.5	423.4	383.0	445.1	428.9
2	421.9	386.1	447.6	429.3
2.5	422.2		450.2	430.5
3	423.2	395.0	455.3	431.8
3.5		398.6		433.6
4		402.2	460.8	435.4
4.5		405.7		434.1
5		409.2	466.7	
5.5		413.5	471.4	438.9
6		416.0	475.0	
6.5				443.1
7		420.0	480.6	444.2
7.5			484.6	447.8
8		426.7	487.0	449.6
8.5			484.5	452.6
9		427.2	479.9	455.4
9.5			469.2	458.3
10				460.3
10.5			466.4	463.1
11				468.7
11.5			461.9	
12				
12.5			458.0	476.5
13			456.8	
13.5			454.8	480.8
14				
14.5				491.2
15				
15.5				497.8
16				
16.5				502.0
17				
17.5				
		66.6	61.0	134.3

RUN #I.

Wt.	Water	60.958 g.	
"	CaO	.804 "	- 1.23%
"	SO_2	3.395 "	- 5.21%
"	Wood (dry)	7.23 "	

SO_2 in liquid phase at start of cook - 3.280 g. - 5.03%

SO_2 " " " after 8 hours - 3.266 G. - 5.015%

Ratio liquor / wood - 9.02

VP of liquor calculated at 25°C. - 34.2 cm.
VP " " and wood found " " " - 32.5 "
Difference - 1.7 "

VP of liquor calculated at 130°C. - 471 cm.
VP " " and wood found " " " - 412 cm. at start
VP " " " " " " " " - 457 cm. after 8 hours.

Yield pulp 48%

Lignin 1.9%

<u>RUN #2.</u>

Wt. Water	41.992 g.	
" CaO	0.535 "	- 1.2%
" SO_2	2.082 "	- 4.67%
" Wood (dry)	8.26 "	-

SO_2 in liquid phase at start of cook - 1.921 g. - 4.31%
" " " " after 11 hours - 1.873 " - 4.20%
" " " " " 13 " - 1.882 " - 4.22%

Ratio liquor / wood - 5.4

VP of liquor calculated at 25°C. - 27.5 cm.
VP " " and wood found 25°C. - 26.8 "
Difference - 0.7 "

VP during cooking 130°C.	Calculated	Found
At start	401 cm.	348 cm.
" 11th hour	393 "	392 "
" 13th "	395 "	383 "

VP after run at 25°C. Calc. 27.5 Found 61.8 cm.

Yield pulp 48%

Lignin 1.03%

RUN #3.

Wt. Water 44.000 g.

" CaO 0.605 g. - 1.29%

" SO_2 2.486 g.

" Cellulose 3.262 g.

SO_2 in liquid phase during cook 2.361 g. - 5.02%

Ratio liquor / cellulose -14.4

VP of liquor calculated at 25°C. 31.5 cm.

VP " " & cel. found " 25°C. 28.5 cm.

Difference 3.0 cm.

VP during cooking at 130°C. Calculated Found

480 cm. 420 cm.

VP after run at 25°C. Calc. 31.5 cm. Found A.33.5 B.33.4 cm.

Yield pulp 3 g. - 92%

RUN #4

Wt. water 47.340 g.

" CaO .5982 " - 1.18%

" SO_2 2.530 " - 5.03%

50.468 grams.

SO_2 in liquid phase during cook 2.285 g. - 452%

VP of liquor calc. at 25°C. 27 cm.

VP " " found " 25°C. 26 "

VP " " calc. " 130°C. 435 "

VP " " found " 130°C. 423 "

RUN #5.

Wt. water	47.586 g.	
" CaO	.6004 "	- 1.19%
" SO_2	2.266 "	- 4.49%
" wood	7.94 "	
Wt. SO_2 in liquid phase	2.074 "	
% " " " "	4.12%	

VP of SO_2 at 25°C. Calculated 26.0 cm. Found 24.3 cm. at start
" 66.6 " " end.

Max. Pressure 427 cm. found
420 " calcium.

RUN #6.

Wt. water	48.200 g.	
" CaO	.5979 "	- 1.16%
" SO_2	2.6274 "	- 5.12%
" wood (dry)	6.938 "	

% SO_2 in liquid phase at 130°C. 4.87%

VP at room temperature. Calculated 34.5 cm. Found 31.5 at start
" 61 after 1st step.
" 134 after 2nd step.

VP at 130°C. Calculated 483 cm. Found 487 cm.

DISCUSSION OF RESULTS

PART I

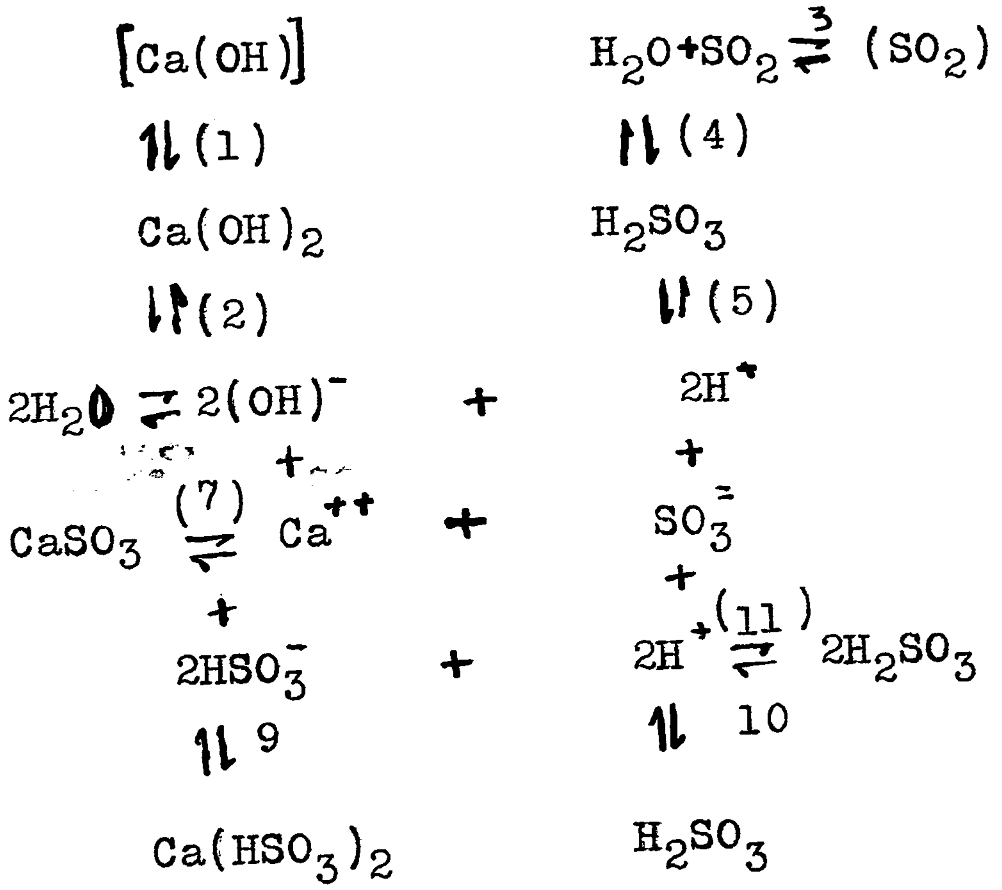
The System CaO - SO_2 - H_2O.

It has been stated above that the object of this part of the research was to obtain data to permit the determination of the various unknown equilibria existing in the system SO_2 - CaO - H_2O. Sufficient data on vapour pressures and conductivities of this system have been obtained, in order to check the work of Gurd (2) and to make it possible to correlate the results of Campbell (41), Gurd and the writer. Vapour pressures and conductivities are now known over a wide temperature and concentration range.

Where comparison was possible, the agreement was good. The best place to compare the results with Gurd's data is at 1% CaO concentration and the results given above at 1.2% CaO. In practically all cases, the results checked to better than 2%. The one marked digression was the conductivity values at about 3% SO_2. In graph 9, specific conductivities were plotted against temperature. In graph 10, specific conductivities were plotted against per cent SO_2 for temperatures of 25°C., 50°c, 70°C. and 90°C. It was found that the 3% value of B_2 did not fit this curve, but fell considerably above it. The interpolated value, however, agreed with that of Gurd.

In the vapour pressure and conductivity curves correlating the work of Campbell and Gurd with the present results, interpolation had to be relied upon to a considerable extent. The widest area in this regard was between 0 and 1% CaO. The possible errors resulting from this lengthy interpolation were minimized to a considerable extent, because the values at 1.2% CaO served to fix the direction of the curves. It was found that in some cases there was a straight line relationship with all points falling on this line, and in others the curvature was small. Some uncertainty, however, is cast on the direction of the conductivity curves at the higher calcium oxide concentrations and especially at the higher temperatures. The chief reason for this was the behavior of the specific conductivity at the precipitation point. This will be dealt with in a later section.

The very nature of the system CaO - SO_2 - H_2O introduces many difficulties. An indication of the number of equilibria involved may be obtained from the following diagram:



Gaseous SO_2 is in equilibrium with the SO_2 dissolved in the water. This equilibrium may be expressed as

$$[SO_2] \text{ soln} = h [SO_2] \text{gas} = hp$$

Where h = Henry's constant

p = partial pressure of SO

The SO_2 in solution is partially converted to H_2SO_3.C. Maass (3) has evaluated this constant:

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

and has found that it increases rapidly with increase in temperature, thus showing that the dissolved SO_2, which is present as H_2SO_3, decreases as the temperature rises.

The first equilibrium of immediate interest is that of the ionization of sulphurous acid.

$$H_2SO_3 \rightleftarrows H^+ + HSO_3$$

Campbell (1) has determined the hydrogen ion concentration over a wide range of sulphur dioxide concentrations at temperatures from 5°C to 90°C. His values were used as a starting point in the calculation of the hydrogen ion concentration of the three component system CaO - SO_2 - H_2O.

A study of the equilibrium diagram above will indicate the role played by CaO when added to system SO_2- H_2O. The CaO forms the hydroxide which is slightly soluble and which ~~ranges~~ ionizes to some extent. In the presence of a small amount of SO_2, the insoluble salt $CaSO_3$ is formed. In the presence of an excess of SO_2, the CaO passes into solution. It has, up to the present, been assumed that bisulphite ($Ca(HSO_3)_2$) is formed and the first part of the following calculations will be based on this assumption. However, in a later part of this discussion a more critical attitude will be adopted and quantitative deductions will be submitted in support of this attitude.

The system Ca O-SO_2 - H_2O can, under various conditions, contain a wide variety of compounds distributed throughout three phases. Before the system could be dealt with in a quantitative manner, it was necessary to simplify it as much as possible and even to make some assumptions which were admittedly false. However, after first approximations of the hydrogen ion, the calcium ion and the bisulphite ion concentrations had been made, the nature of the assumptions was examined and, by the aid of lengthy calculations, a close approximation to the correct ionic concentrations was made. It will be necessary to present the theory upon which these calculations were made in considerable detail.

The solution was first dealt with under concentration and temperature conditions in which no solid was present. The total SO_2 concentration in the liquid phase may be expressed as:

$$[C_{SO_2} = [SO_2] + [H_2SO_3] + [Ca(HSO_3)_2] + [HSO_3^-{}_{(Ca)}] + [HSO_3^-{}_{(H)}] \cdots\cdots (1)$$

where

$[SO_2]$ = concentration of dissolved SO_2

$[H_2SO_3]$ = " " sulphurous acid

$[Ca(HSO_3)_2]$ = " " calcium bisulpite

$[HSO_3^-{}_{(Ca)}]$ = " " bisulphite ions due to Ca ion

$[HSO_3^-{}_{(H)}]$ = " " bisulphite ions due to H ion.

In order to arrive at afirst approximation of the hydrogen ion concentration, the solution was arbitrarily considered to be made up of two distinct parts, which, for the purpose of the first calculation, had no influence on one another. The calcium was considered to be present in the form of dissolved calcium bisulphite. It was assumed that the excess sulphur dioxide was present as SO_2, H_2SO_3 and as ionized H_2SO_3 and that the calcium bisulphite did not influence the equilibria in this system.

Campbell has determined the sulphite ion and hydrogen ion concentration for solutions of SO_2 in H_2O within the concentration and temperature range used in this work. For any solution of CaO and SO_2, the amount of SO_2 in excess of that required to form calcium bisulphite may be calculated from the following equation:

$$C_{SO_2} - C_{Ca} = [SO_2] + [H_2SO_3] + [HSO_3^-]_{(H)} \quad ....2$$

but

$$[SO_2] + [H_2SO_3] = hp \quad ....3$$

where h = Henry's constant

p = partial pressure of sulphur dioxide.

By using Campbell's data, the value for hp was determined and substituted in equation (2). C_{SO_2} and C_{Ca} were known; (C_{Ca} when expressed as equivalents throughout simplifies later calculations) and $[HSO_3^-]$ (H) could be determined. This value was equal to $[H^+]$ as H_2SO_3 is known to ionize appreciably only in one direction, i.e.,

$$H_2SO_3 \rightleftarrows H^+ + HSO_3^- \quad ....4$$

The value for the hydrogen ion concentration will be too high since the influence on the equilibrium in equation (4) of (HSO) due to the ionization of calcium bisulphite has been ignored. A first approximation for the calcium ion concentration can be made from the following equation:

~~$1000K = n_1u_1(\tfrac{1}{2}Ca^{++}) + n_2u_2[H^+] + n_1u_3(HSO_{3(Ca)}^-) + n_2u_3(HSO_{3(H)}^-)$~~ (5)

$$1000K = n_1u_1+n_2u_2+n_1u_3+n_2u_3$$

where

K = specific conductivity

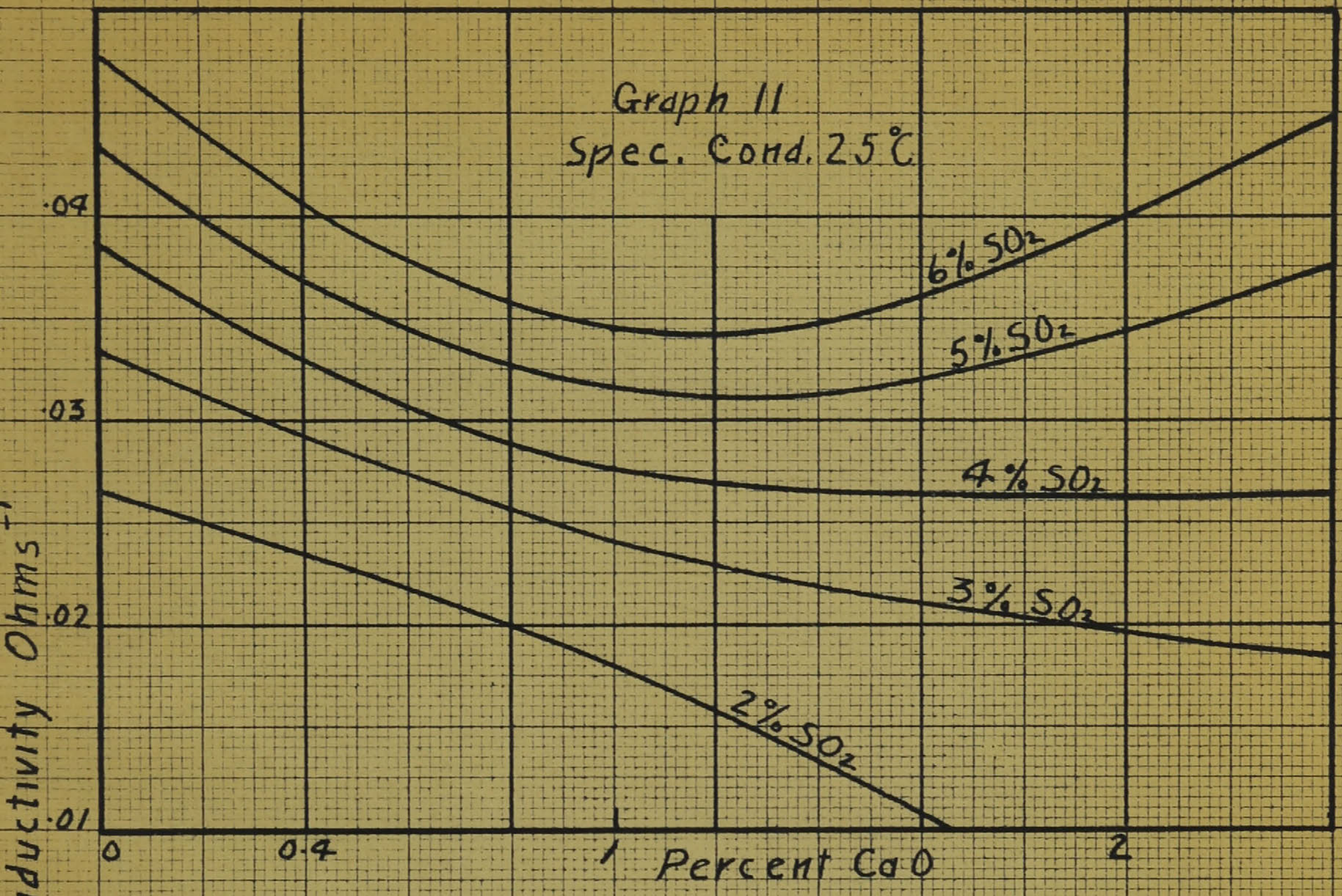
N_1 = concentration of calcium ion expressed in equivalent weights,

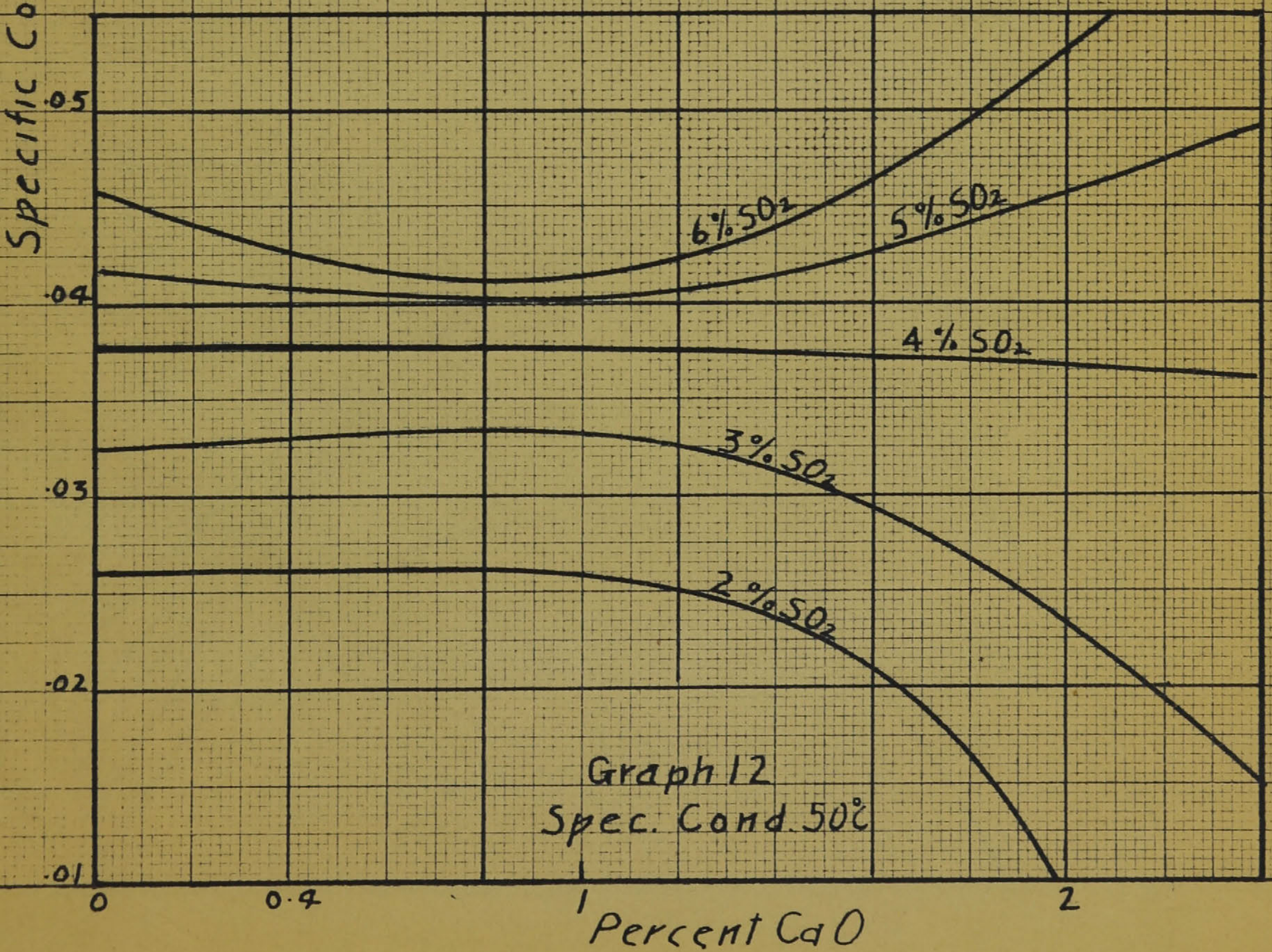
N_2 = concentration of hydrogen ion

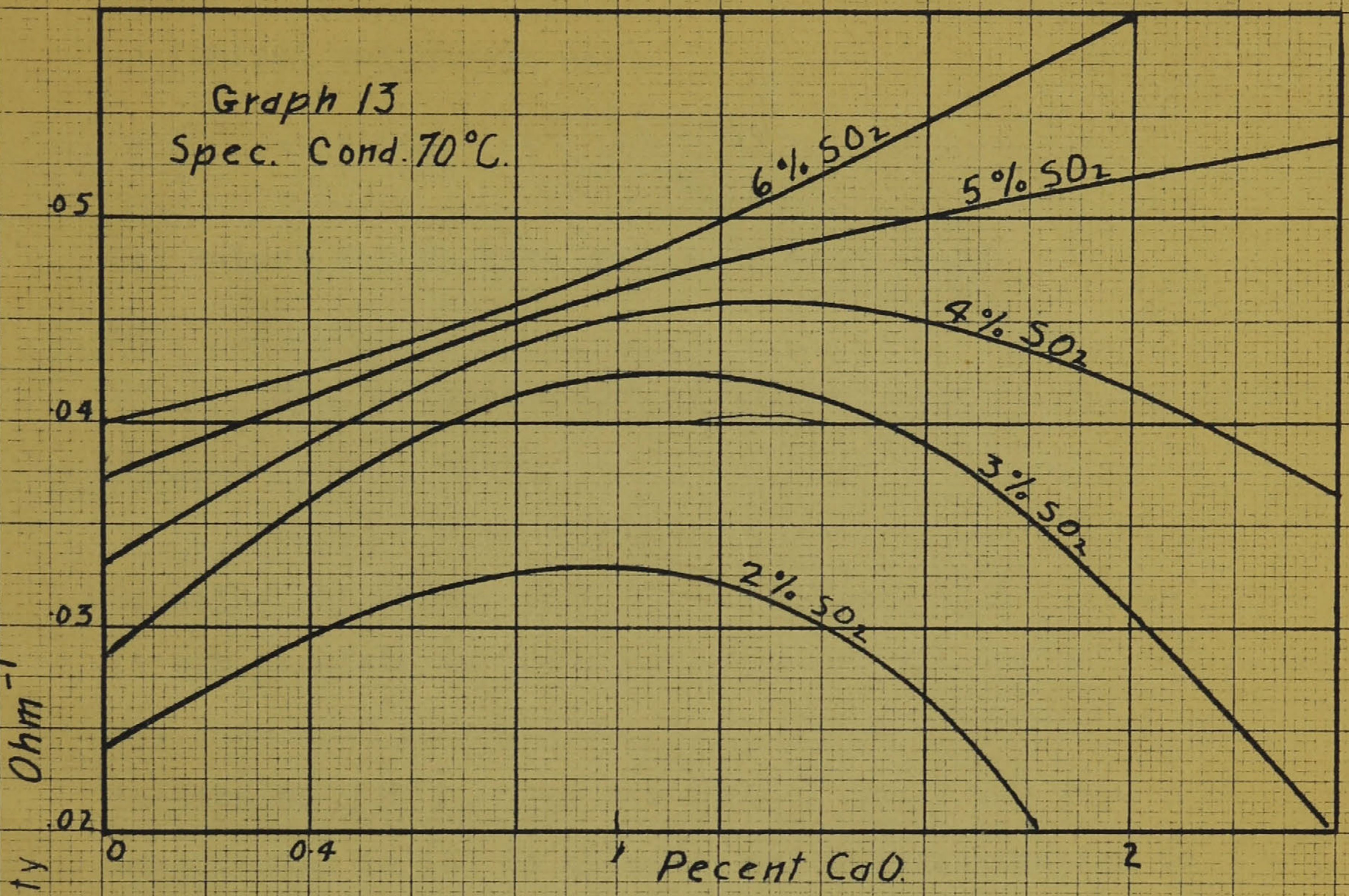
u_1, u_2 and u_3 = the mobility of the calcium, hydrogen and bisulphite ion respectively.

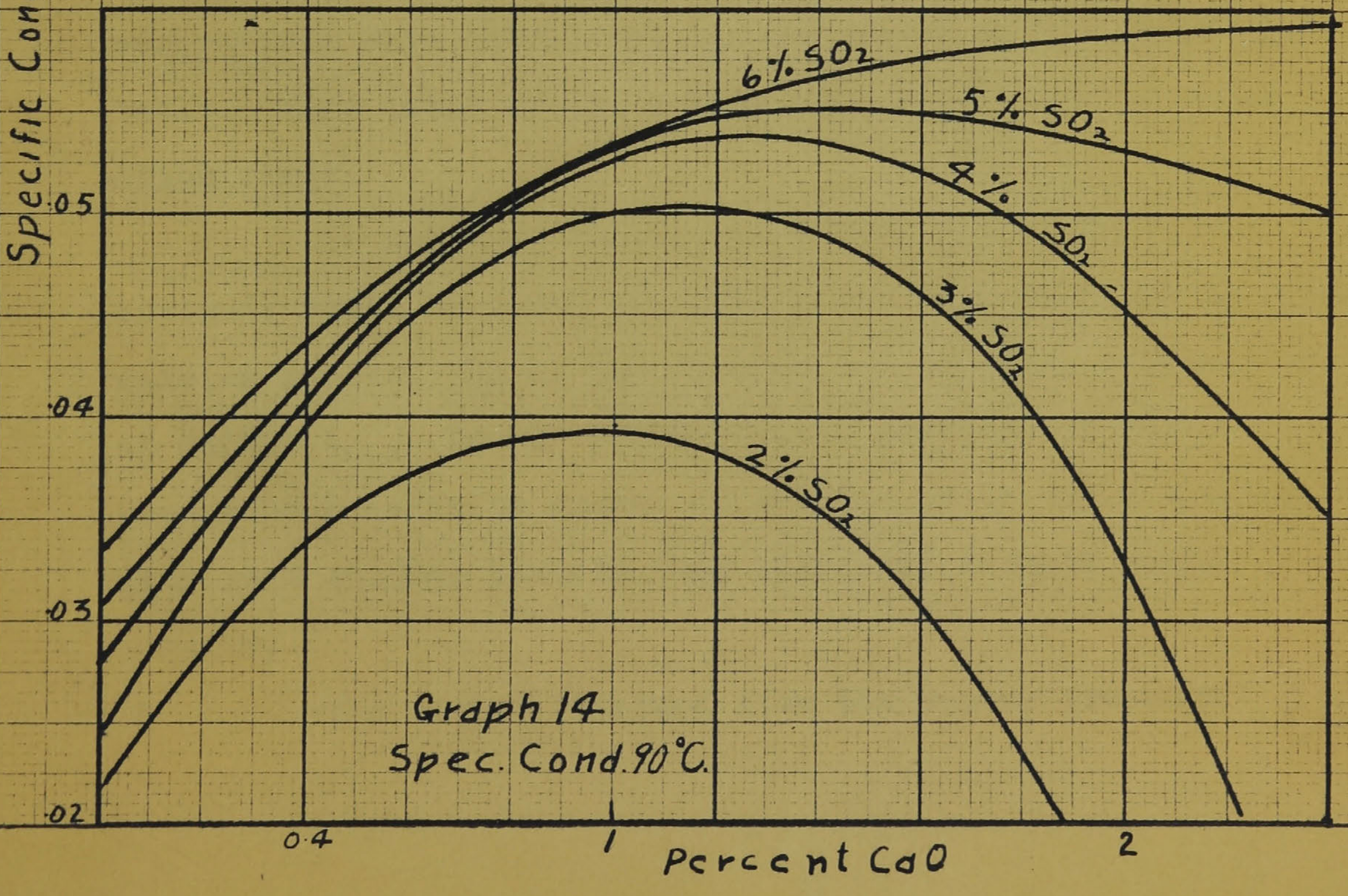
The specific conductivity values have been given in table (12) and also in graph No's. 11 to 14. The mobilities are known, the hydrogen ion concentration has been calculated and, therefore, the calcium ion concentration can be determined. The concentration of the bisulphite ion is equal to the sum of the calcium and hydrogen ion concentrations.

These values, however, have been calculated on the assumption that the ionization of calcium bisulphite does not influence the hydrogen ion concentration. The excess bisulphite ions, however, will tend to depress the hydrogen ion concentration. A quantitative means of determining this influence was available. Campbell (42) has used the following equation to express the ionization


Graph 11
Spec. Cond. 25°C
6% SO2
5% SO2
4% SO2
3% SO2
2% SO2
·04
·03
·02
·01
0
0·4
1
2
Percent CaO
Specific Conductivity Ohms⁻¹


6% SO2
5% SO2
4% SO2
3% SO2
2% SO2
Graph 12
Spec. Cond. 50°C
·05
·04
·03
·02
·01
0
0·4
1
2
Percent CaO


Graph 13
Spec. Cond. 70°C.
6% SO2
5% SO2
4% SO2
3% SO2
2% SO2
.05
.04
.03
.02
0
0.4
1
2
Pecent CaO.
Specific Conductivity Ohm⁻¹


6% SO2
5% SO2
4% SO2
3% SO2
2% SO2
.05
.04
.03
.02
0.4
1
2
Graph 14
Spec. Cond. 90°C.
Percent CaO

of H_2SO_3 . In this it was known that only a part of the sulphur dioxide was present as sulphurous acid, and as ionized sulphurous acid.

$$Ka = \frac{[H^+][HSO_3^-]}{Cso - [HSO_3^-]} \quad \ldots\ldots\ldots\ldots 6$$

The values for Ka have been determined (43)

Let

Cso_2 = totalamount of sulphur dioxide in the liquid phase

$[HSO_3^-]$ = total concentration of bisulphite ions.

By using the values for $[HSO_3^-]$ obtained from equation (5), it was possible to obtain a new value for $[H^+]$. This value was then used in equation (5) to obtain a second approximation to $[H^+]$. The new $[HSO_3^-]$ value was once more substituted in (6) to obtain a third approximation to $[H^+]$. Two more similar approximations yielded a constant value for $[H^+]$, $[\frac{1}{2}Ca^{++}]$ and $[HSO_3^-]$. The first and final concentrations were calculated and are shown in the following table. This table covers a wide temperature and concentration range.

It has been stated above that a more critical attitude would be taken concerning the form in which dissolved calcium exists. Up to the present, it has been represented as $Ca(HSO_3)_2$. In the precipitation studies, on two occasions a definite amount of calcium oxide was dissolved with less sulphur dioxide than the above formula would require.

The values obtained from the vapour pressure studies served as a quantitative means for studying this phase of the problem. If a solution be considered, in which there are 2 gram - molecular weights of SO_2 per gram - molecular weight of CaO, it would be expected that the vapour pressure of the solution remain no greater than that of water at the temperature under consideration. This was not found to be the case. At a 2 to 1 ratio, the vapour pressure was considerably higher than that of water. Again, if a solution be considered in which there are more than 2 gram - molecular weights of sulphur dioxide per gram - molecular weight of calcium oxide, it would be expected that the total vapour pressure should not be greater than that due to the excess sulphurous acid. A higher vapour pressure than the above would indicate was found in all cases. As an example, a solution containing 0.5 % CaO, and 3% SO_2 at 25°C was found to have a vapour pressure of 18 cm.. Of the 3% SO_2, 1.14% was required to combine with the CaO, leaving 1.86% free SO_2. From the data of Campbell (44), it was found that at 25°C a vapour pressure of 18 cm. was produced by a 2.1% SO_2 solution. This would indicate that instead of $Ca(HSO_3)_2$, a compound is formed requiring fewer molecules of SO_2 per molecule of CaO in order to bring the CaO into solution.

The following compound is postulated and sufficient evidence will be given in the following table to establish its composition. Structurally, it may be represented as:

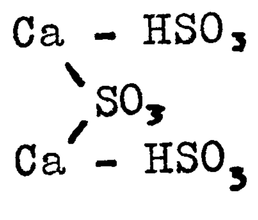


Table XVI

C_{SO_2} %	$[H^+]$	$[\frac{1}{2}Ca^{++}]$	$[HSO_3^-]$	$[H^+]$	$[\frac{1}{2}Ca^{++}]$	$[HSO_3^-]$
	Initial	0.5% CaO - 50°C.		Final Approximation		
3	.0470	.0437	.0907	.0206	.125	.145
4	.0571	.0379	.0950	.0254	.137	.162
5	.0638	.0310	.0948	.0413	.113	.155
		0.5% CaO - 70°C.				
3	.0356	.0606	.0962	.0121	.128	.149
4	.0433	.0548	.0981	.0138	.137	.151
5	.0475	.0491	.0966	.0232	.119	.142
6	.0556	.0293	.0849	.0230	.119	.142
		0.5% CaO - 90°C.				
3	.026	.0858	.1118	.0078	.119	.127
4	.031	.0722	.103	.0094	.127	.136
5	.034	.0634	.0988	.0128	.121	.134
6	.041	.0529	.0927	.0164	.113	.129
		1.0% CaO - 50°C.				
3	.0255	.110	.136	.0177	.137	.155
4	.0465	.071	.117	.0240	.142	.166
5	.0560	.057	.113	.0311	.145	.176
		1.0% CaO - 70°C.				
3	.0200	.127	.147	.0083	.162	.170
4	.0342	.109	.143	.0122	.167	.178
5	.0423	.085	.127	.0179	.154	.172
6	.0487	.069	.118	.0223	.144	.166
		1.0% CaO - 90°C.				
3	.015	.133	.148	.0048	.159	.164
4	.025	.115	.140	.0069	.162	.169
5	.030	.104	.134	.0092	.158	.167
6	.035	.092	.127	.0120	.150	.162
		1.5% CaO - 50°C.				
3						
4	.024	.139	.164	.0229	.145	.168
5	.043	.108	.151	.0304	.146	.176
6	.054	.089	.143	.0380	.131	.169
		1.5% CaO - 70°C.				
3						
4	.0160	.156	.172	.0113	.170	.181
5	.0326	.126	.159	.0140	.180	.194
6	.0412	.114	.155	.0172	.183	.200

Table XVI (continued)

C_{SO_2} %	$[H^+]$	$[\frac{1}{2}Ca^{++}]$	$[HSO_3^-]$	$[H^+]$	$[\frac{1}{2}Ca^{++}]$	$[HSO_3^-]$
	Initial	1.5% CaO - 90°C.		Final Approximation		
3						
4	.0110	.157	.168	.0064	.169	.175
5	.0244	.129	.153	.0083	.171	.179
6	.0293	.123	.152	.0105	.172	.183

and the evidence supporting this structure is the same as that used to disprove the old structure of $Ca(HSO_3)_2$. Using the above structure, it is found that a solution containing 0.5% CaO and 3% SO_2 should have 2.14% free SO_2. This checks with Campbell's value of 2.1% SO_2, as shown above. A large number of cases were tested and found to comply with this structure. These are not all included in the accompanying table (17). However, the results given cover a temperature range of 25°C to 90°C and the concentration range can be seen to pass diagonally throughout the entire range of concentrations studies.

Above each separate table, the concentration of calcium oxide and sulphur dioxide is given, together with the uncombined sulphur dioxide. The three columns of each table contain (1) the temperature, (2) the vapour pressure for the given concentration and temperature, (3) the sulphur dioxide required (according to Campbell's data), in order to produce the vapour pressure as shown in column (2).

There is one marked exception to the general agreement, which is found at the end of the last table. (CaO 2%, SO_2 6% Temp. 90°C.), The free sulphur dioxide found was 3.4%, which is much higher than the estimated value. At the precipitation temperature, there is a marked increase in the slope of the vapour pressure curve. Therefore, at a concentration and temperature in the neighborhood of a precipitation point, this relationship cannot hold. This is also found, but to a lesser extent in the table

Table XVII

CaO - 0.5% Total SO_2 - 3% Free SO_2 - 2.14%

Temp. °C.	V.P. c.m.	SO_2 %
25	19	2.1
50	46.5	2.1
70	85	2.04
90	140	1.93

CaO - 1.0% Total SO_2 - 4% Free SO_2 - 2.3%

Temp. °C.	V.P. c.m.	SO_2 %
25	27	2.5
50	52	2.33
70	91	2.20
90	152	2.2

CaO - 1.5% Total SO_2 - 5% Free SO_2 - 2.43%

Temp. °C.	V.P. c.m.	SO_2 %
25	29	2.3
50	56.5	2.6
70	102	2.5
90	180	2.8

CaO - 2.0% Total SO_2 - 6% Free SO_2 - 2.58%

Temp. °C.	V.P. c.m.	SO_2 %
50	55	2.6
70	110	2.8
90	210	3.4

immediately above that under discussion.

A second method of establishing the existence of the double calcium salt was to recalculate the hydrogen ion, the calcium ion and the bisulphite ion concentrations. In this calculation, the first approximation will naturally be different, but, since the structure of the undissociated calcium salt in no way can influence further approximations, the final approximations should be equal to those obtained in table (16). The truth of this is shown in the following table (18).

A study of this table and a comparison with graphs 11 to 14 will serve to give a picture of the various components in solution. It can be seen that at low temperatures, the hydrogen ion concentration is at its greatest. The addition of CaO to a sulphurous acid solution at 25°C, will, therefore, have a greater effect on the conductivity than at higher temperatures. This is shown in graph 11. The calcium oxide will dissolve with the formation to some extent of calcium and bisulphite ions. The increase in conductivity, however, due to these ions, will not be sufficient to compensate for the loss of conductivity, due to a decrease in the hydrogen ion concentration and, therefore, the specific conductivity will decrease with addition of CaO. However, at the higher SO_2 and CaO concentrations, the rate of decrease of hydrogen ions, with addition of CaO is more than compensated for by the increase in calcium and bisulphite ions. This is reflected in the inflection

Table XVIII

C_{SO_2} %	$[H^+]$	$[\frac{1}{2}Ca^{++}]$	$[HSO_3^-]$	$[H^+]$	$[\frac{1}{2}Ca^{++}]$	$[HSO_3^-]$
	Initial			Final	Approximation	
			0.5% CaO - 50°C.			
3	.0500	.034	.084	.0186	.131	.140
4	.0601	.0316	.092	.0244	.142	.166
5	.0692	.0126	.083	.0374	.109	.146
			0.5% CaO - 70°C.			
3	.0377	.0543	.0920	.0107	.131	.142
4	.0450	.0491	.0941	.0151	.134	.149
5	.0513	.0391	.0904	.0214	.140	.142
6	.0569	.0259	.0828	.0270	.111	.138
			0.5% CaO - 90°C.			
3	.0272	.0755	.1027	.0060	.131	.137
4	.0322	.0688	.1010	.0087	.131	.140
5	.0367	.0600	.0967	.0118	.125	.137
6	.0410	.0524	.0934	.0150	.121	.136
			1.0% CaO - 50°C.			
3	.0392	.0706	.1098	.0170	.139	.156
4	.0517	.0557	.1074	.0254	.131	.156
5	.0615	.0353	.0968	.0370	.115	.152
			1.0% CaO - 70°C.			
3	.0300	.1004	.1304	.0083	.162	.170
4	.0392	.0877	.1269	.0117	.166	.178
5	.0461	.0715	.1176	.0168	.155	.172
6	.0523	.0578	.1101	.022	.145	.167
			1.0% CaO - 90°C.			
3	.0230	.1173	.1403	.0054	.160	.165
4	.0281	.1100	.1381	.0065	.167	.174
5	.0330	.0995	.1325	.0088	.164	.173
6	.0375	.0878	.1253	.0115	.157	.169
			1.5% CaO - 50°C.			
4	.0411	.0788	.1199	.0245	.140	.164
5	.0530	.0763	.1293	.0302	.148	.178
6	.0626	.0655	.1281	.0381	.141	.179
			1.5% CaO - 70°C.			
4	.0312	.1123	.1435	.0113	.169	.180
5	.0403	.1034	.1437	.0143	.178	.192
6	.0470	.0969	.1439	.0174	.182	.199

Table XVIII (continued)

C_{SO_2} %	$[H^+]$	$[\frac{1}{2}Ca^{++}]$	$[HSO_3^-]$	$[H^+]$	$[\frac{1}{2}Ca^{++}]$	$[HSO_3^-]$
			1.5% CaO - 90°C.			
	Initial			Final Approximation		
4	.0237	.1233	.1470	.0064	.166	.172
5	.0286	.1179	.1465	.0083	.171	.179
6	.0355	.1120	.1455	.0102	.174	.184
			2.0% CaO - 50°C.			
5	.0418	.1344	.1762	.0229	.193	.216
6	.0535	.1379	.1914	.0236	.231	.255
			2.0% CaO - 70°C.			
5	.0317	.1372	.1689	.0130	.191	.204
6	.0405	.1472	.1877	.0136	.224	.238
			2.0% CaO - 90°C.			
5	.0237	.1233	.1470	.0089	.163	.172
6	.0290	.1289	.1579	.0099	.179	.189

of the 6% and 5% SO_2 curves.

At 70 °C. (graph 13) and 0% CaO, only hydrogen and bisulphite ions are present. The specific conductivity for a given SO_2 is considerably lower than at 25° C.. The decrease in ionic concentration has had a greater influence on the conductivity than an estimated increase due to an increased mobility at this temperature. When CaO is added, the hydrogen ion concentration is decreased, but the concentration of calcium and bisulphite ion is great enough to cause a rise in the specific conductivity.

When CaO is added to a 3% SO_2 solution at 70°C., a maximum is reached at about 1.2% CaO. The hydrogen ion concentration continues to decrease with further addition of CaO, whereas the solution appears saturated with regard to calcium ions. At some point beyond 1% CaO, their relative ratios will be such as to cause precipitation to take place. The change in the conductivity properties of the solutions, with change in temperature, can be seen from the graphs 11 to 14 to be a gradual one.

It is of interest to compare solutions of 1% CaO concentration at 50°C. and 90°C., and to determine what influence a change in SO_2 concentrations has on the conducting properties of the solution (graph 12 and 14). If SO is added to a solution containing 1% CaO and 2% SO_2 it can be seen that an increase to 3% SO_2 causes a large increase in specific conductivity both at 50°C and 90°C. If the concentration of SO_2 is increased to 4%, the increase is not so great. At 90°C. a further increase in SO_2 concentration will not influence the specific conductivity. Any increase in hydrogen ion concentration is offset by a decrease in the calcium ion. At 50°C., the influence of the hydrogen ion is greater and the specific conductivity continues to rise.

Precipitation Temperatures.

A solution containing the dissolved calcium salt will suddenly precipitate out when heated up. The precipitation temperature depends on the relative concentrations of the calcium oxide and sulphur dioxide in the solution. The amount of precipitate formed at the precipitation temperature has not been determined analytically. The work was carried out in glass bombs, and it could be observed that when precipitation did occur, a considerable fraction of the calcium present appeared as solid calcium sulphite.

One method of arriving at an estimate of the amount of calcium sulphite precipitated, was available. At one concentration, the vapour pressure curve was studied just below and above the precipitation temperature. This is represented below in Graph 17. The vapour pressure was determined at 60°C., and the solution slowly heated to 65°C., where a second vapour pressure determination was made. The solution was heated up very slowly and at 65.4°C. precipitation began. The pressure immediately increased and continued to rise as calcium sulphite was precipitated. Vapour pressures were then determined above the precipitation temperature. This part of the curve has a steeper slope. In a former trial experiment with the same solution, precipitation had not occurred until a temperature of 75°C. had been reached. It would appear that the quantity of precipitate formed depends upon the degree of supersaturation. The true precipitation temperature was arrived at by extrapplating the second part of the curve back to where it cut the first part. It was found to be 60.4°C. There is evidence to show that, had precipitation occurred at 60.5°C., the amount fo formed would have been very slight. On Page 81 of this thesis, in example 2A, the formation of a slight precipitate at 97°C. was described. In this case, the amount of precipitate increased rapidly with increase in temperature.

Consider Graph 17 at 70°C. Over a small temperature range the curves were found to be practically straight lines, therefore, extrapolation of the lower curve to 70°C. is permissible. In the absence of precipitation, the vapour pressure would have been 113 cm. Due to precipitation it actually was 135 cm. The solution under review contained 6.8% SO_2 and 2.35% CaO (calculated on the same basis as that used in the precipitation temperature determinations). No data have been included in this thesis for solutions containing more than 6% SO_2, but determinations could be made with data which have been obtained. The concentration of SO_2 in solution remained almost constant before and after precipitation, but the amount of CaO decreased due to the formation of calcium sulphite. The amount of calcium removed from solution can, therefore, be found by determining the amount of calcium oxide required to produce the known change in vapour pressure. At this degree of supersaturation 0.5%, (more than one fifth of the CaO present), had precipitated out. At 65°C., approximately one-half of this amount precipitated out.

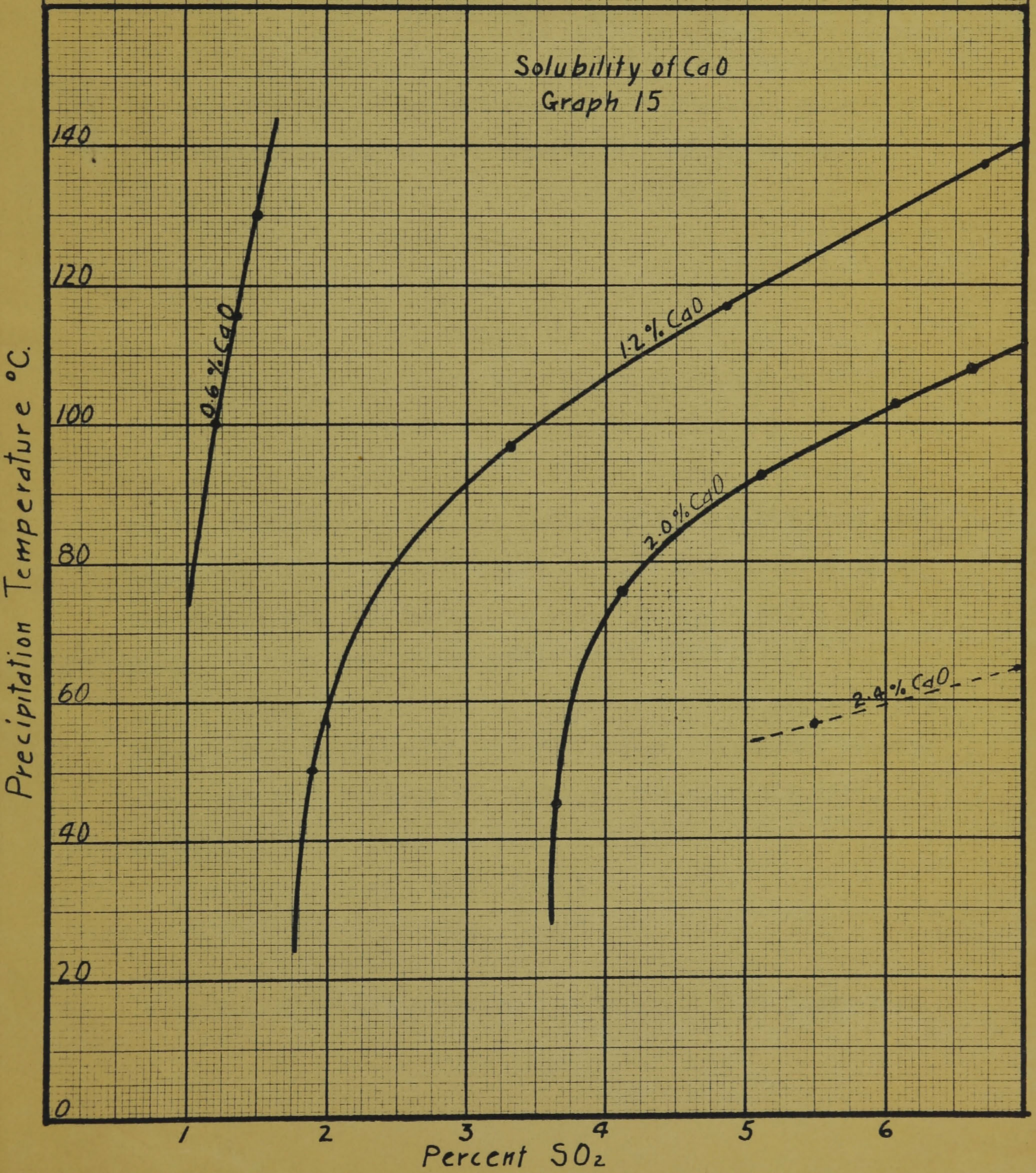
Precipitation temperatures can be studied by means of conductivity measurements. It can be seen in Graph 9, curves B_1 and B_2, that at 95°C. there was a sharp bend in each curve. In B_2 a conductivity determination was made at 100°C., with no precipitate present. Precipitation took place between 100°C. and 110°C., and beyond this temperature the conductivity values were much lower. By extrapolating the post-precipitation values, it is found that the first part of the curve is intersected at 95°C. This gives the true precipitation temperature.

Two questions require answering.

(1) Why does precipitation take place?

(2) Why is the conductivity lowered so abruptly after precipitation has taken place?

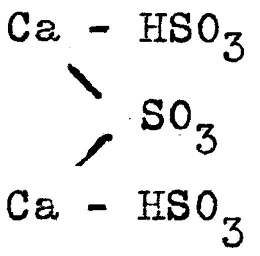
The answer to (1) is found by a study of Table 18. From this table it can be seen that for any solution the hydrogen ion concentration decreases with increase in temperature. Eventually, depending on the amount of CaO and SO_2 present, a temperature is reached at which the solute cannot all exist in solution. The determination of hydrogen ion concentrations was quite involved, due to the large number of different substances present, and it was considered inadvisable to attempt a quantitative study of the system in the



Solubility of CaO
Graph 15

precipitation area. However, this area was approached (i.e., high CaO concentrations at high temperatures). and it was seen that a reduction in hydrogen ion concentration played an important role in determining the solubility of the calcium compounds present.

Question (2) can be answered by a description of the mechanism of precipitation. It has been shown that undissociated calcium occurs as a complex, expresed as -

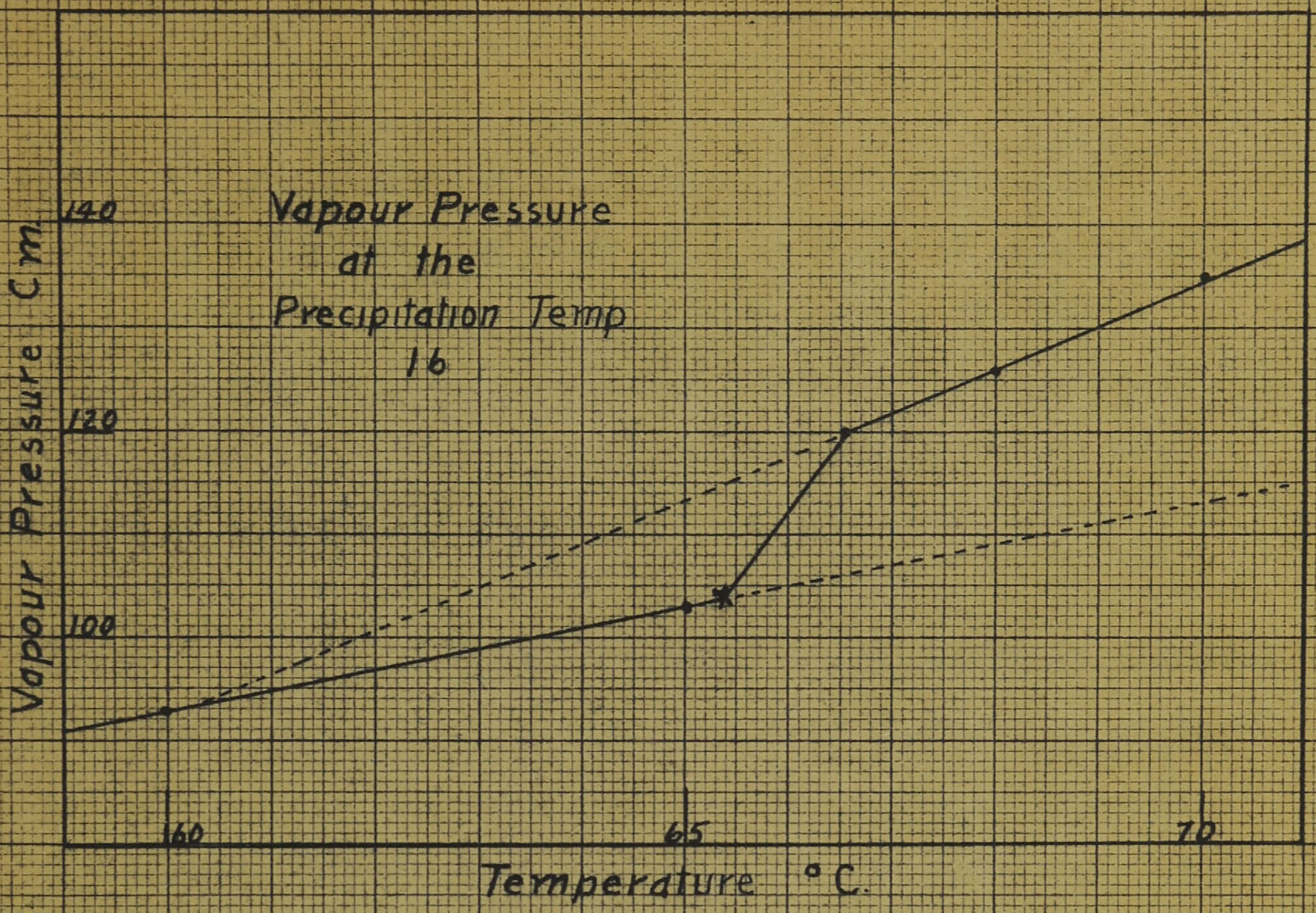


Saunderson (21) has shown that the precipitate is calcium sulphite ($CaSO_3$). When one molecule of $CaSO_3$ precipitates, one calcium ion andtwo bisulphite ions are liberated. The sudden formation of a large number of bisulphite ions will cause two things to take place - (1) The equilibrium of the system will be shifted to cause an increase in the amount of free sulphur dioxide, which will result in a sudden increase in pressure. The increase in pressure has already been described. (2) The sudden increase in bisulphite ions will depress the hydrogen ion concentration. Quantitatively, it may be expressed as -

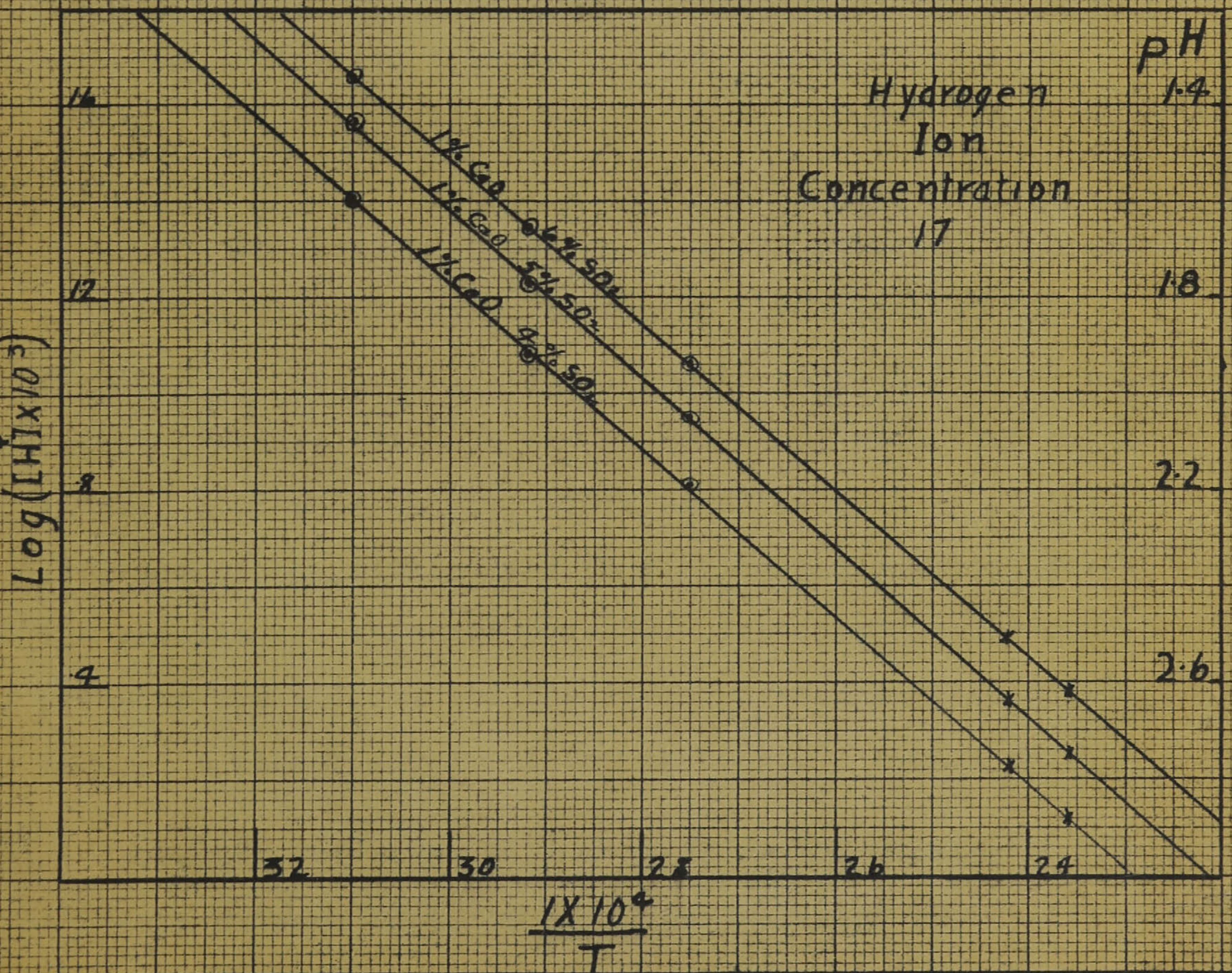
$$Ka = \frac{[H^+]\ [HSO_3^-]}{C_{SO_2} - [HSO_3^-]}$$

The mobility of the hydrogen ion is about five times that of the bisulphite or calcium ion and, therefore, a sudden decrease in the hydrogen ion concentration will cause a marked decrease in the conductivity at and beyond the precipitation temperature.

Graph 15 shows precipitation curves for 0.6%, 1.2% and 2% CaO. Precipitation temperatures found by Gurd and by the writer in their studies of vapour pressures and conductivities at about 1.2% CaO, were in agreement with the curve shown in the graph for this concentration of CaO. It can be seen that a decrease to 0.6% CaO causes a marked increase in the slope of the curve. Two of the values at 2.35% CaO are shown and at the concentrations used the curve is almost flat. An increase in CaO concentrations from 2.0% to 2.4% caused a very considerable lowering of the precipitation temperature.



Vapour Pressure
at the
Precipitation Temp
16



Hydrogen
Ion
Concentration
17

PART III.

COOKING EXPERIMENTS.

The mechanism involved in sulphite cooking has been the subject of much study. This has been briefly reviewed in the introduction of the thesis. It was believed that a careful study of the vapour pressures of the system CaO - SO_2 - H_2O in the presence of wood, might serve as a means of determining the mechanism. This work serves two purposes. (1) It completes a study of the system CaO - SO_2 - H_2O. (2) It introduces a new method of studying cooking. The two are closely related, however, as in the latter case one more component, namely wood, is added to the system. In the time available, it was impossible to do a large number of experiments. The chief object of the work was to develop a technique for the study of this system. Aside from this, several matters of interest have been observed.

In experiment #4 no wood was present. The object of this experiment was to determine the length of time required to reach equilibrium, and to ascertain whether the vapour pressure obtained was in agreement with that obtained in part I of this thesis. This acted as a check on the accuracy of the method used in filling the reaction cell. The results are shown on page 89. The calculated vapour pressure was 435 cm. and the vapour pressure obtained was 423cm. A closer agreement was expected. A part of the

---

Frequent reference will be made to the cooking data on page 86 to 90, and also to graph 18.

discrepancy was possibly due to the fact that in the latter work no stirring of the solution took place. This difference will cast some doubt on the accuracy of the absolute values obtained in the absence of stirring, but the relative values in the runs described above are accurate to within 2 cm.

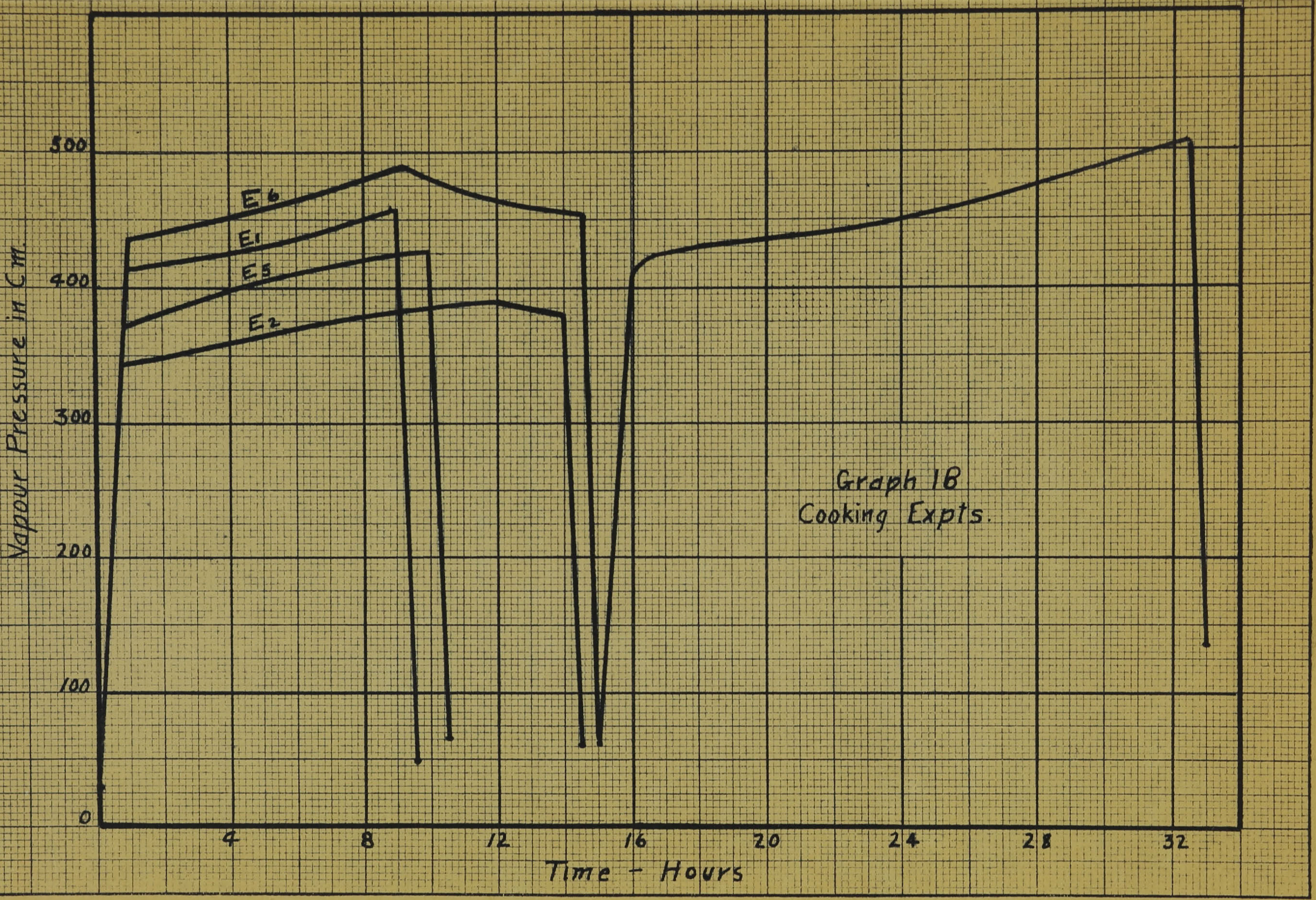
In experiment #4, equilibrium was reached in 2 hours. In experiment #3 in which pure cellulose was used, equilibrium was not reached until the fourth hour. This run was repeated and the two vapour pressure curves obtained were parallel to one another. Two factors were responsible for the time required to reach equilibrium. In the first place, there was no means of stirring the contents of the reaction cell. In the second place, the cellulose hindered the attainment of equilibrium still further.

In experiments containing wood, the vapour pressure obtained at 25°C. before an experimental cook was started, were slightly lower than those calculated on the basis of the amount of CaO and SO_2 present. There is a reason for this. After the mixtures of wood CaO - SO_2 - H_2O had been prepared, they were allowed to stand over night, in order to reach equilibrium and it is believed that adsorption of sulphur dioxide on the wood and cellulose had taken place to some extent, causing a lowering of the vapour pressure. This has been studied by Saunderson (46).

In all the curves, Graph #18, it can be seen that after a temperature of 130°C. was reached, the vapour pressure continued to rise slowly for 8 to 10 hours, until a maximum was reached. There are three factors governing the slope of this part of the curve. (1) For at least a part of the time, the vapour pressure continues to increase, due to the fact that the liquor is slowly reaching equilibrium. (2) There is a tendency for the pressure to be lowered, because sulphur dioxide is being removed because of reaction taking place with the lignin. (3) Carbon dioxide is being formed and this will tend to increase the pressure. No quantitative study has been made of the CO_2 produced during the first part of a cooking experiment, but its existence will be proven at a later part of the discussion. The subject of CO_2 formation has been the cause for much controversy in the past. Technical experts in charge of commercial digesters have even claimed that none is formed. In most cases, their error can be traced to faulty sampling. Their samples have been taken during the blowing down of a digester, and it is only during the first part of blowing that CO_2 is present in the relief gases.

Three phases of the sulphite cooking of wood will be considered.

(1) It is usually considered that, in the delignification of wood, two molecules of SO_2 are used up per molecule of CaO. In order to determine whether this research lent itself to a quantitative study of the mechanism of sulphite cooking, a calculation was made in an attempt to either prove or disprove the above statement. The data of experiment # 5 were used because there was no maximum in the



Graph 18
Cooking Expts.

vapour pressure curve and, therefore, the wood was not over cooked. This eliminated such complications as excess polymerization of lignin which is assumed due to a depletion of lime.

Yorston (45) has calculated that the amount of SO_2 consumed in a sulphite cook was approximately equal to 4.8% of the weight of dry wood present. In Run 5, the liquor contained 0.6004 gms. CaO and 2.074 gms. SO_2. There were 7.9 gms. of dry wood present. Assuming that the ratio of SO_2 to CaO is 2 to 1, it was found that 0.38 gms. SO_2, and0.166 gms. CaO were required. These values were subtracted from the total CaO and SO_2 present in the liquid phase and with the aid of the data in Part I of this thesis the resultant vapour pressure was determined. It was calculated to be 360 cm. at 130°C. The measured vapour pressure at 130°C. was 427 cm. The excess pressure af 67 cm. was assumed to be due to CO_2. This was known to be partly in error, due to the presence of volatile bi-products, but no corrections were made. Similarly, at 25°C., the calculated vapour pressure after the cook was 18 cm., and that found, was 66 cm. Therefore, at room temperature, the system had an excess pressure of 48 cm. assumed to be due to CO_2. Since volume changes of the system due to changes in temperature were known, it was possible to calculate what the CO_2 pressure would be at 130°C., using the data obtained at 25°C. The CO_2 pressure by this method of calculation, was 68 cm., which is in very close agreement with that found at 130°C. (i.e., 67 cm.).

The same method can be used to show that CaO and SO_2 do not react with lignin in the ratio of 1 to 1. If this were so, the amount of CaO used would be doubled. If experiment 5 is used for a second calculation, 0.38 gms. SO_2 and 0.33 gms. CaO would be required. The resultant vapour pressure would be 404 cm. at 130°C., whereas, that found was 427 cm. This would result in a pressure of 23 cm. due to CO_2. Similarly at 25°C., the pressure due to CO_2 would be 45 cm. A pressure of 45 cm. at 25°C. in the system used corresponds to a pressure of 64 cm. at 130°C. This certainly does not check with the pressure obtained (i.e., 23 cm.#, and, therefore, shows that CaO and SO_2 are not used up in the ratio of 1 to 1.

Up to the present, organic chemistry has been the tool used to study the mechanism of sulphite cooking. The above calculations indicate that a careful study of vapour pressures at different temperatures and concentrations serves as a new form of attack on this problem.

(2). It has been shown that CO_2 is produced during cooking, and a method has been described whereby CO_2 pressures can be determined. In the experiments performed, the volume of the vapour phase was known, making it possible to calculate the weight of CO_2 produced during different stages of the cooking reaction. Unfortunately, the pressures at room temperatures have not been determined for cooks lasting for about 4 hours. However, experiment 6 was cooled down to room temperature after 13 hours cooking in order to determine the vapour pressure at 25°C. The reaction cell was then heated up to 130°C., and the cook was continued for 17 hours. A calculation has been made of the CO_2 per gram of wood. It was found that after 13 hours, 0.006 gms. CO_2 were produced per gram of wood, and after 30 hours 0.02 gms. CO_2 were produced.

It is of interest to determine whether the CO_2 was due to the decomposition of lignin or of cellulose. In experiment 3, Page 89, pure cellulose was cooked in two steps. The first step lasted 10 hours, while the second required half that time. After the first 10 hours, the vapour pressure was determined at 25°C., and it was found to be 5 cm. higher than at the beginning of the cook, but only 2 cm. higher than the calculated value. During the secondstep, no CO_2 was produced. However, when wood was cooked under the same conditions, the pressure due to CO_2 was found to be approximately 40 cm. This indicates clearly that CO_2 is a reaction product of the lignin in the wood, and not of the cellulose.

It was possible to observe the color of the liquor during these experiments. At the end of the normal 8 to 9 hour run, the liquor was still a clear straw colored yellow. However, after this period (beyond the maximum point on the curves, graph 18), the liquor rapidly darkened, indicating that a number of more or less complicated reactions involving polymerization, were taking place. The change in the slope of the curves would indicate that these reactions consumed a large amount of SO_2. A study of curve E_6, Graph 18, shows that after the pressure has continued to drop for several hours it tends to remain constant and then to rise. It has been shown above that the final increase in pressure is due to CO_2 formation. After the 30 hour cook (E_6) the contents of the reaction cell were black.

(3). Calculations have been made in Part I of the hydrogen ion concentration for the system CaO - SO_2 - H_2O. These calculations cover a wide temperature and concentration range. The concentrations included those used in the sulphite cooking of wood, but calculations were made for temperatures no higher than 90°C.

There has been a great variety of opinion regarding the hydrogen ion concentration of sulphite liquor at the cooking temperature (140°C. to 150°C.). The early belief was that the solution was quite acid. Campbell and Maass (1) have shown that even when large amounts of SO_2 are dissolved, only a small amount of hydrogen ion is formed; the higher the temperature, the smaller the amount. It was assumed by some therefore, that the addition of CaO would make the solution basic. The present data make it possible to determine the hydrogen ion concentration of sulphite liquor at the cooking temperature.

An example is shown in graph 17. The log of the hydrogen ion concentration was plotted against the reciprocal of the absolute temperature for temperatures of 50°C., 70°C. and 90°C. for a concentration of 1% CaO and concentrations of 4%, 5% and 6% SO_2. A straight line was obtained for each SO_2 concentration. These could be extrapolated to any desired temperature. A number of hydrogen ion concentrations of interest to the pulp and paper industry are given below:

% CaO	% SO_2	Temp. Deg. C.	pH	Temp. Deg. C.	pH
1	4	140	2.78	150	2.88
1	5	140	2.64	150	2.75
1	6	140	2.51	150	2.62

This shows that the sulphite cook is distinctly acid although the pH is quite small. The liquor acts as a buffer solution, so that the pH does not vary greatly with either temperature or concentration. It has been reported at times that calcium hydroxide is actually deposited. Saunderson (46) has shown that the precipitate was calcium sulphite. The above calculations show that the pH is such that calcium hydroxide cannot precipitate.

SUMMARY.

1. Vapour pressures have been determined for the system CaO - SO_2 - H_2O at concentrations of 1.2% and 2.3% CaO and for concentrations of 0 to 6% SO_2 within the temperature range 25°C. to 130°C.

2. Conductivities have been determined for the system CaO -SO_2 - H_2O at concentrations of 1.2% CaO and 0 to 6% SO_2 within the temperature range 25°C. to 130°C.

3. The vapour pressure and conductivities of Campbell and of Gurd have been combined with those of the writer to cover the following concentration and temperature ranges. Vapour pressures were obtained for concentrations of 0 to 2.5% CaO and 0 to 6% SO_2 within the temperature range 25°C. to 130°C. Conductivities have been obtained for the same concentration ranges for the temperature range 25°C to 90°C. All of the above data have been systematically tabulated for the first time.

4. The above values were used to determine the mechanism of the equilibria existing in the system CaO - SO_2 - H_2O.

5. A new complex has been shown to exist in the above mentioned system.

6. Hydrogen ion concentrations, calcium ion concentrations and bisulphite ion concentrations have been calculated for the first time for this system. These calculations cover a wide concentration and temperature range.

7. A method has been developed whereby these values can be used to determine the pH of sulphite liquor at cooking temperatures. Determinations have been made for the first time.

8. A new technique has been developed for the study of precipitation temperatures of the system $CaO - SO_2 - H_2O$. Precipitation temperatures have been determined for solutions containing 0.6% CaO, 1.2% CaO and 2.0% CaO. For each of these CaO concentrations, a wide range of SO_2 concentrations was used. The temperature range extended from 25°C to 140°C..

9. The nature of precipitation has been studied and a description of the mechanism of precipitation has been given. The influence of the hydrogen ion concentration on precipitation has been described. Supersaturation has been discussed, and a method developed whereby a quantitative determination of the amount of precipitate formed for any degree of supersaturation can be calculated.

10. A new technique has been developed to study changes in the system $CaO - SO_2 - H_2O$, caused by the cooking of wood.

11. It has been shown by a new method that during cooking, CaO and SO_2 are used up in the ratio of 1 to 2.

12. It has been shown that CO_2 is produced during cooking and a new method has been developed to calculate the weight of CO_2 formed per gram of wood.

13. A new electrical apparatus has been designed and constructed for measuring the consistency of pulp in water. A description appears below in the form of an appendix.

14. It has been shown that CO_2 is produced from the lignin and not the cellulose during cooking.

Note- The above summary serves as a statement of claim to original research.

1. Campbell, W. B. and Maass. O. Can. Jour. Research. <u>2</u>, 42, (1930).
2. Gurd, G. W. Thesis, McGill University, (1932).
3. Maass, C. and Maass, O. J.A.C.S. <u>50</u>, 1352, (1928).
4. Morgan, O. M. and Maass, O. Can. Jour. Research. <u>5</u>, 162, (1931).
5. Hudson, J. C. J. Chem. Soc. <u>127</u>, 1332, (1925).
6. Lindner, C. Monatsh, <u>33</u>, 613, (1912).
7. Ostwald, W. J. Prakt. Chem. <u>33</u>, 357, (1886).
8. Maben, Pharm. J. Trans. <u>14</u>, 505, (1848).
9. Lamy. Compt. rend. <u>86</u>, 333, (1878).
10. Hertzfeld. Z. ver. Rubenzucker - Ind. 818, (1897).
11. Guthrie. J. Soc. Chem. Ind. <u>20</u>, 223, (1901).
12. Moody. J. Chem. Soc. <u>93</u>, 1722, (1908).
13. Haslam, Calingaert and Taylor. J.A.C.S., <u>46</u>, 311, (1924).
14. Miller, L. B. and Witt, J. C. J. Phys. Chem., <u>32</u>, 285, (1929).
15. Grieve, A. C. Thesis, McGill University, (1932).
16. Larocque, G. L. Thesis, McGill University, (1933).
17. Schwartz andMiller-Clemm, Zeit. fur. Angew. Chemie. <u>34</u> 272, (1921).
18. Smith and Pankhurst, J.A.C.S., <u>44</u>, 1918, (1922).
19. Farnell. Jour. Soc. of Chem. Ind., <u>44</u>, 530, 2T, (1925).
20. Conrad and Beuschlein, J.A.C.S. <u>56</u>, 2554, (1934).
21. Saunderson and Maass, O. Can. Jour. Research <u>10</u>, 24, (1934).
22. Blasdale. J. Ind. Eng. Chem. <u>12</u>, 164, (1920).
23. Hulett and Allen. J.A.C.S. <u>24</u>, 667, (1902).
24. Wislicenus. Kolloid Zeitschrift <u>27</u>, 213, (1920).

25. Kurschner,. Tappi Papers 100, (1928).

26. Jonas. see Ref. 24, P. 290. (Zeitschr. f. Angew. Chem. 34, 290, (1921).

27. Pauly. Austrian patent. 3069-18 Klasse 12-e.

28. Saunderson, Johnston and Maass. Can. Jour. Research, 8, 415, (1933).

29. Montigny and Maass. Can. Forest Service Bulletin #87, (1935).

30. Mitcherlick and Frank. Ref. 25, P. 103. Papier Zeitung (1887(

31. Hagglund and Carrick. Cellulose Chemie, 15, 20, (1934).

32. Miller and Swanson. Chemistry of the Sulphite Process, (Tappi) P. 80.

33. Hagglund, Zellstoff u. Papier, 13, 6, (1933).

34. Nepenin and Sapraigina. Zellstoff u. Papier 14, 316, (1934).

35. Eliashbert andMartuinov. Trans. All. Union Sci. Research Inst. Paper Cellulose Ind. 1, 5, (1931).

36. Klasen. Schriften des Vereina der Zellstolf - und Papierchemiker, Heft 2, S. 25 ff.; Berichte des Vereins der Zellstoff - und Papierchemiker S, 67, (1909).

37. Hagglund. Tech. - Wiss. Teil., Papier fabr. 24, 775, (1926).

38. Michel andJaffard. Papier 35, 1051, (1932).

39. Housekeeper. J. Am. Inst. Elect. Eng., 42, #9, (1923).

40. Kohlrauch, Holborn and Dusselhorst. Landolt - Bornstein Tables Vol II, Page 1098, (1923).

41. Campbell, W. B. Thesis, McGill University, (1929)

42. " " " ibid. - P. 89.

43. " " " ibid. - P. 90.

44. " " " ibid. - P. 29.

45. Yorston - Private communication.

46. Saunderson. Thesis, McGill University. (1932)

APPENDIX

AN ELECTRIC METHOD FOR THE DETERMINATION OF THE CONCENTRATION OF PULP IN WATER.

Introduction.

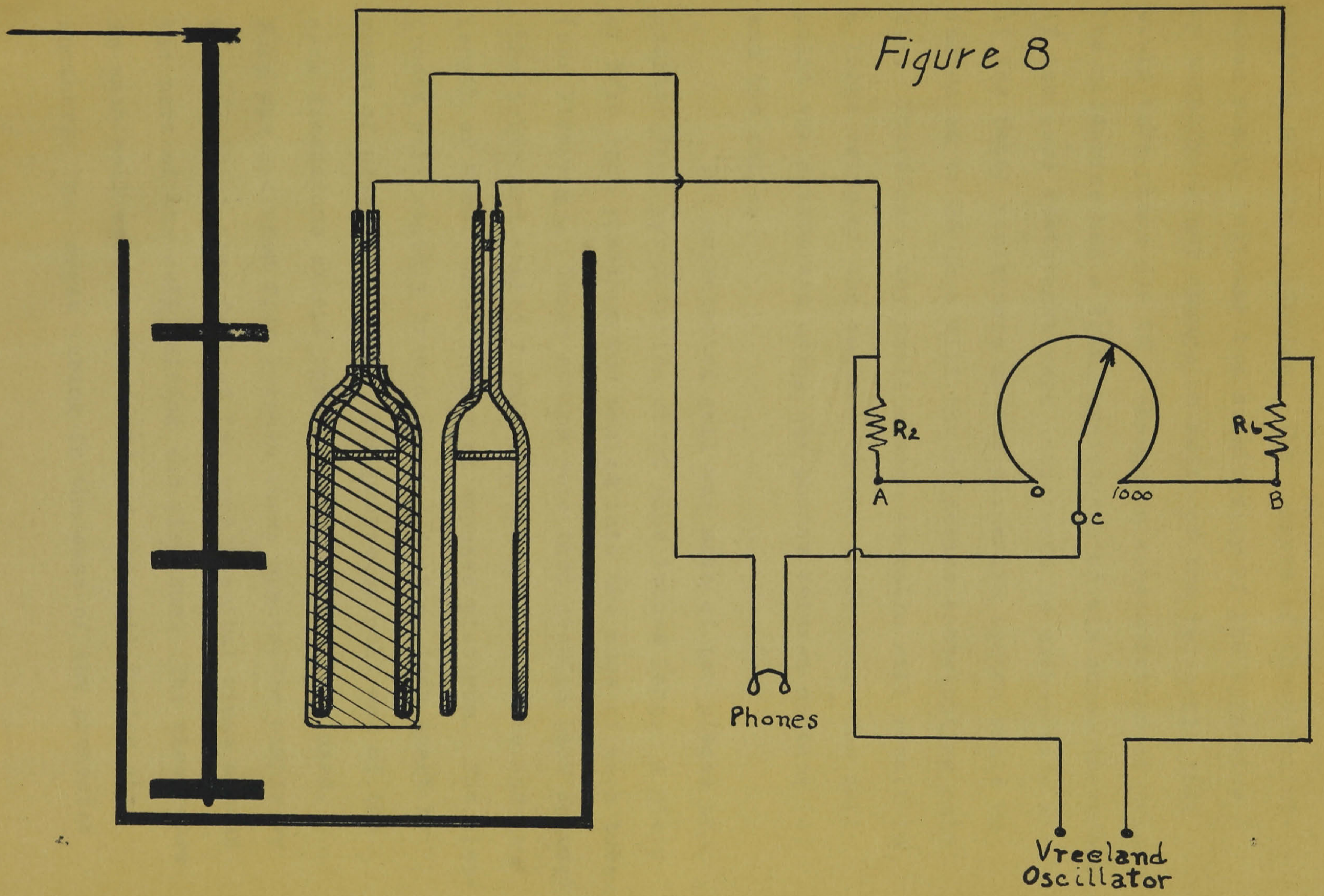
The method for determining the concentration of pulp in water to be described in this paper makes instantaneous determinations possible. The results so far obtained indicate that it should be possible to determine the concentration of pulp to within 0.01%. This means that it will be possible to determine the difference between a 1.00 and 1.01% suspension.

The method of determination is based on the principle that tap water is a conductor of electricity, whereas any pulp dispersed in the same water is not a conductor. If two pairs of platinum electrodes are immersed in ordinary water, the resistance of each to electrical flow can be determined by balancing against a known resistance. If some conducting substance such as a salt is introduced into the water, or if the temperature of the water is changed the resistance of each cell will change but the ratio of the resistances of cell (a) and cell (b) should remain constant. A constant ratio should also be obtainable if the known resistance is cut out of the system and cell (a) is balanced against cell (b). If pulp is added to the water of a well stirred bath containing the two cells, the pulp on passing between the two pairs of electrodes will change the resistance of each but will not change the ratio of these resistances. However, if one pair of electrodes is protected with a screen which prevents pulp from getting into the water between these electrodes and at the same time the other pair of electrodes is unprotected allowing pulp to get into the water between the electrodes, that ratio will be changed. The reason for this is the fact that the volume of conducting liquid (water) between the protected electrodes remains constant because no foreign solid matter is allowed in, whereas, the volume of conducting liquid between the unprotected electrodes is diminished due to the presence of pulp. An apparatus was therefore set up to determine whether these differences were measurable, and if so, to what accuracy.

Apparatus.

The apparatus used was quite simple. It consisted of a battery jar of about 4½ litres capacity which was used to make up the pulp and water mixtures. It contained the two cells and a three paddle stirrer. A high frequency alternating current was used so as to minimize polarization. This was supplied by a Vreeland oscillator. The ratio of the resistances of the cells was determined with a Kohlrausch slidewire arrangement which was somewhat modified by placing two resistances R(a) and R(b) between the point where the current was supplied to the

Figure 8



system, and the slidewire. The purpose of these resistances was to increase the sensitivity of the apparatus by magnifying any change in ratio of the two cells that would take place due to a change in concentration of pulp. The slidewire had a total resistance of six ohms, therefore, if ten ohms resistance were introduced on either side of it the total resistance of the slidewire system would be increased to 26 ohms with the slidewire contributing only six. Therefore, any small change in ratio will result in a large swing of the contact on the slidewire. The null point was determined using ear phones between contact (c) and the cells.

The unprotected cell was made of two pieces of quarter inch pyrex tubing about nine inches long. A strip of 3/16 inch platinum was sealed into the base of each tube (see Figure 8). These strips were then doubled back against the tubes and sealed firmly onto them. Each tube had a length of about three inches of exposed platinum. The electrodes were rigidly braced about 3/4 of an inch apart by means of glass crossbars. The protected cell was of the same dimensions except that half inch tubing was used. Pulp was excluded from between these electrodes simply by winding about five feet of two inch hospital gauze around the part of the cell holding the platinum. The electrodes in each cell were on the inside of the cell facing one another. The larger tubing in the case of the protected cell served to hold the gauze away from the platinum. Contact was made between the platinum seals and the rest of the system by filling the cell tubes with mercury. The electrodes were platinized for the work to be described below.

Procedure.

The constant of the two cells was first determined using a tenth normal solution of KCL. The resistance of the tap water used was determined with the cells at 25°C. and also the actual resistance of various mixtures of pulp in water. However, as actual resistance values were not found necessary to the solution of this problem, this preliminary work will not be dealt with in detail, bu t rather the work carried out with the apparatus as shown in Fig. 81, where cell (a) is balanced against cell (b).

The value of the ratio a/b should remain constant with variation of temperature. Four and a half litres of tap water at 10°C. were poured into the bath, a heater was installed and the water slowly heated. It was found at first that the ratio tended to change but this was due to the fact that the cell covered with gauze did not allow the water to circulate freely between the electrodes and there was therefore a temperature lag. To overcome this, the temperature was held constant until the value on the scale became constant. The temperature was then raised a few degrees and the above procedure repeated. Another much more rapid method of reaching temperature equilibrium was to dip the covered cell in and out of the bath several times before taking a reading. The ratio was tested between 10 and 35^{0}C., and found to remain constant throughout.

The value of the ratio a/b should remain constant for water containing different amounts of dissolved salts. To determine this a small amount of KCL was added to the water and it was stirred until a constant scale reading was obtained. The ratio returned to its former value. It may be added, that after several weeks of work, the ratio was still what it was during the first work undertaken.

The next step was to use a substance which would pass freely and uniformly between the electrodes of the unprotected cell but which could not penetrate the gauze protecting the other cell. Pulp made from poplar by the soda process was used. This was obtained in dry sheet form. Samples weighing ten grams each were disintegrated in the usual manner. The excess water was drained off in a suction funnel leaving a pad which contained 10 grams of pulp and about 20 grams of water. These pads when dropped in small pieces into the water used for the experiment were readily stirred up into a uniform mixture. Unnecessary delays in reaching temperature equilibrium between the inside and outside of the protected cell were usually avoided by having the water at room temperature before starting an experiment.

Several experiments were first made with R(a) and R(b) cut out of the system entirely. Four and a half litres of water at room temperature were poured into the battery jar. The cells and stirrer were set in place and the latter was started. The Vreeland oscillator was started to supply the current and the nul point was determined using the ear phones. In some cases, the correct scale reading was not immediately obtained due either to the fact that the water was slowly heating or cooling, or that a bubble of air had become attached to one of the electrodes. This was readily corrected by dipping the covered cell up and down deveral times. One of the pads containing 10 grams of pulp was then weighed in order to determine the amount of water it contained. It was broken up by hand and dropped into the water where it was soon dispersed. The Vreeland oscillator was again started and a scale reading made on the Kohlrausch slide wire. The change in scale reading was noted. To make sure that this change was due to pulp and not to an upset in the temperature equilibrium or to some conducting substance attached to the pulp, the covered cell was dipped several times before readings. Each pad increased the pulp concentration approximately 0.22%. The stirring arrangement used was found efficient to slightly over 1% pulp. Above that concentration the pulp tended to bunch up about the electrodes. This would not be the case where large volumes are concerned. The results given below deal only with concentrations up to 1%.

Results.

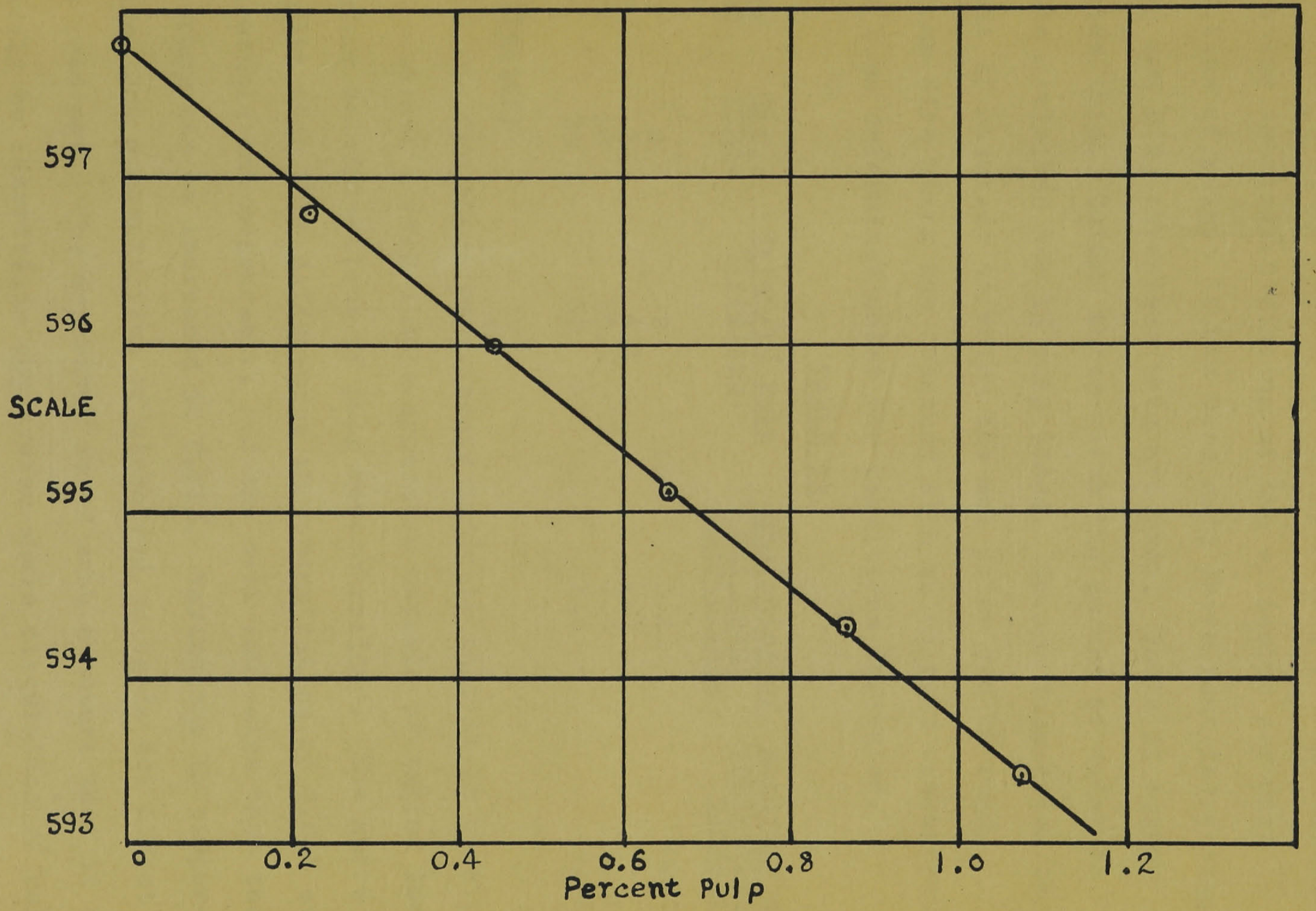
Runs have been made with the concentration of the pulp varying from 0 to 1%. In these experiments the auxiliary resistance R(a) and R(b) on either side of the slidewire have been varied from 0 to 30 ohms. In the case of the higher resistances instead of placing the same resistance in R(a) andR(b) the resistance was so adjusted to bring the scale reading nearer the centre of the slidewire, thus insuring greater sensitivity. It was found that increasing the resistances decreased the sharpness of the end-point but at the same time it greatly increased the scale swing per 1% of pulp added.

The results of one experiment are given in Table I. In this experiment both R(a) and R(b) were set at 3 ohms. The ratio in the final column is obtained in the usual manner, if A is the scale reading, then A/1000-A is the ratio. A graph of these results is also shown below.

TABLE I.

Wt. Pulp.	Wt. Water.	% Pulp.	Scale Reading.	Ratio.
0	4500	0	597.8	1.4863
10	4523	0.22	596.8	1.4802
20	4545	0.438	596.0	1.4752
30	4569	0.653	595.1	1.4697
40	4591	0.864	594.3	1.4649

The accuracy in determining pulp concentration depends on two things, (1) the sharpness of the nul point, GRAPH I 9



i.e., to what fraction of a scale division the nul point can be accurately judged by the operator, (2) the amount of swing in scale divisions of the slidewire per unit addition of pulp. It has been said above that increasing R(a) and R(b) increases this accuracy. Table II illustrates this. Column three gives the amount of swing in scale divisions per 1% pulp added. Column four gives the limit of accuracy to which the nul point can be read. Column five gives the accuracy with which pulp concentration has been determined under the conditions indicated.

TABLE II.

R(a) ohms.	R(b) ohms.	Swing/1% Pulp Divisions.	Sharpness of nul Point Divisions.	Accuracy of Concentration Determination.
0	0	2	0.2	0.10%
3	3	4.1	0.2	0.05
12	10	18.2	0.4	0.025
36	30	60	1.0	0.017

Conclusions.

The above experiments indicate that it is possible to construct a very simple apparatus capable of making instantaneous determinations of pulp concentrations. The above results show that differences in concentration of 0.02% are detectable and measurable , and the work indicates that the accuracy can be increased to 0.01%. Variations in temperature, and concentration of dissolved salts do not affect the readings. The apparatus is of such a nature that it can readily be inserted in any system where circulation of pulp is taking place.