THE SYSTEM

$CaO - SO_2 - H_2O$

"Equilibria Existing in the Three-Component System: Water - Calcium Oxide - Sulphur Dioxide Over the Temperature Range 0° to 25°C."

A Thesis

by

Arthur D.Grieve.

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.

McGill University

Montreal.

Sept. 1932.

TABLE OF CONTENTS.

****

The writer takes this opportunity to acknowledge the debt which he owes to Dr. O Maass for much valuable advice, and many kindnesses received during the course of this research.

INTRODUCTION.

The work to be described in this thesis forms a part of a general investigation which is being carried out in this laboratory on sulphite systems. This series of researches was instituted for two reasons. In the first place, there was very little available data on solutions of sulphurous acid and its salts, and much of what was available was of such a nature as to be open to question. Such experiments as had been carried out were usually confined to a narrow concentration or temperature range. It seemed desirable, therefore, to conduct a systematic research with a view to evaluating the equilibria existing in solutions of sulphur dioxide, calcium hydroxide, calcium sulphite and calcium bisulphite. In the second place. any data which was obtained, in addition to its purely scientific interest would be of value, from a practical point of view, to those who manufacture wood pulp by means of the sulphite process, and to those who use these solutions in the refining of sugar. Sulphite pulp manufacturers have admitted that the data already published is valuable to them and have expressed the belief that the present, and future work should yield additional worth while results.

In the present investigation the specific conductivity and vapour pressure of saturated solutions of calcium hydroxide have been measured over a temperature range from 0^{o} to 25^{o}; in these measurements greater care has been taken than ever before to ensure the purity of the water used and the absence of carbon dioxide from the system. In addition, the specific conductivity and vapour pressure of solutions of calcium hydroxide containing quantities of sulphur dioxide have been measured. Calcium hydroxide solutions, having a concentration of approximately 1% and 2%, were used and successive additions of sulphur dioxide were made until the vapour pressure of the solution approached one atmosphere. This work was carried out over a greater concentration range, solution concentrations have been determined with greater precision, and greater care has been taken to ensure the purity of materials, and the attainment of complete equilibrium than has been the case in any previous work on this system.

Before it was possible to study solutions of calcium sulphite and calcium bisulphite it was necessary to investigate the properties of sulphur dioxide solutions and calcium hydroxide solutions. Sulphur dioxide solutions have been studied in this laboratory by C. E. Maass (1), W. B. Campbell (2), and O. M. Morgan (3). The work on calcium hydroxide forms a part of the investigation to be reported in this thesis.

Maass and Maass (1) measured apparent molecular weights of sulphur dioxide over the temperature range -5° to 35°, the vapour pressures of aqueous solutions of sulphur dioxide over a wide range of concentrations below 27°, and in addition (4), the conductivities of these solutions. Campbell and Maass (2) measured the conductivities and vapour pressures of aqueous sulphur dioxide solutions over the temperature range 23° to 135° and at various concentrations from 0 to 8% sulphur dioxide; They also measured the densities of sulphur dioxide solutions at concentrations varying from 0 to 15%. Morgan and Maass (3) have made the best available measurements of conductivities and vapour pressures of sulphur dioxide soltuions from 0° to 25°, varying concentrations up to such a value as to give a vapour pressure of about one atmosphere.

The conductivity of calcium hydroxide solutions was measured by Ostwald (5). Unfortunately he neglected to mention at what temperature the measurements were made. In a previous paper (6) he reports similar measurements made on a series of acid solutions which were carried out at 25°, so presumably the work on calcium hydroxide was also done at 25°. Ostwald casts some doubt on these measurements, however, for he points out that the distilled water used was probably not as pure as it should have been, and that carbon dioxide may have introduced an error as it was not entirely excluded from the solutions. Miller and Witt (7) measured the conductivity of a saturated calcium hydroxide solution at 30°. Their value is in excellent agreement with the extrapolation to 30° of the values obtained in the present work.

The solubility of calcium hydroxide has been determined by a number of investigators. Determinations have been made over a considerable temperature range by Maben (8), Lamy (9). Herzfeld (10), Guthrie (11), Moody (12), and Haslam, Calingaert and Taylor (13). Miller and Witt (7) determined the solubility at 30°. Between 30° and 100° fair agreement exists between the determinations of the majority of these authors. Below 30° the agreement is very poor; it will be shown in the discussion of results that all the values in this temperature range are open to question.

Some density measurements have been made on solutions of calcium hydroxide by Cavazzi. (14).

The three component system - - calcium hydroxide - sulphur dioxide - water - - has been the subject of a few investigations, some of which have been carried out from the point of view of the use of the system in the process of sugar refining, others from the point of view of the sulphite pulp manufacturer.

The conductivities of solutions of calcium sulphite, calcium bisulphite, and sulphur dioxide in calcium bisulphite have not been measured hitherto.

The solubility of calcium sulphite has been determined by Robart (15), by van der Linden (16) and by Weisberg (17). The values obtained by these authors do not agree with one another.*

Of the investigations on the system calcium oxide - sulphur dioxide - water only the following need be discussed here.

Schwarz and Muller-Clemm (18) have investigated the ratio of free to combined sulphur dioxide in calcium bisulphite solutions. They worked with solutions whose total sulphur dioxide content varied from 3 to 10%, and studied these at temperatures from 2° to 35°. Smith and Parkhurst (19) measured the solubility of sulphur dioxide in water, and in solutions of calcium hydroxide and magnesium hydroxide. Enckell (20) has also measured the solubility of sulphur dioxide in water, and the effect of the presence of calcium bisulphite and other salts on the solubility. Farnell (21) has measured the pH of certain solutions of calcium sulphite and bisulphite; he has also determined the neutralisation curve, i.e. pH plotted against per

* Solubilities have recently been determined by Bain(29). His values are in reasonable agreement with those of van der Linden.

cent neutralisation of sulphurous acid by calcium hydroxide.

All these investigations have been carried out from the point of view of the practical application of the data to industrial problems, rather than as a piece of pure research; as a result certain sources of error can be pointed out in all of them. It is probable that the sulphur dioxide used was impure. In most cases insufficient precautions were taken to ensure the complete removal and exclusion of air from the system. Solution concentrations were determined by titration. It is probable that in most cases insufficient time was allowed to permit the systems to reach equilibrium.

In planning the present work it was decided to carry the investigation over the entire range of temperature from 0° to 130°. To do this as one investigation would have meant constructing an apparatus which was capable of withstanding the high pressures encountered at high temperatures and at the same time of making accurate measurements of the vapour pressures met with at low temperatures. This would have been difficult, if not impossible; therefore, it was decided to divide the work into two parts: one part to consist of the measurements above 25°, the other part to consist of measurements below that temperature. The high temperature investigation has been conducted by G. W. Gurd, and is reported elsewhere (27). The work at low temperature has been performed by the writer.

As has been pointed out in the review of the literature, practically all the work done on sulphite systems, excepting what has been done in this laboratory, must be regarded with some doubt for two reasons; these are, first, uncertainty as to the concentration of sulphur dioxide in the solution, and second, the impurity of materials used. The technique of measuring the components and of preparing the solutions, as it has been developed in this laboratory, has removed any doubt which may exist regarding these two factors.

In addition to these two possible sources of error, it was discovered very early in this work that solutions of calcium hydroxide, calcium sulphite, etc., reach equilibrium with the corresponding solid phase at a surprisingly slow rate, despite thorough stirring of the solution. It is believed that this fact has not been fully appreciated by some authors and consequently the disagreement which exists amongst the available data for, say solubilities, is due to a great extent to the fact that sufficient time was not allowed for the system to reach equilibrium. In the present work it has been found that, at low temperatures, and when solid phase is present, the system reaches equilibrium only after from one to three days of constant stirring. This delay in reaching equilibrium made it impossible to do as much work as had been planned.

The following pages will contain a description of the apparatus used in this work; an outline of the experimental technique will be given, as well as a type of each of the calculations used in determining solution concentration, specific conductivity, etc. Tables of experimental results will be included, and these will be followed by a discussion of the results. The section on discussion will contain any data which is obtained from the literature and which is necessary in the interpretation of the experimental results. Finally, a summary and a bibliography will be presented.

EXPERIMENTAL SECTION

The experimental section will be divided into three parts:

A. Description of Apparatus.
B. Experimental Technique.
C. Type Calculations.

A. - Apparatus

The apparatus will be considered under the following heads:

1. General.
2. The Cell.
3. The Thermostat.
4. The Measurement of Vapour Pressure.
5. The Measurement of Electrical Conductivity.
6. Measurement of the Constituents.
    (a) Sulphur Dioxide.
    (b) Water.
    (c) Calcium Oxide.
7. The purification of the Constituents.
    (a) Sulphur Dioxide.
    (b) Water.
    (c) Calcium Oxide.
8. Auxiliary Devices

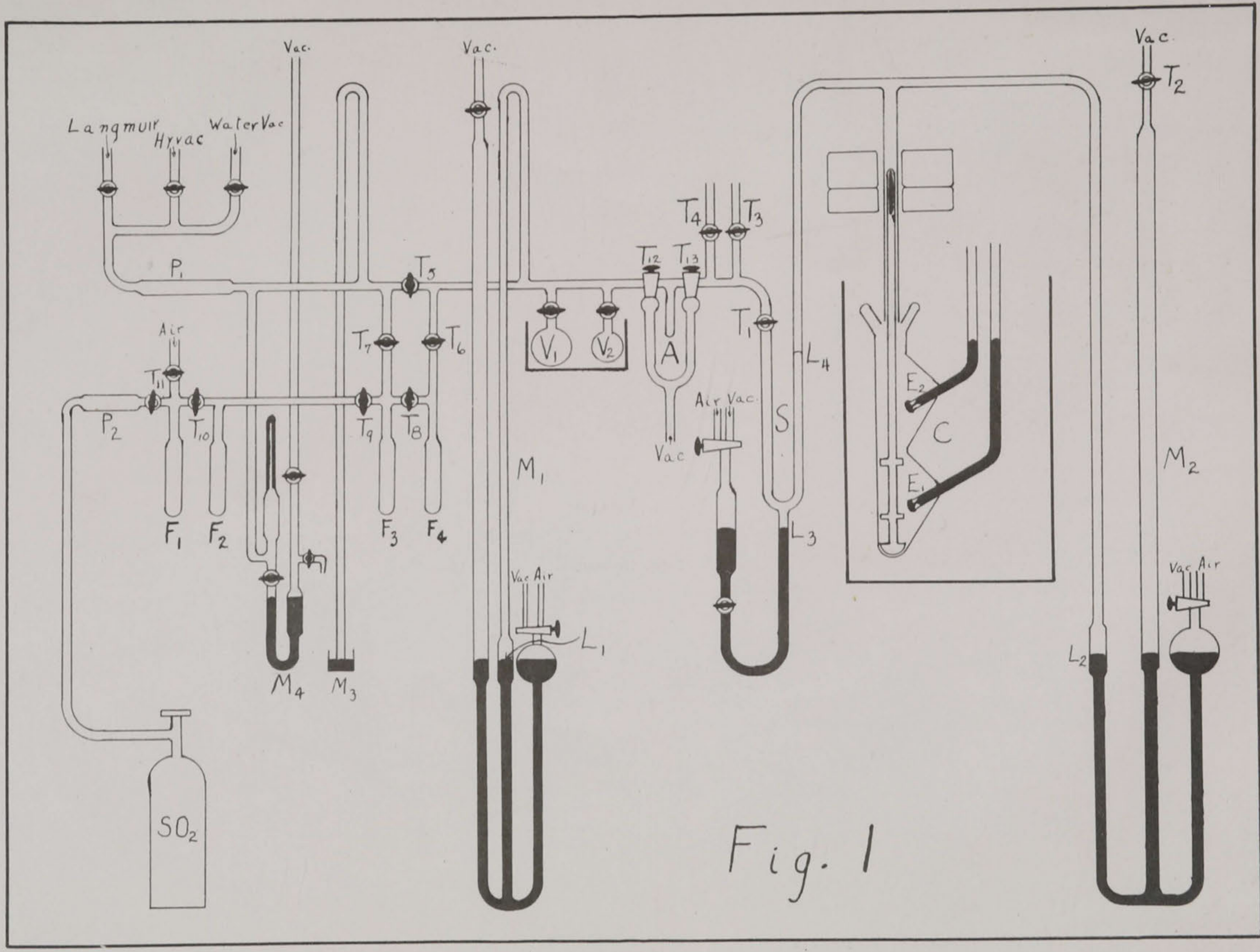


Fig. 1
Langmuir
Hyvac
Water Vac
Vac.
Vac.
Vac.
P1
P2
T1
T2
T3
T4
T5
T6
T7
T8
T9
T10
T11
T12
T13
Air
V1
V2
A
Air Vac
Vac
S
L1
L2
L3
L4
E1
E2
C
F1
F2
F3
F4
M1
M2
M3
M4
Vac Air
Vac Air
SO2

1. General.

The apparatus used in this work is shown diagrammatically in Figure 1.

For the purposes of description it may be considered in three sections: (a) the cell, C, in which the solutions to be studied were prepared; it was so designed that the conductivities and vapour pressures of these solutions could be measured simultaneously; (b) the central portion of the apparatus, consisting essentially of two bulbs of known volume, together with tubing connecting them to one another, to a constant level manometer and to the cell. This section was used to measure the quantities of sulphur dioxide introduced into the cell and, (c) the section for the purification and storage of the sulphur dioxide, consisting of four flasks, F_1, F_2, F_3, and F_4, of which F_4 acted as a storage reservoir for the sulphur dioxide.

In addition to these three main sections there were certain auxiliary devices, such as the MacLeod gauge, M_4, a rough manometer, M_3, a phosphorus pentoxide drying tube and connections to the various vacuum pumps.

In what follows, the apparatus used for the measurement, purification, and storage of the water and calcium oxide, while not an integral part of the apparatus shown in Figure 1, will, for the sake of continuity, be described along with the corresponding apparatus for sulphur dioxide.

2. Cell

Because of the uses to which it was to be put the cell had to be vacuum tight and resistant to the chemical action of the solutions it was to contain; the electrodes had to be so placed as to permit of continuous stirring of the contents of the cell, and a stirrer had to be built in, Provision had to be made for introduction of the lime, water and sulphur dioxide, and for measuring the vapour pressure of the solution.

The cell was made of pyrex glass of about 0.1 cms. thickness. It was about 3.5 cms. in diameter and 12 cms. high. It could be cut off from the remainder of the system by means of a mercury seal, S. When this was done the atmosphere of the cell was completely enclosed in glass except where it was in contact with the mercury surface of the seal and mercury surface of the constant level manometer, M_2.

The electrodes, E_1 and E_2, were made of very thin platinum foil, sealed into pyrex tubing. The electrodes were set in "bay-windows" as shown; the exposed platinum portions projected very slightly into the body of the cell, but not so far as to be in danger of being damaged by the movements of the stirrer. Contact was made with the electrodes by filling the pyrex tubing with mercury, from which copper wires led to the conductivity measuring apparatus.

The electrodes were platinized according to the method outlined by Reilly (22).

The cell constant was determined, using 0. 1 N, and 0.02 N solutions of potassium chloride, which had been purified by three recrystallizations followed by heating for some hours at 110° C. In calculating the cell constant the data of Kohlrausch (23) for the specific conductivity of potassium chloride solutions were used. The atomic weights used in preparing the solutions were those used by Kohlrausch.

The cell constant was independent of the level of the liquid in the cell, provided that that level was always kept above the upper edge of the upper electrode "bay window". During run number 9 the cell head had to be repaired and these repairs altered the cell constant slightly. The two values were: No. I - 1.437; No. II = 1.428.

Since the foil used in the elctrodes was so thin, and the leads to the conductivity measuring apparatus were of considerable length, the lead resistance of the cell was appreciable. This lead resistance was measured by filling the cell with mercury and measuring its resistance with the electrodes short-circuited in this way. It was found that this lead resistance could be determined more accurately than by calculating it from the measured resistance of two solutions of known specific conductivity. In the latter method, any small errors in the determination of total resistance introduce large relative errors in the value of the lead resistance.

The lead resistance was found to be 0.36 ohms.

The cell was completely enclosed, so that in order to stir the solution in the cell, the stirrer had to be actuated from the outside. This was done by placing a soft iron core in the shaft of the stirrer in order that it could be controlled electro-magnetically. The shaft of the stirrer extended into the neck of the cell into which it fitted more or less snugly and was thus prevented from swaying from side to side. The neck of the cell was surrounded by two cylindrical electro-magnets. The current was maintained in the lower magnet at all times when the stirrer was in use; the permanent magnet thus created served to just lift the stirrer from the bottom of the cell and to prevent it dropping back too heavily onto the bottom again during the stirring operation; a drop would have caused damage to the stirrer or to the bottom of the cell. The current in the upper magnet was interrupted at regular intervals; When the current was flowing the stirrer was pulled out of the field of the permanent magnet into the field of the intermittent magnet, when it was broken, the stirrer dropped back into the field of the permanent magnet. During the early part of the work the circuit of the intermittent magnet was made and broken by means of an automatic mercury valve-operated by a water vacuum pump; during the latter part of the work this was accomplished by means of a switch which was opened and closed by an eccentric wheel driven by an electric motor whose speed was reduced by means of a train of pulleys. The current in each magnet could be varied as desired by means of a parallel bank of lamps which was in series with the magnet.

The design of the stirrer was found to be of the utmost importance in obtaining true equilibrium between the solution and the solids which were present. Several month's work had been completed before it was discovered that the solid was not being properly stirred and was consequently not in equilibrium with the solution; the solution appeared to reach equilibrium with the solid phases, as shown by the constancy of the conductivity, but actually the solid calcium hydroxide was merely coated over with a precipitate of calcium sulphite, and the stirrer which was then being used was not suitable for breaking up this solid. An analysis of the data showed that all data relating to the system when a solid phase was present was open to question. It was decided to discard all these data, redesign the cell and stirrer so as to be sure of getting good agitation of the solid, with no pockets into which solid could settle.

With this in mind, the new stirrer was built with a large pestle-shaped base. This dropped into the more or less cup-shaped bottom of the cell, and since the cell was so designed that this was the only place into which solid could settle, the solid was being stirred constantly, thus ensuring a true, instead of a pseudo-equilibrium, as had previously been obtained. Button-like expansions on the shaft of the stirrer served to agitate the upper portions of the solution. The stirrer was constructed entirely of pyrex tubing.

Three tubes gave access to the body of the cell; a central tube, or neck, mentioned above, and two side tubes. The central tube was connected to the manometer for measuring vapour pressures; it was connected to the sulphur dioxide measuring system, and was used to admit the sulphur dioxide; through it the cell could be evacuated. Lime was added through one of the side tubes. Distilled water was added through the other side tube by distillation from a flask sealed to it.

It was necessary to know the volume of the cell with its connecting tubing in order to determine the volume of the dead space over the solution; this latter quantity was necessary in the calculation of corrections to solution concentrations made necessary by the presence of some of the sulphur dioxide and water in the vapour phase.

The total volume of the cell and its connecting tubing, i.e. that volume bounded by stop-cock, T_1, level, L_3, of the mercury seal and level L_2 of the constant level manometer, M_2, was determined by allowing dry air to expand into the previously evacuated cell from the volume measuring system (to be described later). The volume of this system was known, and by measuring the temperature and pressure of the gas before and after the expansion the volume of the cell and its tubing was calculated using the formulae:-

$$v_c = v_2 - v_1$$

$$v_2 = \frac{p_1 \; v_1 \; T_2}{p_2 \; T_1}$$

v_1 = the volume of the gas introduction system.

v_2 = the sum of the volume of the gas introduction system and cell system.

v_c = the volume of the cell system.

p_1 = the pressure of the gas before expansion into the cell.

p_2 = the pressure of the gas after expansion into the cell

T_1 - the temperature of the gas before expansion into the cell.

T_2 - the temperature of the gas after expansion into the cell.

The volume of the cell system was 190.9 cc.

When the mercury seal was closed the volume of the cell system was reduced by a small amount:-the volume of the tubing between T_1, L_3 and L_4 (The mercury in the seal was kept at L_4 during the course of the run.) This volume was determined by measuring the length of the tubing and multiplying the length by the volume per unit lengeth as determined by weighing the amount of mercury necessary to fill a unit length.

The volume of this length of tubing was 8.9 c.c.

The volume of the dead space in the cell system was calculated by subtracting from the volume of the cell system the sum of the volume of the solution and the volume of the tubing cut off by closing the mercury seal.

3. The Thermostat

The cell was immersed in a constant temperature bath, which consisted of a large glass jar well lagged with wool. The temperature of the bath was controlled by means of a toluene over mercury thermo-regulator which, operating through a relay, controlled a heating coil in the bath. The heating coil consisted of a coil of nichrome resistance wire which was placed inside a pyrex tube and covered with oil. The current in the heating coil could be varied by varying the external resistance in series with it. The temperature of the laboratory was at all times higher than the temperature of the bath. To prevent the temperature of the bath rising as a result of warmer surroundings, a copper cooling coil was placed in the bath and tap water was circulated through it.

The bath was filled with water which was stirred by a motor driven stirrer.

4. The Vapour Pressure Manometer.

The vapour pressure of the solution in the cell was measured on the manometer, M_2. One arm of this manometer was kept at a constant level, L_2, by applying pressure or vacuum to the mercury reservoir of the manometer. The other arm was evacuated from time to time by means of a Langmuir diffusion pump and closed off by means of stop-cock, T_2.

The scale of the manometer was etched on glass. It was compared with an invar scale; minor errors were found, especially in the upper portions of the scale. A curve was made of these which was used in applying the necessary corrections to the vapour pressure readings.

Vapour pressures could be measured to within 0.02 cms.

5. The Conductivity Measuring Apparatus.

The apparatus for measurement of the conductivity of the solution consisted of Leeds and Northrup helical slide wire, Serial No. 195,767 and Leeds and Northrup resistance box No. 135,712. The slide wire was graduated in half divisions from 1 to 1000. The resistance box read in steps of 1 ohm from 1 to 1000 ohms. Both these devices had been checked for accuracy and found satisfactory. One end of the slide wire was grounded to the laboratory plumbing. A variable condenser was connected in parallel with the resistance box to balance any capacity in the cell.

A Vreeland oscillator was used as the source of current. It operated at a frequency of 1000 cycles and gave a pure sine wave without harmonics. A set of Murdock headphones was used to detect the balance point in setting the slide wire.

6. Measurement of Components.

(a) Sulphur Dioxide.

The apparatus for the measurement of the amount of sulphur dioxide consisted of two bulbs, V_1 and V_2, of known volume, tubing bounded by stop-cocks T_1, T_3,

T_4, T_5, T_6 the level, L_1 on the manometer, and the manometer, M_1, for the measurement of the pressure of the gas.

The volumes, V_1 and V_2, were calibrated by weighing them empty and filled with water and calculating the volume of each after applying the necessary corrections. The volume of the connecting tubing was determined by allowing dry air to expand into the evacuated tubing, measuring the pressure and temperature of the gas before and after the expansion. The volume of the tubing was calculated from these data using the same type of formula as that given in the description of the determination of the volume of the cell system. The volume of V_1, V_2 and the tubing were:-

V_1 = 587.8 cc.
V_2 = 126.9 cc.
Tubing = 83.3 cc.
Total = 797.0 cc.

The manometer, M_1, was similar in construction to the manometer, M_2, which was described above in the section on vapour pressure measurement.

The bulbs, V_1 and V_2, were immersed in a water bath in order to obtain accurately their temperatures.

Two thermometers were attached to the connecting tubing in order to obtain its average temperature.

The T-shaped section, A, in addition to forming part of the gas measuring system, also was used as a means of injecting sulphur dioxide into the cell. The vertical portion was so designed to permit the sample of sulphur dioxide to be condensed in it. T_{12} and T_{13} were pressure stop-cocks and hence it was possible to allow the sulphur dioxide to develop considerable pressure as it warmed up; this pressure carried it into the cell against any pressure that existed there.

(b) Water.

The quantity of water introduced was determined by weighing it in a weight pipette.

(c) Calcium Oxide.

The quantity of calcium oxide introduced was determined by weighing it in a covered weighing bottle.

7. Purification and Storage of Materials.

(a) Sulphur Dioxide.

The apparatus for the purification of the sulphur dioxide consisted of four flasks F_1, F_2, F_3, F_4. These could be connected to one another or cut off from one another through stop-cocks T_8, T_9, T_{10}. They could be evacuated through stop-cock T_7. The two way stop-cock, T_{11}, led on the one hand to the atmosphere through a tube which projected through the laboratory window, and on the other hand to a stock cylinder of sulphur dioxide through a phosphorus pentoxide drying tube, P_2.

(b) Water.

A pyrex distilling flask, sealed to one of the side arms of the cell, was used to purify the water.

(c) Calcium Oxide.

An electric muffle furnace was used in the preparation of the calcium oxide. It was stored in a stoppered weighing bottle in an evacuated desiccator over phosphorus pentoxide and fused potassium hydroxide.

8. Auxiliary Devices.

Three types of vacuum pumps were used: water vacuum pump, Cenco hyvac pump, and Langmuir mercury diffusion pump. The system was so designed that any one of these pumps could be used to evacuate any portion of it.

The water vacuum pump was used for adjusting mercury levels in the manometer reservoirs, and the mercury seal, and for removing as much as possible of the sulphur dioxide from the system when it became necessary to evacuate it; it was thus possible to avoid passing large quantities of it through the hyvac pump.

The hyvac pump was used when a more complete evacuation of the system was necessary; it was also used in conjunction with the Langmuir diffusion pump.

The Langmuir diffusion pump was of the usual type. It was capable of reducing the pressure of the system to 0.0003 cms. of mercury in about twenty minutes. It was used for the complete evacuation of the system and especially for the evacuation of the low pressure arm of each manometer.

Low pressure measurements were made on a MacLeod gauge, M_4.

A rough manometer , M_3, was found useful as a means of giving an approximate measure of pressures, especially in the distillation of sulphur dioxide; being open at the bottom, it served as a convenient safety valve in these distillations whenever the pressure became too great.

A phosphorus pentoxide drying tube was used to remove traces of water vapour from the system and to dry the air that had to be admitted during volume calibration operations.

B. Experimental Technique.

This part of the experimental section will consist of a description of the experimental methods used in carrying out this work. This will be divided into two heads:

1. Preparation and Purification of Materials.
2. Preparation of Solutions, and Measurements made on them.

1. Preparation and Purification of Materials.

(a) Sulphur Dioxide.

Sulphur dioxide was procured in liquid form in steel cylinders from the Matheson Chemical Company.

It was passed slowly over phosphorus pentoxide and condensed in the flask, F_1, by surrounding it with a mixture of acetone and solid carbon dioxide. As soon as a sufficient quantity had been condensed it was allowed to warm up and evaporate. The "head" portion was discarded, the middle portion was condensed into the flask, F_2, the "tail" portion was discarded. This procedure was repeated twice.

The final product was free from sulphur trioxide and water. It was stored until needed in the flask, F_4.

(b) Water.

Water was procured from the distilled water supply in the laboratory. If the water is allowed to run from the tap for a short time, a sample is procured having a specific conductivity of about $4x10^{-6}$. This water contained considerable amounts of dissolved air.. This, if left in the water, would tend to come out of solution at the low pressures met with during the run, and introduce an error in the vapour pressure measurements.

The air was removed in the following manner: A pyrex distilling flask was sealed to one of the side arms of the cell, the sample of water was added from a weight pipette and the neck of the flask was sealed off. The flask was surrounded with a mixture of acetone and carbon dioxide; when the water was frozen the flask was evacuated through the cell. Stop-cock, T_1, was closed and the ice allowed to melt. Under the reduced pressure the dissolved gases readily came out of solution. The cycle of freezing, evacuation, and melting was repeated at least twice, or until no further gas was evolved as indicated by reading the manometer, M_2.

Considerable difficulty was experienced in freezing the water without breaking the flask. A narrow cylindrical flask was used at first, but with rather unsatisfactory results. Later a 250 cc. distilling flask was used and it proved satisfactory if the cooling was done in the proper manner. If the level of the freezing mixture were slowly raised about the flask,ice formed in the flask above the level of the freezing mixture and when the latter was raised, the glass, on being still further cooled, contracted, and was broken because it could not compress the ice inside it. If, on the other hand, the level of the freezing mixture was brought at the outset to a point above the level of the water, the glass was completely cooled before any appreciable amount of ice had formed. In melting the ice, it has been found advisable to free the ice from the glass immediately by surrounding the flask for a few minutes with water at about 40°.

When the gas was completely removed from the water, the latter was distilled into the cell. This distillation was done slowly and at low temperature by surrounding the cell with ice water and maintaining the flask at 25° to 30° C.

(c) Calcium Oxide.

Calcium oxide was prepared from calcium carbonate which was obtained from Messrs Eimer and Amend in the form of "clear select" crystals of Iceland spar. The crystals were crushed, placed in a platinum crucible and heated in an electric muffle furnace at about 1000°C. for from ten to fifteen days.

The calcium oxide formed was tested for freedom from carbon dioxide in two ways In the first method a sample of the calcium oxide was placed on a microscope slide and covered with a film of gelatin solution. A microscope was focussed on the sample and a few drops of hydrochloric acid were placed on the gelatin. The acid soon diffused through the gelatin to the calcium oxide where it reacted with it; if any calcium carbonate were present the acid liberated carbon dioxide which was trapped under the gelatin and could be seen in the form of a bubble. In the second method a sample of the calcium oxide was dissolved in water, concentrated hydrochloric acid was added to liberate any carbon dioxide which might be present. A few cubic centimeters of chloroform were added, and the mixture was heated gently; the vapour was bubbled through a saturated solution of barium hydroxide. Carbon dioxide is quite insoluble in the acid solution used and the bubbles of chloroform vapour facilitate its removal from the solution and carry it into the barium hydroxide where it forms a precipitate of barium carbonate. Care was taken to have all reagents free from carbon dioxide and a blank was run before each sample was tested.

Both methods showed that the calcium oxide was entirely free of carbonate.

2. Preparation of Solutions, and Measurements Made.

This section will contain a description of all the steps necessary in carrying out a "run".

In each run, water and calcium oxide were placed in the cell and quantities of sulphur dioxide were added; after each addition of sulphur dioxide the specific conductivity and vapour pressure of the solution were measured at 0°, 10°, 18°, and 25°C.

The cell was cleaned with nitric acid and thoroughly rinsed and dried. It was sealed to the apparatus; this could be done without changing the volume of the cell system appreciably. The cell was evacuated and tested for possible leaks; this was important because each run extended over such a long period that even the slightest leak would admit considerable amounts of air.

The flask for the purification of the water was cleaned with nitric acid, rinsed, dried, and sealed to one arm of the cell. A constriction was made at the point at which the flask was to be sealed off to permit this being done under reduced pressure.

Distilled water was added to the flask from a weight pipette and the ~~flask~~ neck was sealed off.

The other side arm of the cell was opened and the desired amount of calcium oxide added. This operation was carried out as quickly as possible to prevent the calcium oxide reacting with the water vapour and carbon dioxide of the air. The side arm of the flask was sealed off.

The water was freed of air and distilled into the cell as described in the section on purification of water. The distillation flask was sealed off.

The conductivity and vapour pressure of the calcium hydroxide solution thus prepared were measured over the temperature range from 0° to $25^{\circ}C$. These measurements form part of a separate investigation in themselves. They will be treated separately in the discussion.

When the calcium hydroxide investigation was complete, a quantity of sulphur dioxide was added to the cell. This was done as follows: The system for the measurement of sulphur dioxide was completely evacuated, then flushed two or more times with pure sulphur dioxide from the storage flask. The system was filled with sulphur dioxide; several minutes were allowed to permit the gas to come to the temperature of the surroundings. The pressure of the gas was read, the temperature of the bulbs and of the connecting tubing was read. The bulb of section A was surrounded with a carbon dioxide-acetone mixture and the desired amount of sulphur dioxide was condensed into it. Stop cocks T_{12} and T_{13} were closed and the liquefied gas was allowed to warm up. T_1 and T_{13} were opened and sulphur dioxide rushed into the cell. This process was repeated until all the gas was added. Stop cock, T_1, was closed, the mercury seal was closed. Stop cocks T_{12} and T_{13} were opened and the temperature and pressure of the remaining gas were read as before.

During the addition the cell was packed in ice to increase the solubility of the gas and the solution was vigorously stirred to increase the rate of solution.

The temperature was held at 0° and the conductivity, vapour pressure, bath and tubing temperatures were recorded at intervals of from fifteen minutes to half an hour until equilibrium was reached. If the conductivity did not change during an hour the system was regarded as being in equilibrium. The temperature was then raised to 10° and the measurements repeated; the same procedure was followed for 18° and 25°.

C. Type Calculations.

In this section a sample of each of the calculations used in determining solution concentration, specific conductivity and vapour pressure will be given.

As a preliminary to the calculation of the quantity of sulphur dioxide introduced, the pressure measurements were reduced to centimeters of mercury at $0^oC.$, using the data from the "International Critical Tables", (24). Isothermals for the variation with pressure of the apparent molecular weight of sulphur dioxide were plotted from the data of Cooper and Maass (25). The apparent molecular weight of sulphur dioxide at any pressure and temperature could be read from these curves.

The weight of sulphur dioxide introduced into the cell was calculated using the formula:

$$W = \left(\frac{p_1 M_1}{T_1} - \frac{p_2 M_2}{T_2}\right) \frac{v}{R}$$

where w = the weight in grams of sulphur dioxide introduced.

p_1 = the initial pressure of the sulphur dioxide.

p_2 = the final pressure of the sulphur dioxide.

M_1 = the apparent molecular weight of the sulphur dioxide at pressure p_1 and temperature T_1.

M_2 = the apparent molecular weight of the sulphur dioxide at pressure p_2 and temperature, T_2.

v = the volume of the gas introduction system.

R = the gas constant in appropriate units.

T_1 = the average initial temperature of the sulphur dioxide.

T_2 = the average final temperature of the sulphur dioxide.

These average temperatures were obtained by averaging the readings of the thermometer in the bath surrounding the bulbs, V_1 and V_2, and the thermometers attached to the connecting tubing, weighting the readings according to the volumes which they represented. Calculations using this method were found to check calculations in which the bulbs and tubing were considered separately and since the former method is less laborious it was used in place of the latter.

At higher concentrations of sulphur dioxide the partial pressure of sulphur dioxide above the solution was sufficient to necessitate correcting the solution concentration for the quantity of sulphur dioxide in the vapour phase. This was calculated from the formula.

$$m_{SO_2} = \frac{p_{SO_2} \; M \; v}{R \; T}$$

Where m_{SO_2} = the weight of sulphur dioxide in the vapour phase.

p_{SO_2} = the partial pressure of the sulphur dioxide.

M = the molecular weight of sulphur dioxide at that temperature and pressure.

v = the volume of the cell dead space.

R = the gas constant

T = the average temperature of the dead space.

The weight of the sulphur dioxide in the solution was given by:

$$w_{SO_2} = w - m_{SO_2}$$

where w_{SO_2} = the weight of sulphur dioxide in solution.

w = the weight of sulphur dioxide introduced.

m_{SO_2} = the weight of sulphur dioxide in the vapour phase.

Percentage of sulphur dioxide was given by:

$$\text{percent } SO_2 = \frac{w_{SO_2} \times 100}{w_{H_2O} + w_{CaO} + w_{SO_2}}$$

in which w_{H_2O} = the weight of water.

w_{CaO} = the weight of calcium oxide

w_{SO_2} = the weight of sulphur dioxide.

The number of moles of sulphur dioxide was calculated from:

$$n_{SO_2} = \frac{w_{SO_2}}{M}$$

where n_{SO_2} = the number of moles of sulphur dioxide.

w_{SO_2} = the weight of sulphur dioxide.

M_{SO_2} = the true molecular weight of sulphur dioxide.

= 64.06 g.

The number of moles of sulphur dioxide per mole of calcium oxide was given by:

$$N = \frac{n_{SO_2}}{\dfrac{w_{CaO}}{M_{CaO}}}$$

where N = the number of mols of sulphur dioxide per mol of calcium oxide,

n_{SO_2} = the number of mols of sulphur dioxide.

w_{CaO} = the weight of calcium oxide.

M_{CaO} = the molecular weight of calcium oxide,

= 56.07

The weight of water was corrected for buoyancy using the formula from "International Critical Tables" (26):

$$m_{H_2O} = S + (v_m - v_s)d.$$

Where m_{H_2O} = the true weight of the water.

S = the mass of the weights.

v_m = the volume of the water.

v_s = the volume of the weights.

d = the density of air.

The weight of water was also corrected for the amount of water vapour contained in the distillation flask when it was sealed off.

The total vapour pressure of the solution was reduced to centimeters of mercury at 0°C. The calibration corrections of the scale were also applied. Partial pressures of sulphur dioxide were calculated by subtracting the vapour pressure of the solution of calcium hydroxide at that temperature from the total vapour pressure.

The specific conductivity was calculated from the formula:

$$k = \frac{C}{R\frac{A}{1000-A} - r}$$

where k = the specific conductivity.

C = the cell constant.

R = the reading of the resistance box.

A = the slide wire reading

r = the lead resistance.

RESULTS.

Measurements have been made on saturated solutions of calcium hydroxide, and on the three- component system, water - calcium oxide - sulphur dioxide. In studying this three-component system two different calcium oxide concentrations were used. All the measurements made on the system for a given calcium oxide concentration constitute a "run". In run No. 4 the calcium oxide concentrations was approximately 1 gm. calcium oxide per 100 gm. of water + calcium oxide, in run No. 9, approximately 2 gm. per 100 gm. Run No. 9 was done in two parts. This was necessary because of a break in the neck of the cell. This break occurred just after the measurements at sulphur dioxide concentration 9i had been completed. After repairs had been made and the constants of the cell redetermined, a second solution was prepared having the same concentration as the previous one. The calcium oxide concentration of this second solution was within 0.1% of that of the first.

As sulphur dioxide was being added to this new solution, conductivity and vapour pressure measurements were made at some of the concentrations at which measurements had been made on the first solution. It was found possible to check previously obtained values to within 1%.

These measurements not only served to prove that it was quite permissible to do the run in two parts, but also served to establish the reproducibility of the data obtained in this work.

Conductivity and vapour pressure measurements have been made on saturated solutions of calcium hydroxide at 0°, 10°, 18°, and 25°. (In all this work the 0° values had to be obtained by making the measurements at 0.1° and extrapolating to 0°). These values are given in Table 1 and Fig. 2. In addition to the experimental data, Table 1 also contains certain values which have been calculated from them, or found in the literature. Temperatures are given in degrees centigrade, vapour pressures in centimeters of mercury, specific conductivities in reciprocal ohms. The solubilities given in column four are taken from an average curve drawn from values found in the literature; this curve will be treated in greater detail in the discussion. λ_c, the equivalent conductivity at a given concentration, was calculated from the specific conductivities and the concentrations as given by the solubilities. λ_0, the equivalent conductivity at infinite dilution, was calculated from the data of Kohlrausch for the mobility, and temperature coefficient of mobility, of calcium and hydroxyl ions. α, the degree of dissociation, is given by the ratio of λ_c to λ_0 K, the dissociation constant, was calculated from

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

$$= \frac{\alpha N \alpha^2 N^2}{N(1-\alpha)}$$

$$= \frac{\alpha^3 N^2}{1-\alpha}$$

where α is the degree of dissociation,

N is the normality as found from the solubility.

The data obtained in run No. 4 are given in tables 2, 3, 4, and 5 and graphically in figures 3 and 4, the data for run No. 9 in tables 6, 7, 8 and 9 and in figures 5 and 6.

In the tables the concentration of sulphur dioxide is expressed in two different ways; in column 2 it is expressed as the ratio of the number of molecules of sulphur dioxide to the number of molecules of calcium oxide; in column 3 it is expressed as per cent, i.e. grams of sulphur dioxide per 100 grams of water + calcium oxide + sulphur dioxide. At higher concentrations of sulphur dioxide a correction had to be made for the amount of the gas which was in the vapour phase. p, the total vapour pressure of the solution, and p_{SO_2}, the partial vapour pressuresof the

TABLE No. 1.

System: Calcium Oxide-Water.

t °C	p. cms.	$k \times 10^2$	solubility, gms. CaO/ l. of soln.	λ_c
0	0.47	0.585	1.351	121.5
10	0.94	0.720	1.322	152.7
18	1.55	0.799	1.272	176.1
25	2.37	0.856	1.207	198.8

λ_o	α	$K \times 10^3$
145.9	0.832	7.97
189.9	0.804	5.89
225.0	0.783	4.55
255.8	0.777	3.90

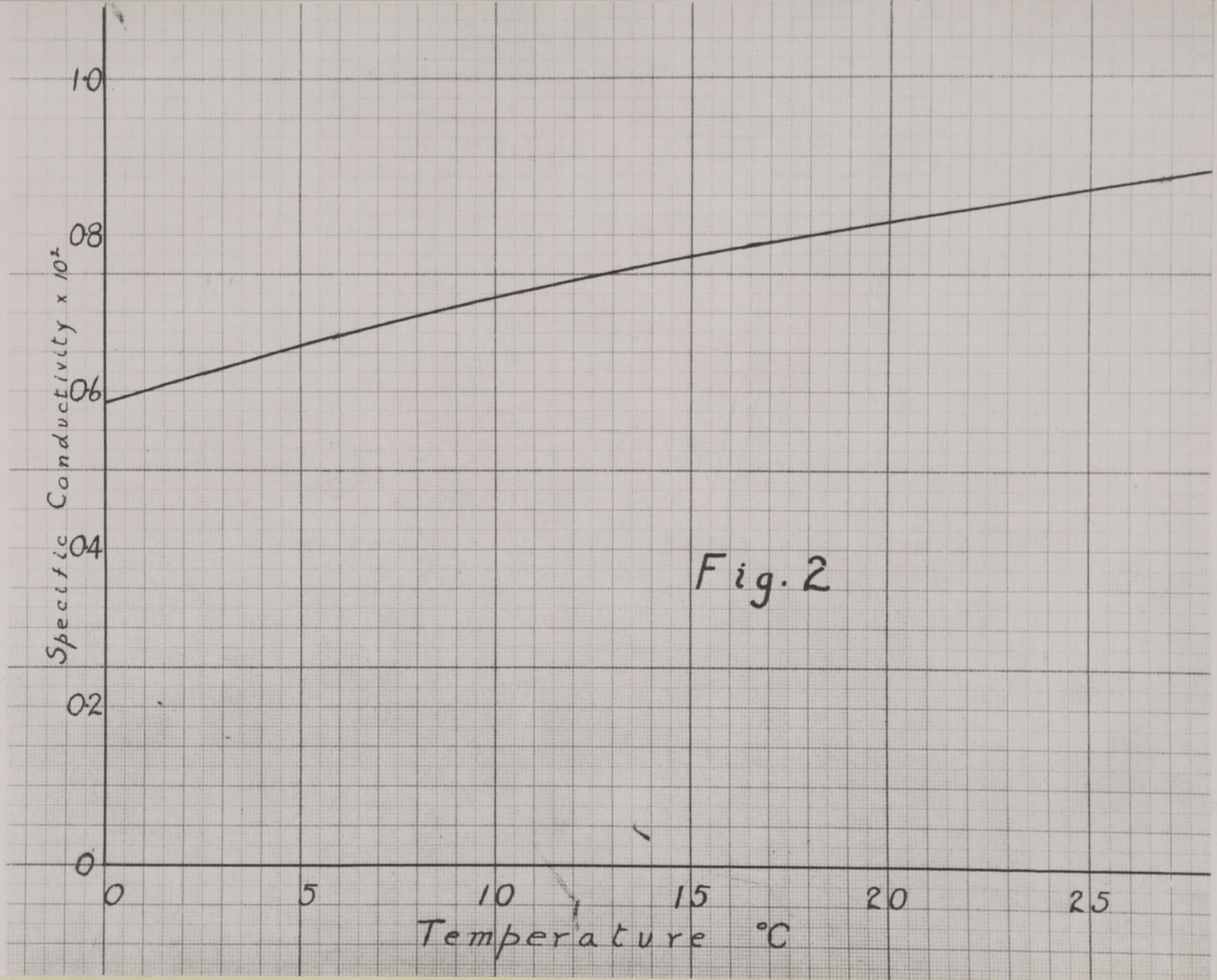

1·0
0·8
0·6
0·4
0·2
0
Specific Conductivity x 10²
0
5
10
15
20
25
Temperature °C

Fig. 2

sulphur dioxide, are given in centimeters of mercury. p_{SO_2} was calculated from p by substracting the vapour pressure of the saturated calcium hydroxide solution from the values found for p; this method is not rigorous, especially at the higher sulphur dioxide concentrations, because the partial pressure of water above such solutions will be less than the vapour pressure of water over a saturated calcium hydroxide solution. The error thus introduced is small enough to be neglected in this work.

TABLE 2.

Run No. 4 - 0° C.

No.	SO_2 Conc.		$k \times 10^2$	p, cms	pso_2, cms
	Moles/Mole	%			
4	0.0	0.0	0.585	0.47	0.0
4(a)	0.084	0.099	0.586	0.47	0.0
4(b)	0.511	0.600	0.566	0.47	0.0
4(c)	0.791	0.934	0.540	0.47	0.0
4(d)	0.900	1.053	0.200	0.47	0.0
4(e)	0.951	1.112	0.014	0.48	0.01
4(f)	1.000	1.169	0.085	0.54	0.07
4(g)	1.107	1.294	0.228	0.58	0.11
4(h)	1.378	1.604	0.535	0.75	0.28
4(i)	1.947	2.252	1.062	1.24	0.77
4(j)	2.084	2.404	1.159	1.54	1.07
4(k)	2.365	2.722	1.299	2.54	2.07
4(l)	2.770	3.172	1.479	4.13	3.66
4(m)	3.846	4.351	1.939	8.52	8.05
4(n)	7.782	8.430	3.258	25.16	24.69

Weight of water = 111.642 g.

Weight of calcium oxide = 1.168 g.

TABLE 3.

Run No. 4 - 10°C.

No.	SO_2 Conc. Moles/Mole	%	k x 10^{2}	p, cms.	p_{SO_2}, cms.
4	0.0	0.0	0.720	0.94	0.0
4(a)	0.084	0.099	0.709	0.93	0.0
4(b)	0.511	0.600	0.692	0.94	0.0
4(c)	0.791	0.934	0.668	0.94	0.0
4(d)	0.900	1.053	0.257	0.95	0.01
4(e)	0.951	1.112	0.019	0.96	0.02
4(f)	1.000	1.169	0.116	1.02	0.08
4(g)	1.107	1.294	0.307	1.07	0.13
4(h)	1.378	1.604	0.717	1.25	0.31
4(i)	1.947	2.252	1.404	2.08	1.14
4(j)	2.084	2.404	1.529	2.39	1.45
4(k)	2.365	2.722	1.681	4.00	3.06
4(l)	2.770	3.172	1.878	6.53	5.59
4(m)	3.838	4.343	2.358	13.45	12.51
4(m)	7.767	8.407	3.699	39.25	38.31

Weight of water = 111.642 g.

Weight of calcium oxide = 1.168 g.

TABLE 4.

Run No. 4 - 18° C.

	SO$_2$ Conc.				
No.	Moles/Mole	%	k x 10^2	p, cms	p_{SO_2}, cms.
4	0.0	0.0	0.799	1.55	0.0
4(a)	0.084	0.099	0.791	1.56	0.01
4(b)	0.511	0.600	0.783	1.56	0.01
4(c)	0.791	0.934	0.753	1.56	0.01
4(d)	0.900	1.053	0.307	1.56	0.01
4(e)	0.951	1.112	0.021	1.57	0.02
4(f)	1.000	1.169	0.142	1.64	0.09
4(g)	1.107	1.294	0.375	1.72	0.17
4(h)	1.378	1.604	0.871	1.91	0.36
4(i)	1.947	2.252	1.688	3.16	1.61
4(j)	2.084	2.404	1.852	3.44	1.89
4(k)	2.365	2.722	2.004	5.64	4.09
4(l)	2.757	3.157	2.202	9.19	7.64
4(m)	3.830	4.334	2.655	18.71	17.16
4(n)	7.732	8.382	4.003	54.11	52.56

Weight of water = 111.642 g.

Weight of calcium oxide = 1.168 g.

TABLE 5.

Run No. 4 - 25°.

	SO_2 Conc.				
No.	Moles/Mole	%	k x 10^2	p, cms.	p_{so_2}, cms.
4	0.0	0.0	0.856	2.37	0.0
4(a)	0.084	0.099	0.851	2.38	0.01
4(b)	0.511	0.600	0.848	2.37	0.00
4(c)	0.791	0.934	0.814	2.37	0.00
4(d)	0.900	1.053	0.355	2.37	0.00
4(e)	0.951	1.112	0.024	2.37	0.00
4(f)	1.000	1.169	0.165	2.40	0.03
4(g)	1.107	1.294	0.437	2.52	0.15
4(h)	1.378	1.604	1.022	2.76	0.39
4(i)	1.947	2.252	1.936	4.53	2.16
4(j)	2.084	2.404	2.149	4.64	2.27
4(k)	2.365	2.722	2.305	7.55	5.18
4(l)	2.754	3.155	2.473	12.15	9.78
4(m)	3.822	4.326	2.930	24.44	22.07
4(n)	7.707	8.344	4.213	69.79	67.42

Weight of water = 111.642 g.

Weight of calcium oxide = 1.168 g.

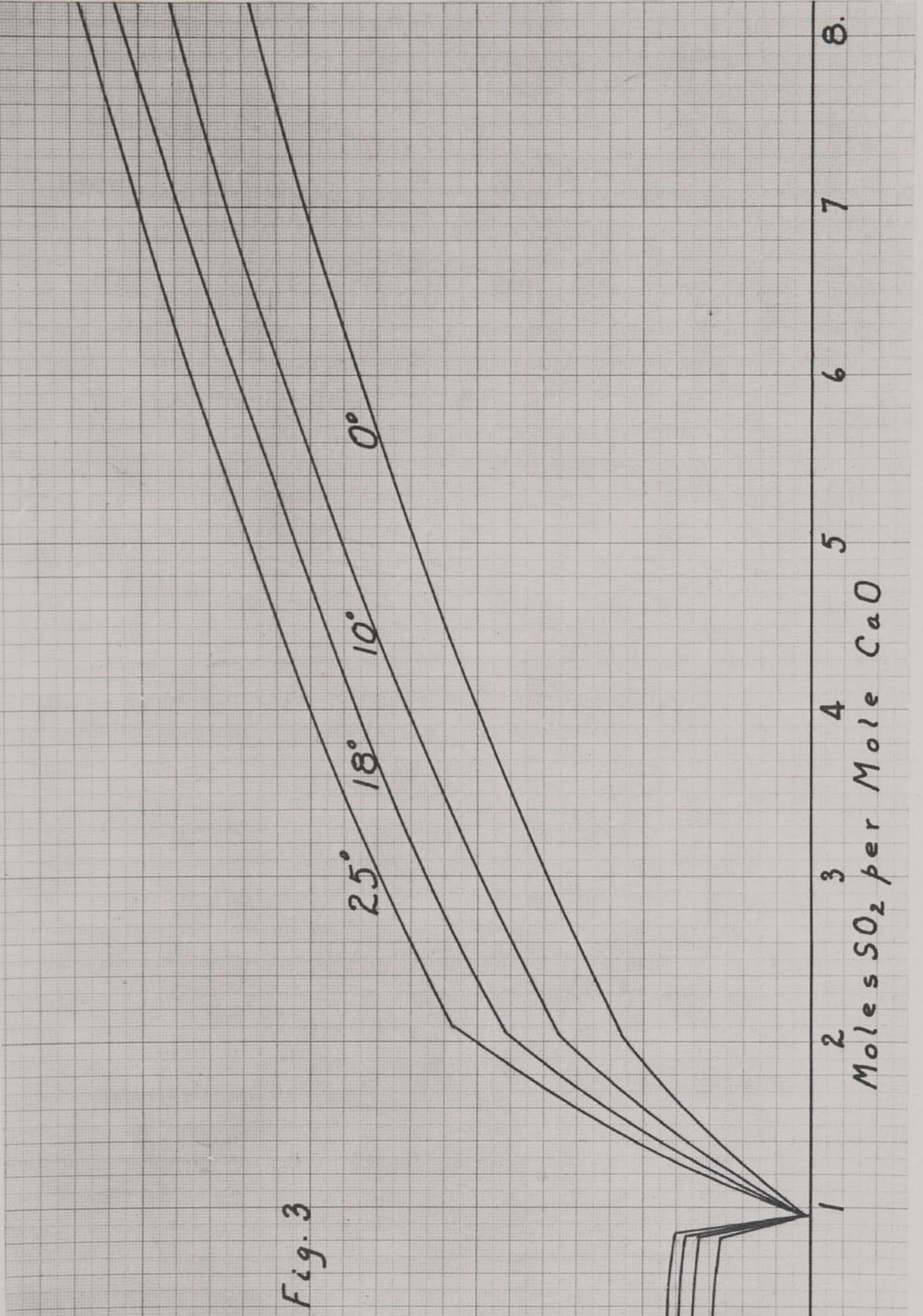


Fig. 3

Spec. Cond. x 10^2, Ohms^{-1}
0
1.
2.
3.
4.
Moles SO_2 per Mole CaO
0
1
2
3
4
5
6
7
8.
25°
18°
10°
0°

TABLE 6.

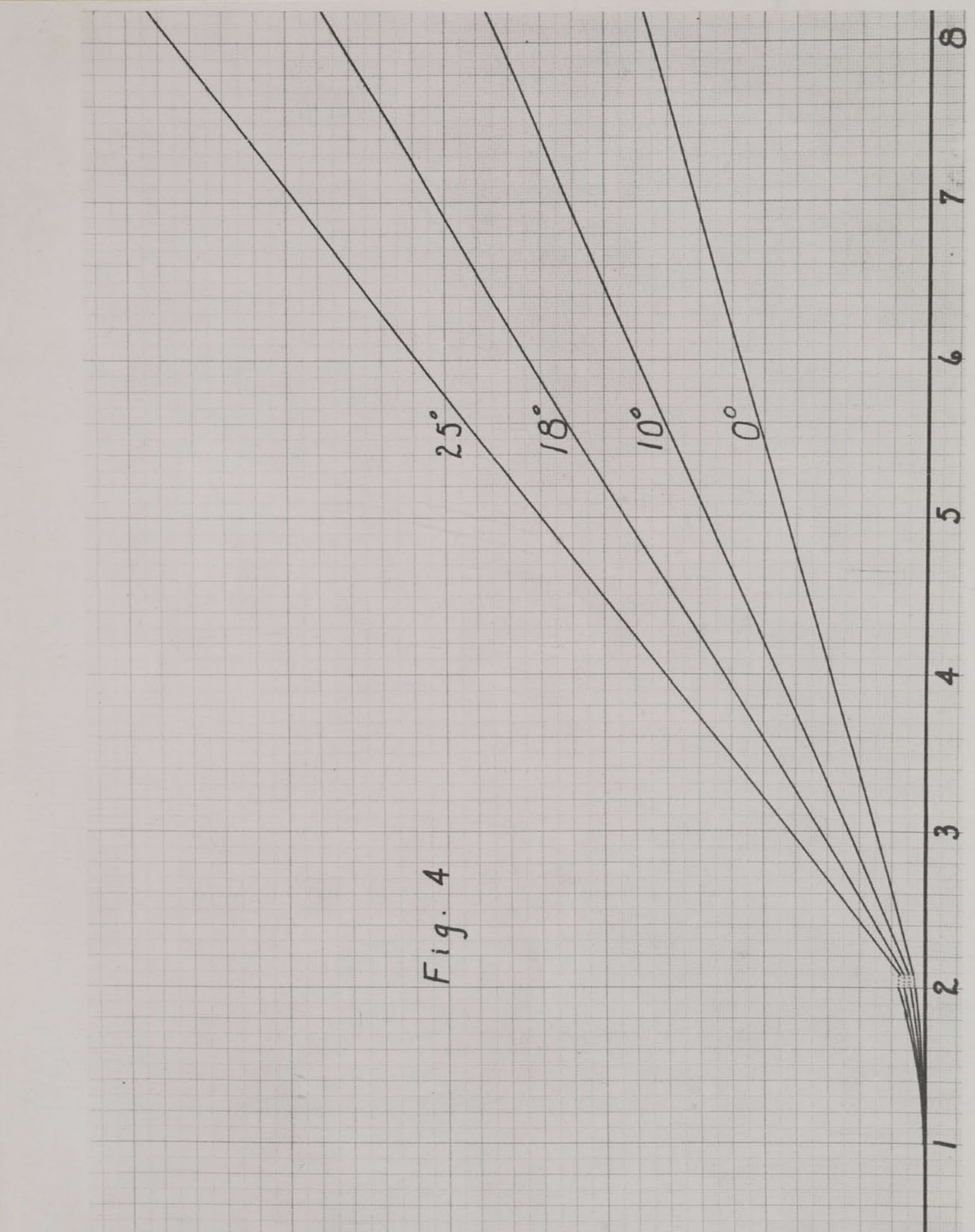


Fig. 4

TABLE 6.

Run No. 9 - 0°C

No.	SO_2 Conc. Moles/Mole	SO_2 Conc. %	k x 10^2	p, cms	p_{SO_2}, cms.
9	0.0	0.0	0.585	0.47	0.0
9(a)	0.203	0.452	0.581	0.46	0.0
9(b)	0.793	1.742	0.563	0.47	0.0
9(c)	0.886	1.941	0.418	0.47	0.0
9(d)	0.929	2.034	0.126	0.46	0.0
9(e)	0.965	2.111	0.060	0.46	0.0
9(f)	1.158	2.523	0.512	0.57	0.10
9(g)	1.664	3.557	1.328	1.29	0.82
9(h)	1.959	4.195	1.674	2.06	1.59
9(i)	2.060	4.401	1.788	2.25	1.78
9(j)	2.295	4.898	1.997	3.67	3.20
9(k)	2.981	6.271	2.355	9.58	9.11
9(l)	3.779	7.814	2.730	16.61	16.14
9(m)	5.116	10.29	3.260	28.38	27.91

Weight of water = 109.622 g.

Weight of calcium oxide = 2.188 g

TABLE 7.

Run No. 9 - 10° C.

No.	SO_2 Conc. Moles/Mole	SO_2 Conc. %	k x 10^2	p, cms.	p_{SO_2}, cms.
9	0.0	0.0	0.720	0.94	0.0
9(a)	0.203	0.452	0.711	0.92	0.0
9(b)	0.793	1.742	0.692	0.94	0.0
9(c)	0.886	1.941	0.528	0.94	0.0
9(d)	0.929	2.034	0.160	0.94	0.0
9(e)	0.965	2.111	0.081	0.94	0.0
9(f)	1.158	2.524	0.684	1.08	0.14
9(g)	1.664	3.557	1.751	2.17	1.23
9(h)	1.959	4.195	2.210	3.32	2.38
9(i)	2.060	4.401	2.362	3.64	2.70
9(j)	2.295	4.898	2.606	5.78	4.84
9(k)	2.976	6.262	2.965	15.00	14.06
9(l)	3.773	7.801	3.343	25.78	24.84
9(m)	5.103	10.26	3.875	43.89	42.95

Weight of water = 109.622 g.

Weight of calcium oxide = 2.188 g.

TABLE 8.

Run No. 9 - 18°C.

No	SO_2 Conc. Moles/Mole	SO_2 Conc. %	k x 10^2	p, cms.	p_{SO_2}, cms.
9	0.0	0.0	0.799	1.55	0.0
9(a)	0.203	0.452	0.794	1.56	0.01
9(b)	0.793	1.742	0.780	1.56	0.01
9(c)	0.886	1.941	0.621	1.56	0.01
9(d)	0.929	2.034	0.189	1.55	0.0
9(e)	0.965	2.111	0.099	1.56	0.01
9(f)	1.158	2.524	0.832	1.78	0.23
9(g)	1.664	3.557	2.122	3.18	1.63
9(h)	1.959	4.195	2.655	4.76	3.21
9(i)	2.060	4.401	2.855	5.21	3.66
9(j)	2.295	4.898	3.083	8.12	6.57
9(k)	2.972	6.253	3.466	20.77	19.22
9(l)	3.764	7.780	3.813	35.49	33.94
9(m)	5.089	10.23	4.335	60.11	58.56

Weight of water = 109.622 g.

Weight of calcium oxide = 2.188 g.

TABLE 9.

Run No. 9 - 25°

No.	SO_2 Conc. Moles/Mole	SO_2 Conc. %	k x 10^2	p, cms.	p_{so_2}, cms.
9	0.0	0.0	0.856	2.37	0.0
9(a)	0.203	0.452	0.854	2.38	0.01
9(b)	0.793	1.742	0.856	2.38	0.01
9(c)	0.886	1.941	0.695	2.38	0.01
9(d)	0.929	2.034	0.218	2.37	0.0
9(e)	0.965	2.111	0.116	2.38	0.01
9(f)	1.158	2.524	0.967	2.70	0.33
9(g)	1.664	3.557	2.453	4.47	2.10
9(h)	1.959	4.195	3.094	6.50	4.13
9(i)	2.060	4.401	3.289	7.07	4.70
9(j)	2.295	4.898	3.587	10.72	8.35
9(k)	2.967	6.242	3.913	27.11	24.74
9(l)	3.755	7.764	4.250	45.91	43.54
9(m)	5.075	10.21	4.713	76.92	74.55

Weight of water = 109.622 g.

Weight of calcium oxide = 2.188 g.

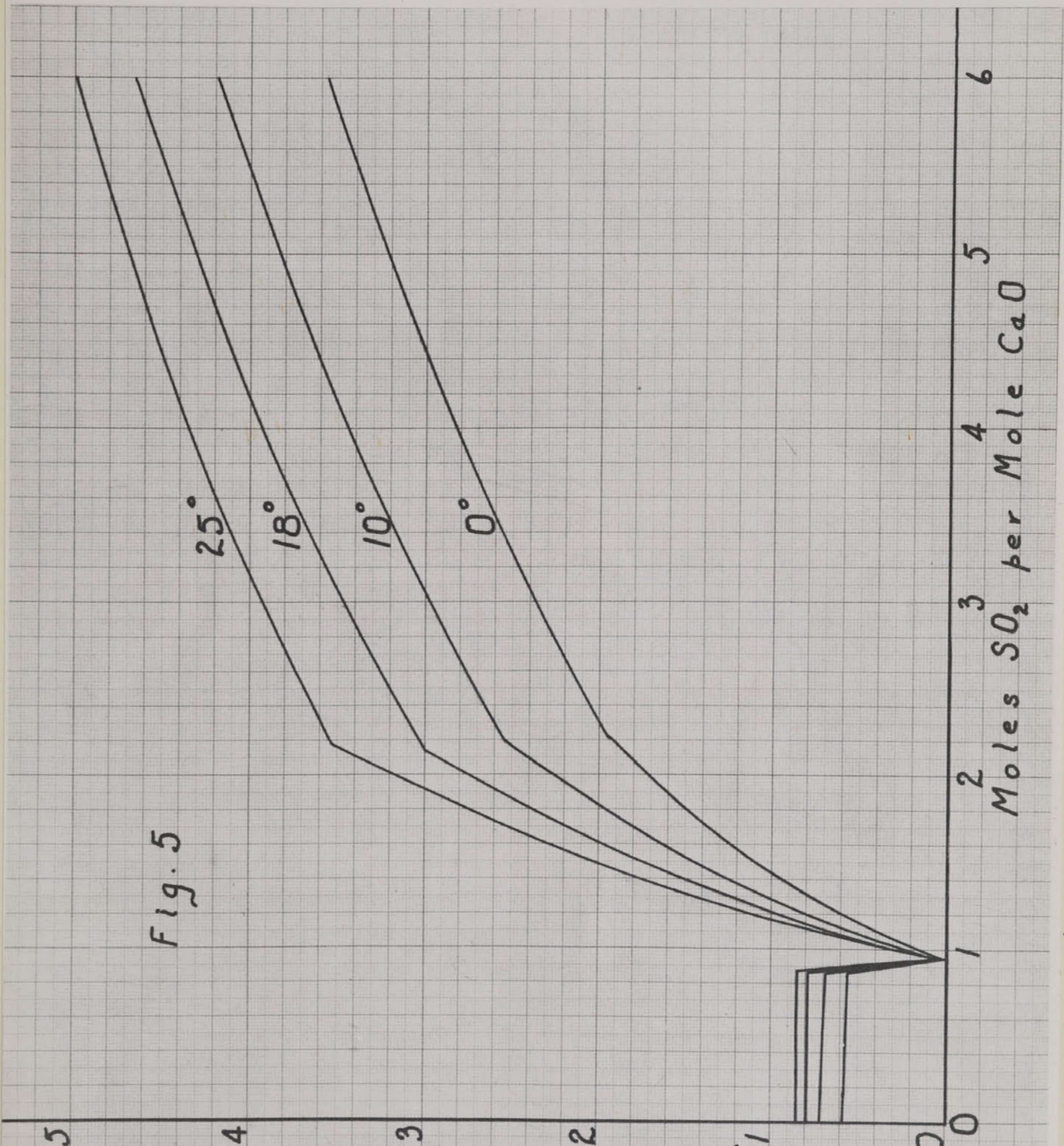


Fig. 5

25°
18°
10°
0°
0
1
2
3
4
5
6
Moles SO_2 per Mole CaO
0
1
2
3
4
5
Spec. Cond. x 10^2, Ohms^{-1}

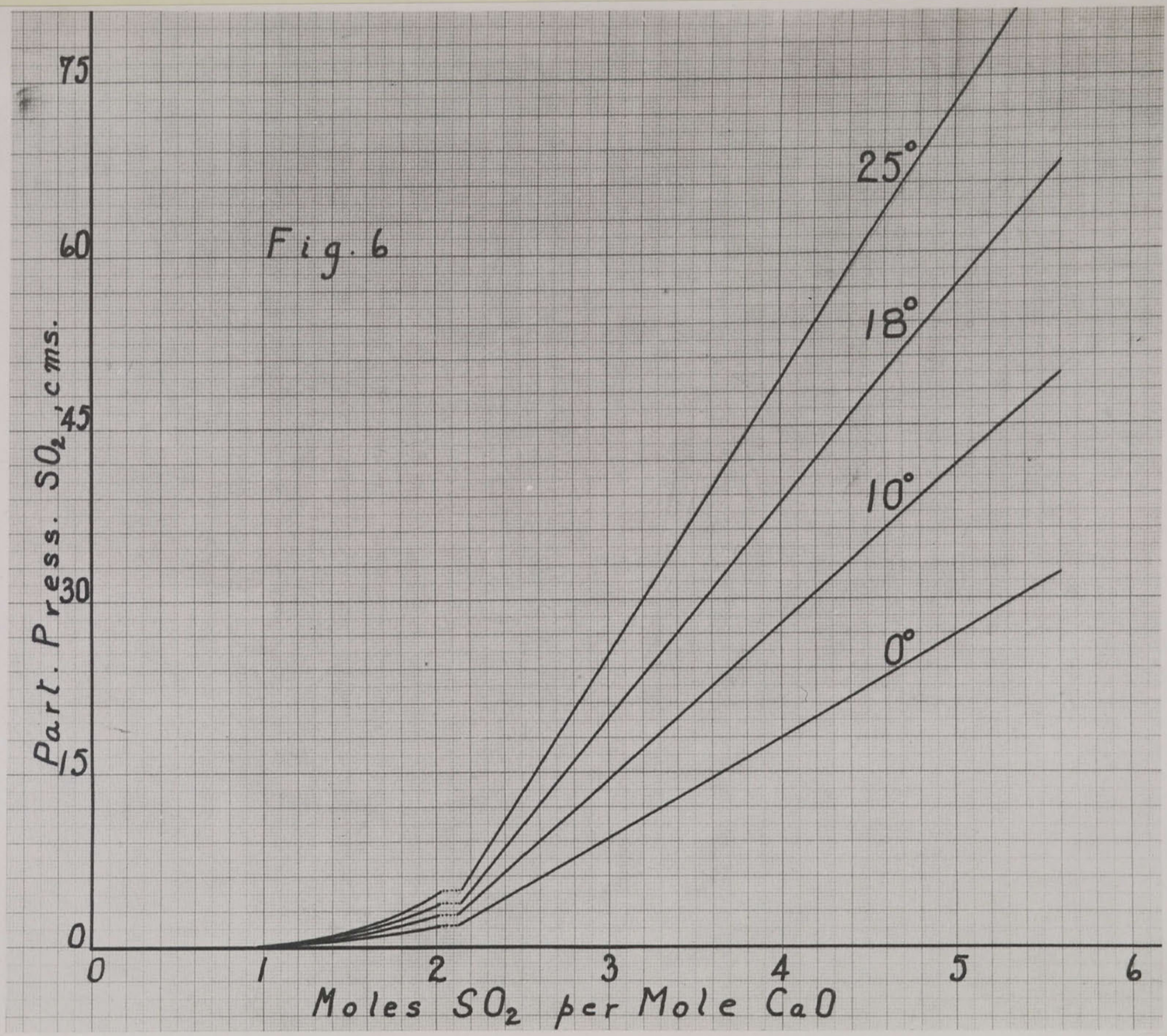


Fig. 6
75
60
45
30
15
0
Part. Press. SO_2, cms.
0
1
2
3
4
5
6
Moles SO_2 per Mole CaO
25°
18°
10°
0°

It has been mentioned in the introduction that G.W. Gurd has carried out in this laboratory an investigation of the systems calcium oxide - water, and calcium oxide - sulphur dioxide - water. His work was done at temperatures from 25°C up to about 130°C, consequently it is possible to compare his values at 25° with those obtained at 25° in the present work. This has been done, and the comparative data are presented in Table 10.

In preparing this table, Gurd's values were taken from the tables presented in his thesis(27), and the values for conductivity and partial pressure of sulphur dioxide found in the present work were picked off curves.

It should be borne in mind that calcium oxide concentrations used in the two cases are not precisely equal, however they are nearly enough equal to permit some comparisons to be made

In the case of the conductivity values the agreement between the data from the two sources is very good. The value given by Gurd for the 1% solution at sulphur dioxide concentration 0.789 moles per mole is very much lower than the value obtained in the present work; however Gurd points out why it is probably in error. This is borne out by the fact that the writer has found it quite difficult to be certain of equilibrium at, and near, that sulphur dioxide concentration. Agreement between values for the partial

TABLE 10.

Comparison of Data of Gurd and Grieve at 25°.

A.

Calcium oxide concentration: Gurd - 1.013%

Grieve - 1.050%

SO_2 Moles/Mole	k x 10^2 (Gurd)	k x 10^2 (Grieve)	p_{so_2}, cms. (Gurd)	p_{so_2}, cms. (Grieve)
0.00	0.850	0.856	0.00	0.0
0.184	0.810	0.850	0.2	0.0
0.271	0.778	0.850	0.2	0.0
0.789	(0.350)	0.810	(0.7)	0.0
1.519	1.480	1.280	3.7	0.6
3.023	2.510	2.594	15.9	12.6
5.032	3.290	3.380	38.5	35.8

B.

Calcium oxide concentrations: Gurd - 2.085%

Grieve - 1.956%

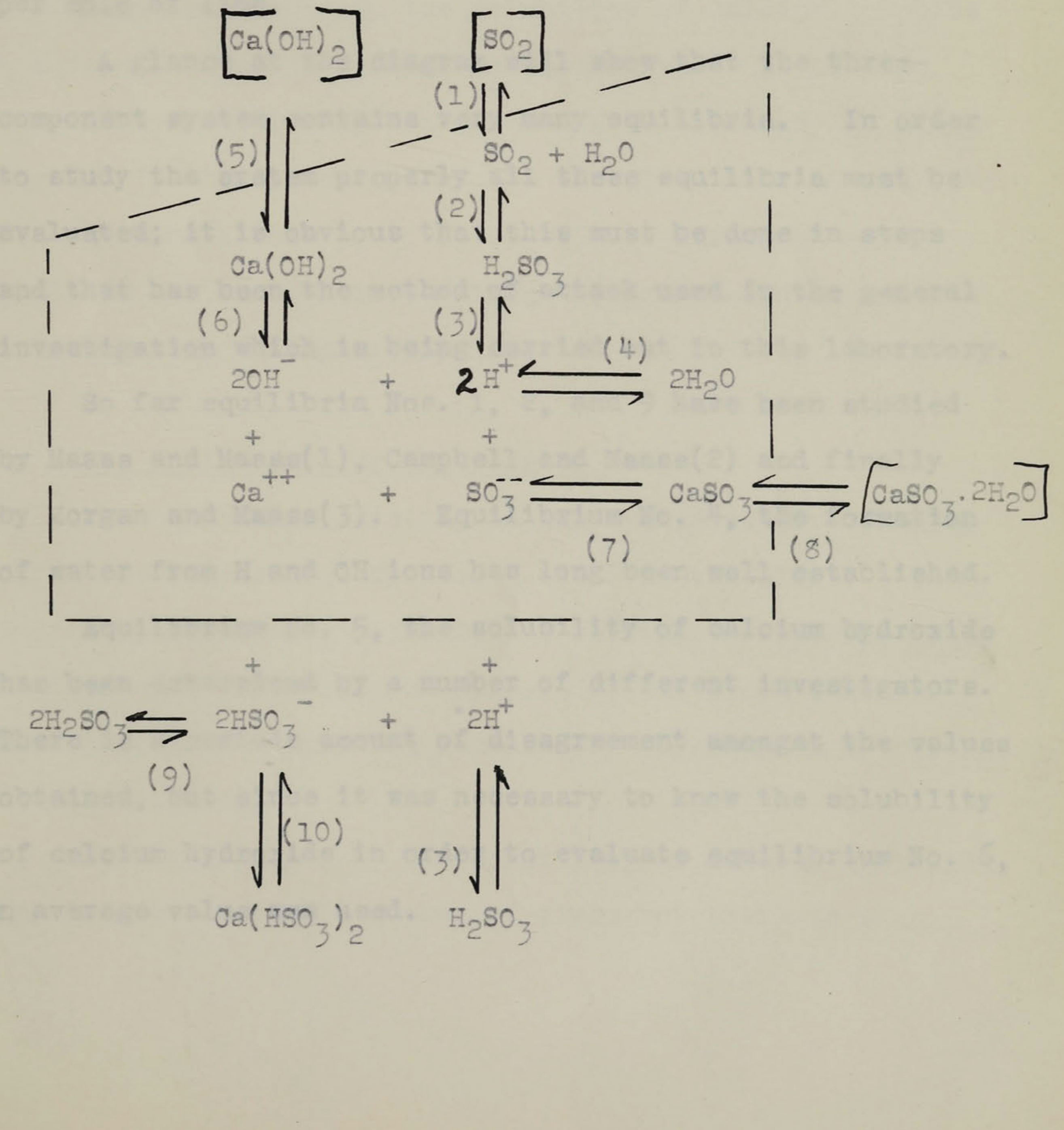
SO_2 Moles/Mole	k x 10^2 (Gurd)	k x 10^2 (Grieve)	p_{so_2}, cms. (Gurd)	p_{so_2}, cms. (Grieve)
0.0	0.850	0.856	0.0	0.0
0.527	0.833	0.850	0.4	0.0
1.048	0.494	0.520	0.7	0.1
1.291	1.410	1.430	1.9	0.5
2.271	3.581	3.575	12.5	8.0
3.018	4.107	3.934	31.0	25.8
4.022	4.463	4.350	57.5	49.6

pressures of sulphur dioxide is not so good, however there is reason to believe that the values obtained in the present work are the more reliable; the manometer used by Gurd was designed to measure vapour pressures up to six or seven atmospheres, and consequently could not make precise measurements at lower pressures

DISCUSSION OF RESULTS.

a. General

Before considering in detail the experimental data which have been obtained it seems advisable to give a schematic representation of the equilibria which are to be expected in the three-component system water - calcium oxide - sulphur dioxide.



In this diagram solid $Ca(OH)_2$, solid $CaSO_3$ $2H_2O$ and gaseous SO_2 are distinguished from the materials in solution by being placed in square brackets. All the other formulae represent substances which are in equilibrium in solution. The section enclosed by the dotted line contains all the equilibria which will have a measureable effect upon the properties of the system, until sulphur dioxide has been added in such amounts as to exceed approximately one mole per mole of lime.

A glance at the diagram will show that the three-component system contains very many equilibria. In order to study the system properly all these equilibria must be evaluated; it is obvious that this must be done in steps and that has been the method of attack used in the general investigation which is being carried out in this laboratory.

So far equilibria Nos. 1, 2, and 9 have been studied by Maass and Maass(1), Campbell and Maass(2) and finally by Morgan and Maass(3). Equilibrium No. 4, the formation of water from H and OH ions has long been well established.

Equilibrium No 5, the solubility of calcium hydroxide has been determined by a number of different investigators. There is a certain amount of disagreement amongst the values obtained, but since it was necessary to know the solubility of calcium hydroxide in order to evaluate equilibrium No. 6, an average value was used.

Equilibrium No. 6, the ionization of the dissolved calcium hydroxide can be worked out thoroughly - the accuracy of the values obtained being limited by the precision of the measurements; of these, the values for the solubilities are the least precise The treatment of equilibria Nos. 5 and 6 will be discussed in greater detail in the section devoted to the discussion of the calcium hydroxide-water system.

Equilibrium No 8, the Solubility of Calcium Sulphite has been studied by several investigators. As in the case of the calcium hydroxide, No. 8 is necessary to evaluate No. 7, the ionization of the dissolved calcium sulphite. The equilibria Nos. 3, 7, 8, 10 will be discussed more fully in the section on the three component system water - calcium oxide - sulphur dioxide.

b. The System Calcium Oxide-water.

The equilibria existing in the system water - calcium oxide are represented by Nos. 5 and 6 in the chart In addition, of course, there is the reaction of calcium oxide with water to form calcium hydroxide, but since that reaction goes to completion immediately it requires no further discussion here.

Equilibrium No. 5, the solubility of calcium hydroxide, has been determined a number of times but there is some disagreement amongst the values obtained. This disagreement is most pronounced from 0° to about 30°, from 30° to about 100° agreement is fair; above 100° very few determinations have been made. An average value for the solubility over the whole temperature range was obtained by plotting the values of Maben(8), Lamy(9), Herzfeld(10), Guthric(11), Moody(12), Haslam, Calingaert and Taylor(13), and Miller and Witt(7). These values were plotted on a large scale on a single graph, and an average curve was drawn through these points; in drawing this curve, consideration was given to any agreement existing between the values from two or more sources, and to the temperature range, and continuity of a given investigation. Values obtained from this curve are contained in Table 11, a reproduction of the curve is given in figure 7, in which the continuous curve represents the solubility as determined above. The broken line represents certain calculated solubility values, the source of which will be discussed later.

The study of equilibrium No 6, forms a part of the present work. Using the average values obtained for the solubility of calcium hydroxide, the normality of a saturated solution can be calculated for any temperature. These, with the specific conductivities which have been measured, make it possible to calculate the equivalent conductivity

TABLE No. 11.

Solubility of Calcium Hydroxide as Obtained from an Average Curve.

t°C	gms. CaO/l. soln.
0	1.351
10	1.322
18	1.272
25	1.207
30	1.156
40	1.056
50	0.958
60	0.860
70	0.764
80	0.680
90	0.620
100	0.578

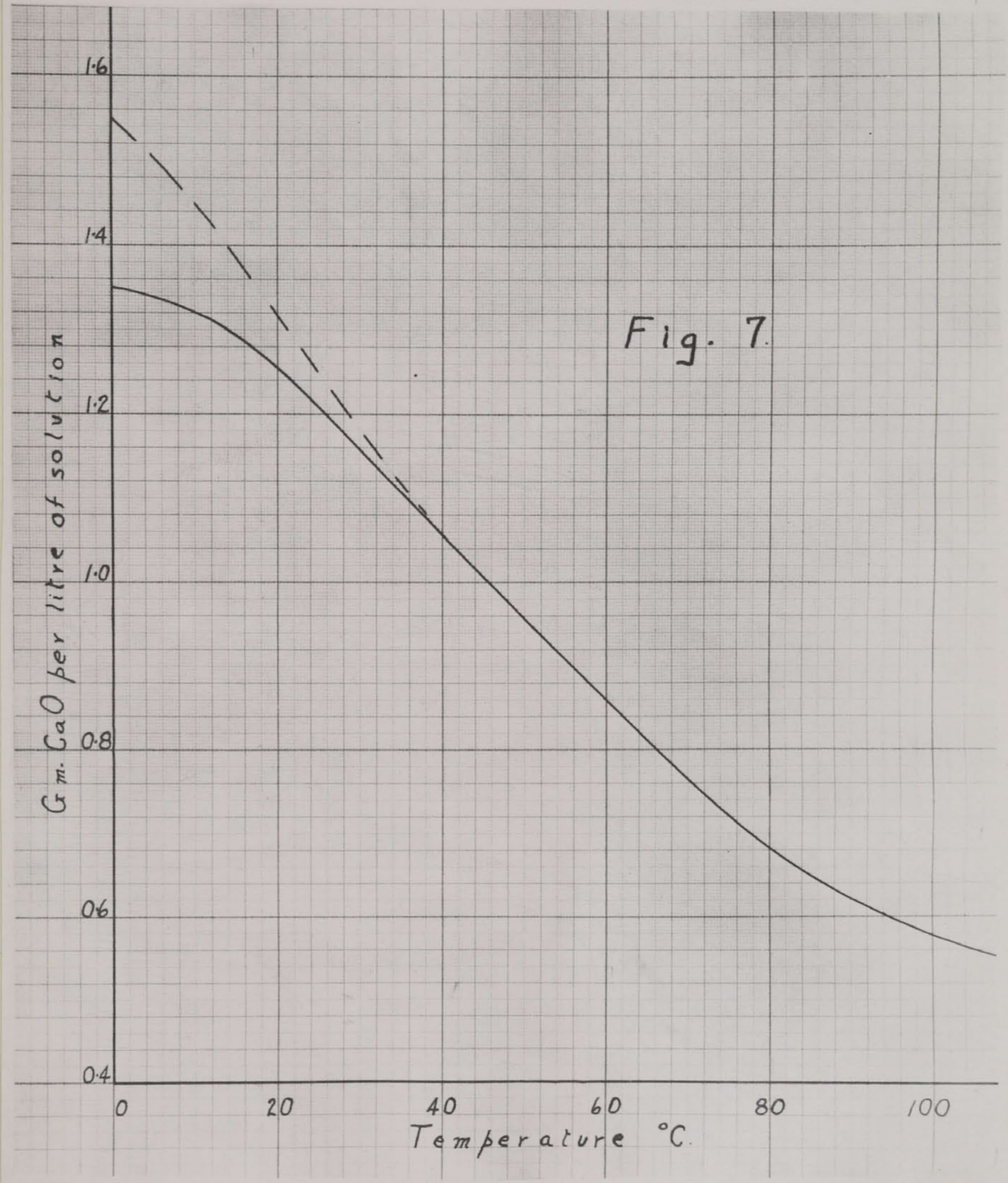


Fig. 7.

1·6
1·4
1·2
1·0
0·8
0·6
0·4
Gm. CaO per litre of solution
0
20
40
60
80
100
Temperature °C.

of a solution which is saturated at a given temperature. From this value, and the equivalent conductivity at infinite dilution at that temperature, the degree of dissociation was calculated, and it, with the solubility, gave the dissociation constant. All these values are listed in Table 1

If these values of the dissociation constant are plotted against temperature, as in figure 8, we get the curve shown by the continuous line which has been drawn from 0° to about 34° (the latter part of this curve is an extrapolation from 25°). On the other hand, the values obtained for K by Gurd(27) (see table 12), when plotted on the same graph, give the straight line extending from 37° to about 100°. Such an abrupt change of form in a

TABLE 12.

Dissociation Constant for Saturated Calcium Hydroxide Solutions. (Data due to Gurd)

t°C.	$K \times 10^3$.
37	2.91
50	2.43
60	2.06
70	1.70
80	1.33
90	0.93
100	0.58

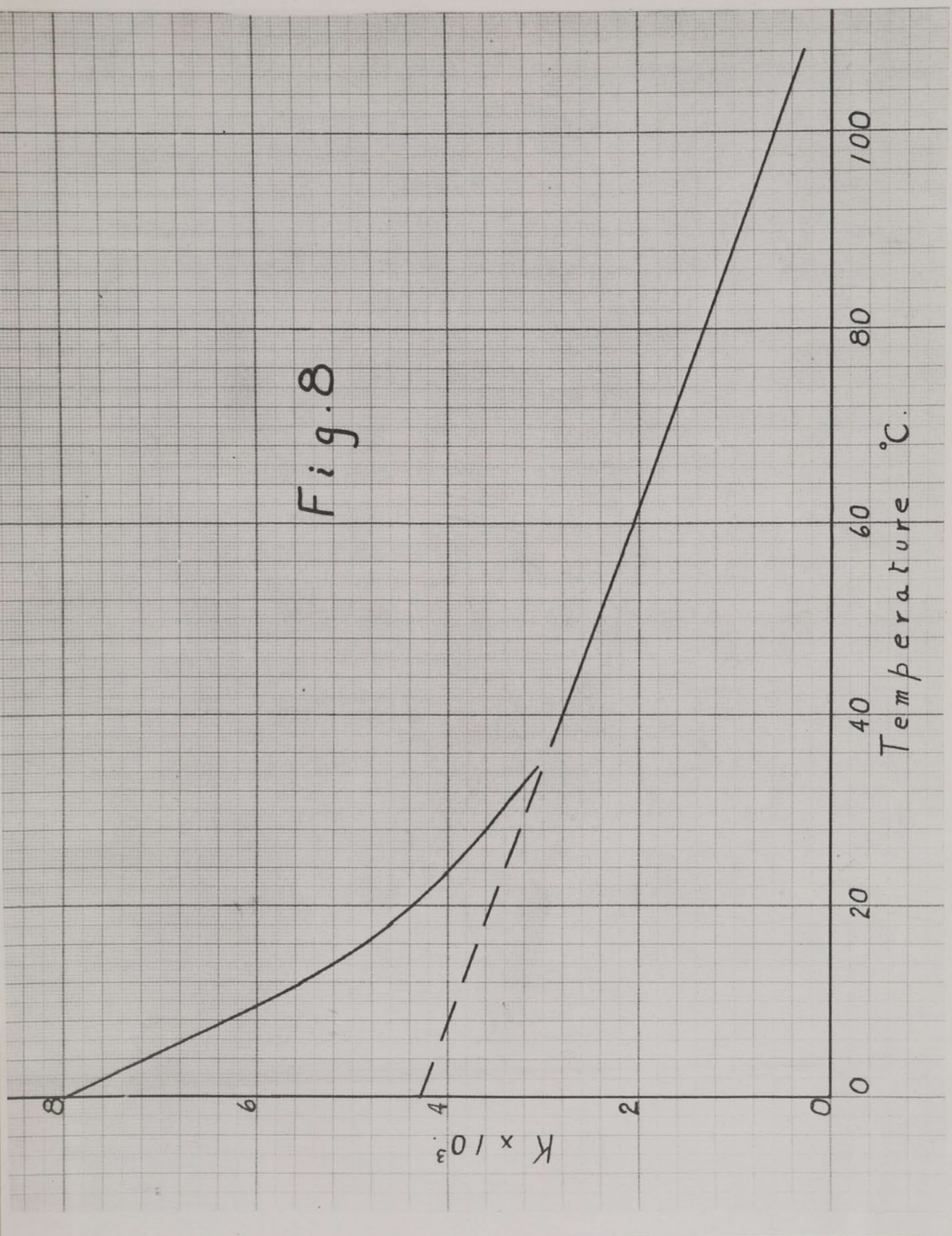


Fig. 8

dissociation constant-temperature curve, without a corresponding abrupt change in composition, or in some other variable in the system, is unusual. Since K is calculated from two sets of data: specific conductivities and concentrations, as given by solubilities, it is necessary to look to one or other of these sources in seeking reasons for this break in the curve. In so far as conductivities are concerned, at 25°, the only point at which direct comparison can be made, our values for specific conductivity agree to within 0.8% and in addition when plotted against temperature our two curves fit together very satisfactorily, hence there is no break in the conductivity data. When we consider solubilities we find, as has been pointed out above, that the agreement amongst various determinations is reasonably good from 30° or 35° to about 100° and that probably, therefore, the solubility curve as drawn is a fairly correct representation of the true values in this temperature range.

If we assume that over this temperature range we have the true values for the solubility, and that K, when plotted against temperature, should continue to give a curve that has the same shape below 37° as it has above that temperature, then we are justified in extrapolating K to 0°, reading values for K from this curve and, from them, calculating the solubility that would be necessary to give these values for K. The extrapolation of K is represented by a dotted line in Figure 8. The values taken from this extrapolation are given in column 2 of table 13, along with the values

TABLE 13.

Calculated Solubilities of Calcium Hydroxide.

t°C.	Ke x 10^3	k x 10^3	λ_o	solubility, calculated, gms CaO/l.soln.
0	4.29	5.85	145.9	1.55
10	3.92	7.20	189.9	1.45
18	3.62	7.99	225.0	1.34
25	3.36	8.56	255.8	1.25

for the solubility which were calculated from these values for K. These solubilities are plotted as a dotted line in figure 7. It is believed that these values are more nearly correct than those obtained from the average of the literature and the following paragraphs will contain confirmation of this.

G.W.Gurd(30) has obtained data by means of which it is possible to determine, indirectly, the solubility of calcium hydroxide. The method is as follows: The specific conductivity of unsaturated solutions of calcium hydroxide, whose concentration is known, is measured over a range of temperature; the values obtained at a given temperature for a series of solutions of different concentrations are plotted against concentration. A curve is drawn through these points and extrapolated until it cuts a straight line drawn parallel to the concentration axis, and through the conductivity of a saturated solution for that temperature. The concentration at the point of intersection gives the solubility at that temperature.

Gurd has obtained data for two different calcium oxide concentrations. These, with the origin, give a series of isothermal curves which are slightly concave toward the concentration axis. The values obtained by extrapolating these curves are given in column 2 of table 14. If one assumes that the upper portions of these curves should be straight lines instead of curves, and that the curvature should occur only at lower concentrations, the values in column 3 can be obtained by drawing a straight line through the two points for which data are available. Column 4 contains the values of the solubility which were calculated from the extrapolated dissociation constant curve; column 5 contains the average of the data from the literature.

A comparison of these values shows that the calculated values are probably more nearly correct than are the average values of the literature, because the values obtained by the straight line extrapolation of the conductivity-concentration curves probably gives the lower limit of the solubility values. (If the true values were any lower the conductivity-concentration curve would have to be S-shaped, which is unlikely.) It is probable that the true values lie between the values obtained from a straight line extrapolation and those obtained by the extrapolation of a curve, in which case the calculated values must be very nearly correct.

TABLE 14.

Comparision of Values for Solubility of CaO

t°C.	Curve	St.Line	Calculated	Ave. Curve
0°	1.66 gms/l	1.45 gms/l	1.55 gms/l	1.35 gms/l
10°	1.57 "	1.39 "	1.45 "	1.32 "
18°	1.43 "	1.30 "	1.34 "	1.27 "
25°	1.25 "	1.22 "	1 25 "	1.21 "

Since values obtained from the literature for the solubility of calcium hydroxide differ as they do, it can be seen that there may be a reason for this disagreement, a reason which would indicate not only why the values obtained could vary, but also, would indicate why the values obtained would be lower than the true value. In measuring solubilities of a substance which is more soluble at low, than at high, temperatures, the sample of solution which is taken for analysis must not be allowedto warm up, or solute will immediately precipitate; if this happens, a variable error is introduced, and the values obtained will always be low. It has not been possible to determine whether the technique used in all cases has been such as to avoid the possibility of this error, because several of the original papers have been inaccessible. However, the assumptions on which the calculated solubilities are based appear to be justifiable and if they are, then the solubilities as calculated should represent the true values more nearly than do the average of the data available in the literature.

c. The Three Component System H_2O-CaO-SO_2.

The data obtained for the three component system will be considered in four sections, as follows: first, the system up to the point at which all the solid calcium hydroxide has dissolved; second, the data obtained at and near 1 mole of sulphur dioxide per mole of lime, with special reference to the minimum in the conductivity curve; third, the data obtained at sulphur dioxide concentrations between 1 mole and 2 moles per mole of lime; and fourth, that data obtained above 2 moles of sulphur dioxide per mole of lime.

In studying the three component system, a suspension of calcium hydroxide in water was taken as the point of departure. In this suspension equilibria Nos. 5 and 6 had been established. To this suspension sulphur dioxide was added; as soon as a small amount had been added, equilibria 1, 2, 3, 4 and 7 established themselves. When sufficient calcium sulphite had been formed to exceed its solubility, solid calcium sulphite was precipitated and equilibrium No. 8 was established. The solubility of calcium sulphite is reached very quickly because its value is so small; according to the work of Bain(29) and of van der Linden(16) it is of the order of 0.06 gm. per litre. This amount of calcium sulphite is approximately equivalent to the amount of sulphur dioxide which, when expressed on a basis of moles of sulphur dioxide per mole of lime, would be given by 0.003 moles per mole in the case of the 1% calcium oxide system and 0.0015 in the case of the 2% system.

From these figures it can be seen that the system is saturated with calcium sulphite as soon as the first trace of sulphur dioxide is added. The addition of more sulphur dioxide now serves to increase the amount of solid calcium sulphite present; this is accomplished by a corresponding decrease in the amount of solid calcium hydroxide. It is to be noted that the solution is at all times saturated with respect to both calcium hydroxide and calcium sulphite. So long as this condition obtains, the addition of sulphur dioxide to the system should cause no change in the properties of the solution. This is found to be true of the vapour pressure of the solution, which remains constant, with the partial pressure of sulphue dioxide equal to zero. As for the specific conductivity, it can be demonstrated that it should remain constant:- Consider the following reaction:-

$$\underset{a}{Ca(OH)_2} + \underset{c}{H_2SO_3} \rightleftharpoons \underset{b}{CaSO_3} + \underset{d}{2H_2O}$$

where a, b, etc. represent the concentrations of the reactants and products in gram moles per liter.

Also the ionizations of these substances:

$$[Ca(OH)_2] \rightleftharpoons \underset{a}{Ca(OH)_2} \rightleftharpoons \underset{e}{Ca^{++}} + \underset{h}{2OH^-}$$

$$[CaSO_3] \rightleftharpoons \underset{b}{CaSO_3} \rightleftharpoons \underset{e}{Ca^{++}} + \underset{f}{SO_3^{--}}$$

$$SO_2 \rightleftharpoons \underset{c}{H_2SO_3} \rightleftharpoons \underset{g}{2H^+} + \underset{f}{SO_3^{--}}$$

$$\underset{d}{2\ H_2O} \rightleftharpoons \underset{g}{2H^+} + \underset{h}{2OH^-}$$

with the small letters, as before, representing concentrations. It is possible to express the equilibrium constant for each of these reactions as follows:

$$\frac{a\ c}{b\ d} = K_1 \qquad (1)$$

$$\frac{a}{e\ h^2} = K_2 \qquad (2)$$

$$\frac{b}{e\ f} = K_3 \qquad (3)$$

$$\frac{c}{g^2 f} = K_4 \qquad (4)$$

$$\frac{d}{g\ h} = K_5 \qquad (5)$$

In addition to these, since all these equilibria exist in the one solution, and since the number of position ions in that solution must be equivalent to the number of negative ions, we may set up another equation:

$$2^{e} + g = h + 2f. \qquad (5)$$

If we substitute in (6) for e from (2), for g from (5) and for f from (3) we get:

$$2\frac{a}{K_2h^2} + \frac{d}{K_5H} = h + 2\frac{b}{e\,K_3} \qquad (7)$$

substituting in (7) for e from (2)

$$2\frac{a}{K_2h^2} + \frac{d}{K_5h} = h + 2\frac{a\,b}{h^2K_2K_3} \qquad (8)$$

K_5, the dissociation constant of water, will be very much larger than any of the other equilibrium constants, consequently the second term of equation (8) will be very small and may be neglected entirely. In addition, a, the solubility of calcium hydroxide is small and b, the solubility of calcium sulphite is very much smaller than a. According to Bain(29) and van der Linden(16) b is only about five per cent of a, consequently the last term in equation (8) will also be small and may be neglected. By making these two approximations (8) reduces to

$$2 \frac{a}{K_2h^2} = h$$

$$2\ a = h^3K_2$$

Substituting for K_2 from (2)

$$2\ a = \frac{a\ h^3}{e\ h^2}$$

therefore $2\ e = h$

Since by making use of these two approximations, equation (6) has been reduced to one containing only terms which are due to the calcium hydroxide, then to a first approximation the conductivity should be due entirely to the calcium hydroxide, and should remain constant as long as solid calcium hydroxide is present. Instead of remaining constant, there is a slight decrease in the conductivity as sulphur dioxide is added. This falling off is probably due to the fact that the calcium hydroxide was not reaching complete equilibrium with the solution. It has been found that with both solid phases present, true equilibrium is reached very slowly in this system; it has also been found that it is possible to reach an apparent equilibrium value, as shown by constancy of conductivity, without ever reaching the true value. These two facts have caused a great deal of difficulty in the handling of this system. As has been pointed out above, improved stirring has eliminated most of the trouble.

As more sulphur dioxide is added to the system, the solid calcium hydroxide is eventually completely used up. At the point at which the last trace of solid calcium hydroxide disappears, the solution is saturated with calcium hydroxide, saturated with calcium sulphite, with a large excess of solid calcium sulphite present. When sulphur dioxide is added to the system at this point it reacts with the calcium hydroxide to form calcium sulphite but since there is no longer any solid calcium hydroxide present, it can no longer be replaced from that source, consequently the concentration of calcium hydroxide is decreased as sulphur dioxide is added. The concentration of calcium sulphite, of course, remains constant.

This decrease in the calcium hydroxide concentration causes a very pronounced decrease in the specific conductivity of the solution. A saturated solution of calcium hydroxide will have a much higher conductivity than one saturated with calcium sulphite, because, first, calcium hydroxide is roughly twenty times as soluble as calcium sulphite, and consequently furnishes many more ions than does the calcium sulphite, and, second, one of its ions is hydroxyl, which has a much greater mobility than either calcium or sulphite ion. (The mobility of sulphite ion is not available, but assuming that it has the same mobility as others of its type, its mobility will be of the same order of magnitude as that of the calcium ion.) As sulphur dioxide is added, the conductivity of the solution drops to the value of the conductivity of a saturated solution of calcium sulphite; this is very nearly zero because of the slight solubility of calcium sulphite and the low mobility of its ions. The value of the conductivity reached at this point is of the same order of magnitude as the value which can be calculated for the specific conductivity, using the solubility date of Bain(29) or of van der Linden(16), the mobility of the calcion ion(28), assuming a reasonable value for the mobility of the sulphite ion, and assuming complete dissociation.

The minimum in the conductivity-sulphur dioxide concentration curve, when the latter is expressed as moles of sulphur dioxide per mole of lime, occurs at a molal ratio of 0.95 or 0 96 to 1 It was at first expected that this minimum would occur at the point where sulphur dioxide and lime were present in equi-molecular proportions; when it did not, all the constants of the apparatus were checked to discover any errors of calibration; no errors were found. The value 0.95 - 0 96 to 1 has been obtained on three different occasions. In run No. 4, the minimum, as found by extrapolation, is at 0.95 moles of sulphur dioxide to 1 mole of calcium oxide. Similarly with the first solution used in obtaining the data of run No. 9, the minimum was found to occur at a sulphur dioxide concentration of 0.95 moles to 1 mole of lime. The preparation of a second solution to complete run No. 9, which was interrupted by a break in the cell, afforded an additional opportunity to determine the exact point at which the minimum occurred. On this occasion sulphur dioxide was added in small amounts as the minimum was approached. The solution was thoroughly stirred during and after each addition, and the conductivity was measured after each addition. By making very minute additions it was possible to obtain a fairly precise evaluation of the concentration at which the minimum occurred. By this method it was found to be at 0.962 moles per mole, ± 0.006 moles per mole.

In addition to this, measurements were made at exactly 1 mole of sulphur dioxide per mole of lime; this solution was stirred, at constant temperature, for eleven hours in an endeavour to find out if any small particles of solid calcium hydroxide were present but coated with calcium sulphite, thus preventing the hydroxide from dissolving (such a condition would account for the minimum at concentrations of sulphur dioxide of less than 1 mole per mole.) During this long period of stirring the conductivity changed by less than one per cent, and the value was within one per cent of the value obtained in the measurements made on the first solution of run No. 9.

It should also be mentioned that the calcium oxide used in preparing these calcium hydroxide suspensions was very finely ground, in order to minimize the possibility which was mentioned in the last paragraph, namely of having small granules of undissolved calcium hydroxide, covered with precipitated calcium sulphite and existing in a solution which was less than saturated with calcium hydroxide. Besides being finely ground, the calcium oxide was hydrated quite rapidly; this gave a very fine suspension of calcium hydroxide. The fineness of the calcium hydroxide was such that in the case of the first suspension used in run No. 9 the material was colloidal, and the solid would not settle appreciably even on standing overnight; this was true, to a lesser extent, of the second suspension in run No. 9. The suspension used in run No. 4, while fine, was not colloidal, consequently it seems very improbable that there was any calcium hydroxide which was not in equilibrium with the solution.

To sum up, the evidence for the minimum occurring at 0.95 to 0.96 moles per mole is as follows: that value has been obtained on three different occasions, the system has been stirred for long periods, not only at that concentration, but also at 1 mole per mole, without changing the values obtained for conductivity or vapour pressure, and last, the calcium hydroxide was very fine and should have reached equilibrium with its solution very quickly. In view of this the writer feels justified in assuming that the value obtained for the concentration at which the minimum occurs in the conductivity curve is the correct one, and that its deviation from 1 mole per mole is due to equilibria existing in the solution and not to any experimental error in preparing or handling the materials.

Considerable space has been devoted to this point, because, in the first place, the results were scarcely expected, and, in the second place no explanation which is entirely satisfactory suggests itself to account for the results.

The equilibra existing at, and near, one mole per mole can be regarded as those equilibria which would exist in a suspension of calcium sulphite to which small amounts of calcium hydroxide or sulphur dioxide are added, depending on whether one is considering conditions at 1 mole of sulphur dioxide per mole of lime, or at slightly less, or at slightly more than this.

In the saturated solution of calcium sulphite, which will be present in such a suspension, the dissolved calcium sulphite may be hydrolysed. Let us assume that it hydrolyses as follows:

$$2\ CaSO_3 + 2H_2O \rightleftharpoons Ca(HSO_3)_2 + Ca(OH)_2.$$

Such a hydrolysis would account for the fact that the conductivity at 1 mole per mole is higher than would be expected for a saturated solution of calcium sulphite, but if calcium hydroxide were added to such an equilibrium, the conductivity of the system would probably decrease, because of the reversal of the reaction shown above, but this decrease would not be sharp because there would always be an excess of calcium hydroxide which, because of the high mobility of the hydroxyl ion, would prevent the conductivity from dropping as sharply or to as low a value as is the case in the results obtained in this work. Therefore such a hydrolysis seems unlikely.

Another type of hydrolysis which might occur in a solution of calcium sulphite is

$$\begin{array}{lclcl}
CaSO_3 & & 2HOH & & \\
\downarrow\uparrow & & \downarrow\uparrow & & \\
Ca^{++} & + & 2OH^- & \rightleftharpoons & Ca(OH)_2 \\
+ & & + & & \\
SO_3^{--} & + & 2H^+ & \rightleftharpoons & H_2SO_3 \rightleftharpoons H_2O + SO_2 \rightleftharpoons [SO_2]
\end{array}$$

If one or other of the products of this reaction were only slightly ionized, then this reaction would take place to an appreciable extent, and if the calcium hydroxide were less highly ionized than the sulphurous acid, this hydrolysis would account rather well for most of the experimental facts.

There is a small partial pressure of sulphur dioxide above the solution at 1 mole per mole. This would indicate the presence of sulphurous acid in the solution, because, if present, it would be in equilibrium with dissolved sulphur dioxide, and the latter would be in equilibrium with sulphur dioxide gas as shown in the equilibrium scheme.

The conductivity when plotted against concentration, gives what is believed to be a smooth curve from the minimum point, through one mole per mole and on to two moles per mole. Since the addition of sulphur dioxide, beyond 1 mole per mole causes no break in the curve, it would seem likely that there was some free sulphurous acid present at 1 mole per mole.

However, all this presupposes that at equivalent concentrations sulphurous acid yields a higher concentration of hydrogen ions than calcium hydroxide yields of hydroxyl ions, whereas the only available evidence (due to Morgan(3), Gurd(27), (30) and the present work) points to the fact that the reverse is true.

Another explanation, which would account for a great many of the observed facts, assumes the formation of a complex between the calcium sulphite and the calcium hydroxide, as follows:

$$x.CaSO_3 + y.Ca(OH)_2 \rightleftharpoons x\ CaSO_3.y\ Ca(OH)_2.$$

The corresponding basic magnesium sulphite has been reported by Seubert and Elten(31). They assign to it the formula 13 $MgSO_3.2Mg(OH)_2.22.H_2O$. In the same paper they report that they failed to isolate a basic calcium sulphite, but their evidence on that point does not seem entirely conclusive.

The formation of such a complex removes calcium hydroxide from active participation in the equilibria existing in the solution. (Calcium sulphite would also be removed, but, since, at and near the equivalence point, it is present in such large excess, this would have no effect on the properties of the system.) The removal of calcium hydroxide, as in a complex salt, would mean that less sulphur dioxide would be necessary to neutralize the remaining calcium hydroxide than would be the case if it were all present as such, consequently the equivalence point, as shown by the minimum in the conductivity curve, would be shifted to lower sulphur dioxide concentrations.

The formation of a complex salt would also explain why the conductivity values begin to fall sharply at lower sulphur dioxide concentrations than would have been predicted. As has been pointed out above, the point at which the conductivity begins to decrease sharply should correspond to the point at which solid calcium hydroxide disappears, consequently the sulphur dioxide, which is added between the point where the break in the conductivity curve occurs, and the point at which all the dissolved calcium hydroxide has reacted with sulphur dioxide, should be equivalent to the amount of lime necessary to saturate the solution. The break in the conductivity curve, therefore, should give a measure of the solubility of calcium hydroxide. However the values thus obtained are nearly twice too big; this would point to the fact that the solid calcium hydroxide is not only in equilibrium with dissolved calcium hydroxide, but also with calcium hydroxide in some other form, for example such a complex salt as has been mentioned above.

These three possible explanations of the equilibria existing at and near the equivalence point have all been presented, because each accounts for some of the experimental facts. Of the three, objections may be offered against the acceptance of either of the first two, the third, while no objections can be raised regarding it, lacks supporting evidence from other sources.

When sulphur dioxide is added to the suspension of calcium sulphite, the conductivity increases very rapidly, and the partial pressure of sulphur dioxide, which first became measurable when the minimum was passed, continues to increase.

The existence of measurable partial pressure of sulphur dioxide above the solution is evidence of the presence of free sulphurous acid in solution, This suggesta a comparison of the present data with the data obtained by Morgan and Maass(3) for solutions of sulphur dioxide in water Such a comparison makes it possible to draw certain conclusions regarding the equilibria existing in the present system.

In order to make the comparison possible, it is necessary to express the sulphur dioxide concentrations of the present work in percentages; from these values for the total amount of sulphur dioxide, have been deducted the amounts necessary to form calcium sulphite; the values so obtained are the percentages to be found in table No. 15 The conductivity values designated "k x 10^2(Grieve)" are the values obtained in the present work and were obtained from tables; the values designated "k x 12^2(Morgan)" are the values of Morgan & Maass(3), obtained from curves plotted from their data; the "difference" columns contain values obtained by substracting the values obtained in the present work from the values of Morgan and Maass. Similar methods have been used in preparing the data for the partial pressures of sulphur dioxide. The data for 10° and 18° have been omitted from this table, because the data for 0° and 25° are typical and at the same time give the greatest temperature interval for studying the effect of temperature on the equilibrium. The values of the differences in conductivity have been plotted against per cent sulphur dioxide in figure 9 and figure 10 gives the corresponding curves for the partial pressure differences.

The equilibria to be expected in a system in which sulphur dioxide is being added to calcium sulphite may be represented;

TABLE 15.

Comparison of Data of Morgan and Maass, and Present Work in Region between 1 and 2 Moles per mole.

Data for 1% (Approx) CaO.

	0°			25°		
% SO_2	k x 10^2 Grieve	k x 10^2 Morgan	k Morgan -k Grieve	k x 10^2 Grieve	k x 10^2 Morgan	k Morgan -k Grieve
0.125	0.23	0.30	0.07	0.44	0.45	0.01
0.435	0.54	0.77	0.23	1.02	1.04	0.02
1.083	1.06	1.43	0.37	1.94	1.81	-0.13
			2% (Approx) CaO.			
0.337	0.51	0.65	0.14	0.97	0.88	-0.09
1.370	1.33	1.66	0.33	2.45	2.07	-0.38
2.008	1.67	2.09	0.42	3.09	2.59	-0.50

1% (Approx) CaO.

	0°			25°		
% SO_2	p_{so_2} Grieve	p_{so_2} Morgan	p_{so_2}Morgan $-p_{so_2}$Grieve	p_{so_2} Grieve	p_{so_2} Morgan	p_{so_2}Morgan $-p_{so_2}$Grieve
0.125	0.1	0.2	0.1	0.2	0.6	0.4
0.435	0.3	0.9	0.6	0.4	2.5	2.1
1.083	0.8	2.5	1.7	2.2	7.7	5.5
			2% (Approx) CaO.			
0.337	0.1	0.7	0.6	0.3	1.9	1.6
1.370	0.8	3.3	2.5	2.1	10.0	7.9
2.008	1.6	5.2	3.6	4.1	15.3	11.2

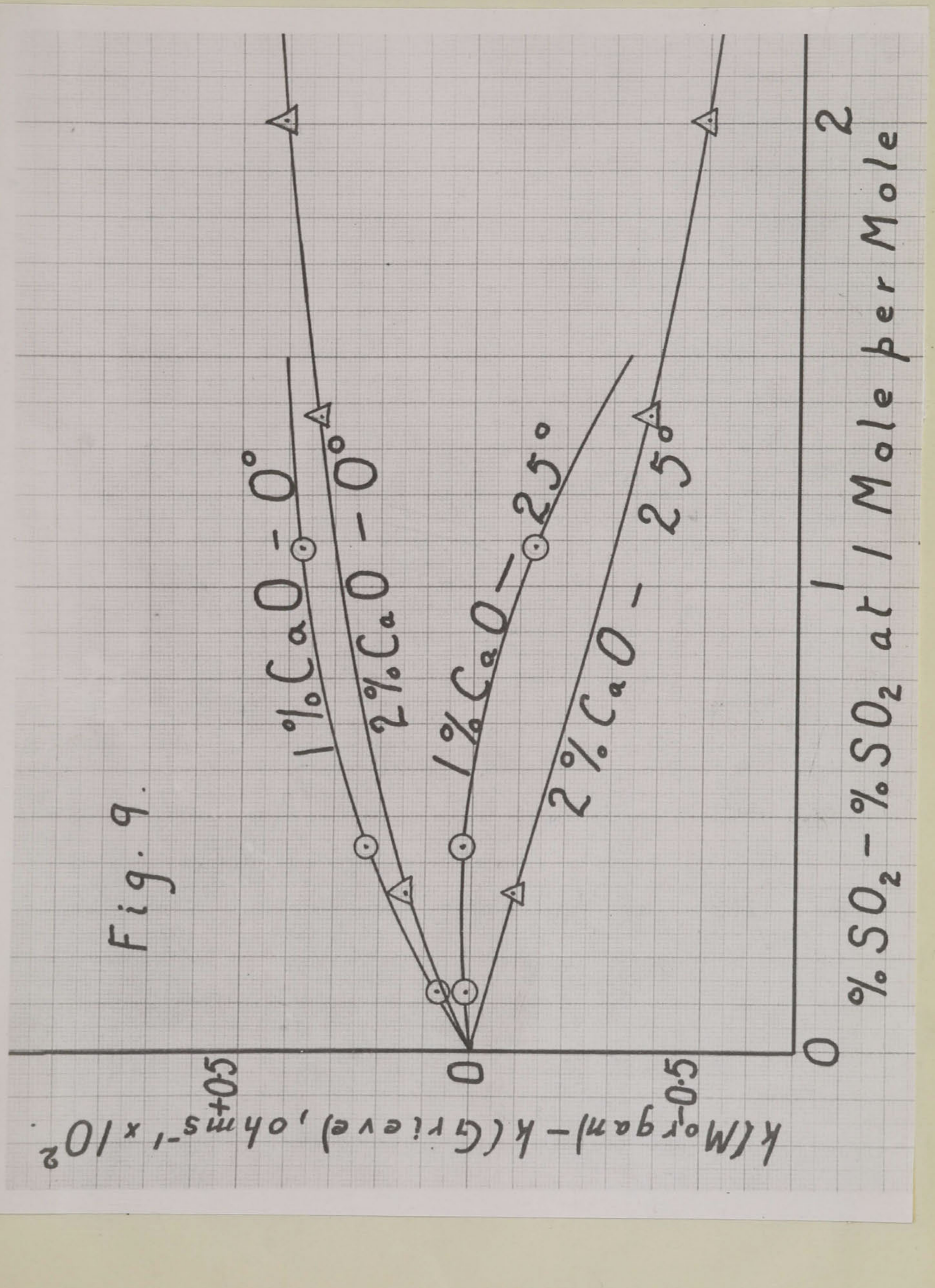


Fig. 9.

1% CaO - 0°
2% CaO - 0°
1% CaO - 25°
2% CaO - 25°
% SO_2 - % SO_2 at 1 Mole per Mole
0
1
2
k(Morgan) - k(Grieve), ohms⁻¹ x 10²
+0.5
0
-0.5

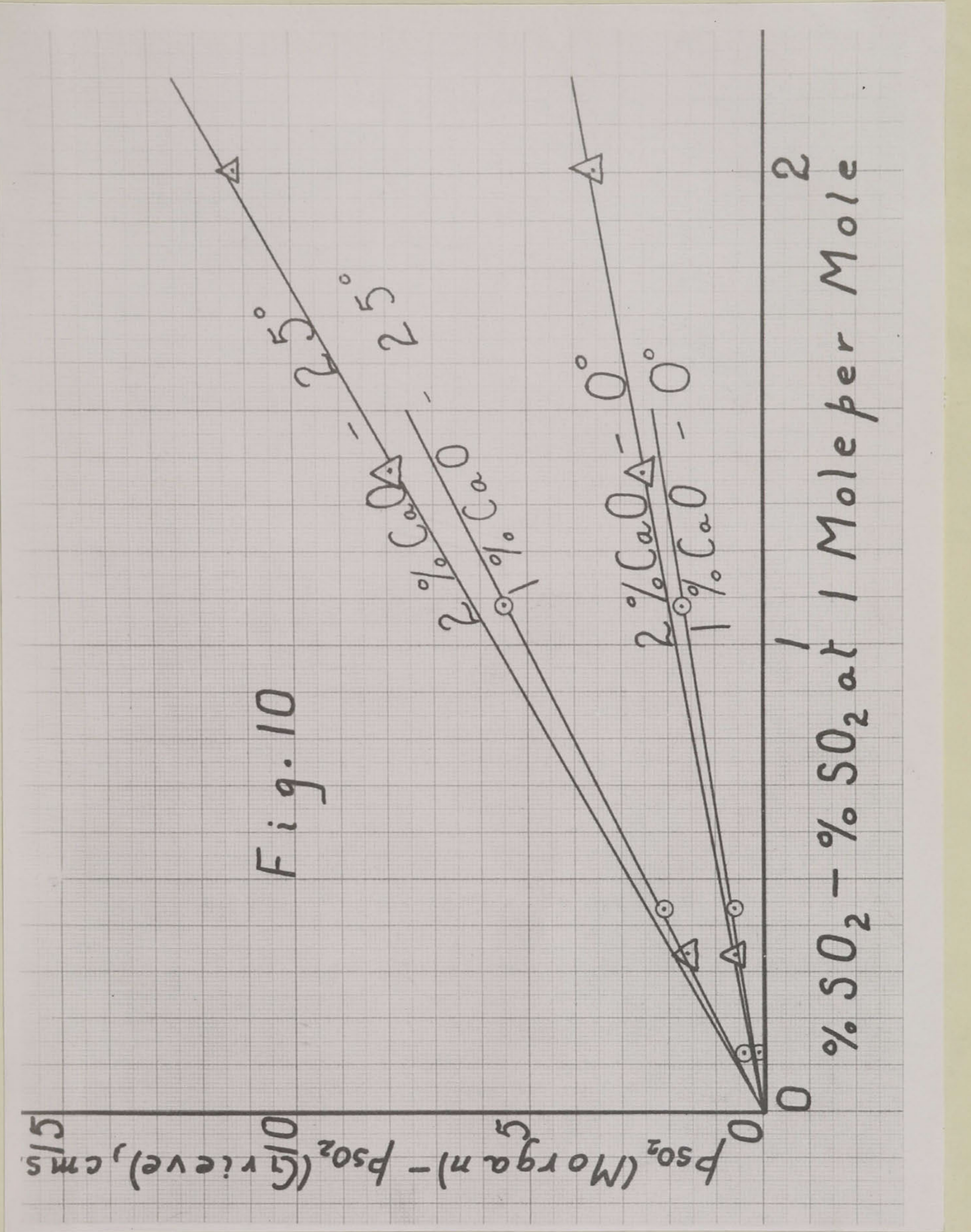
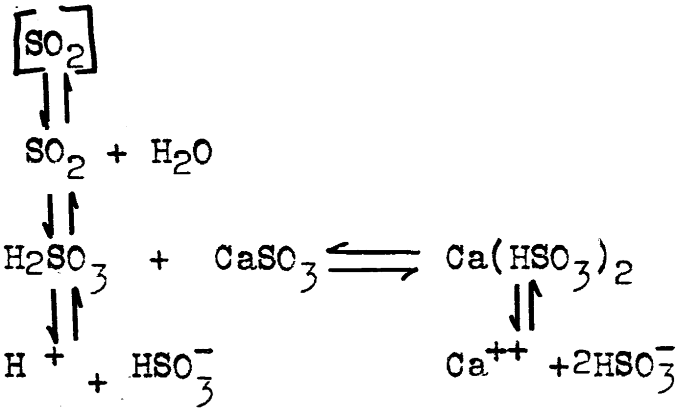


Fig. 10
p_{SO_2}(Morgan) − p_{SO_2}(Grieve), cms
0
5
10
15
% SO_2 − % SO_2 at 1 Mole per Mole
0
1
2
2% CaO − 25°
1% CaO − 25°
2% CaO − 0°
1% CaO − 0°



The main equilibria in a solution of sulphur dioxide in water are:

$$SO_2 \rightleftharpoons SO_2 + H_2O \rightleftharpoons H_2SO_3 \rightleftharpoons H^+ + HSO_3^-$$

Since there is sulphurous acid present in each of these systems, each system will have a partial pressure of sulphur dioxide above it which will be proportional to the amount of sulphurous acid present. A glance at table 15 reveals the fact that the partial pressures of sulphur dioxide obtained in the present work are very much smaller than those of Morgan and Maass(3), consequently, in the present system a considerable amount of the sulphurous acid must have reacted with the calcium sulphite to form calcium bisulphite. For this reason, an increase in temperature causes a much smaller increase in partial pressure in the present system than it does in a sulphurous acid solution. This can be seen in table 15 as well as in figure 10 Increase in the calcium oxide concentration used causes a slight decrease in the partial pressure; this can be best seen in figure 10, in which, at a given temperature, the partial pressure differences for the 1% calcium oxide run are smaller than those for the 2% run.

Examination of the comparative conductivity data also indicates that in the present system considerable of the sulphurous acid has reacted with the calcium sulphite to yield bisulphite. In a solution of sulphur dioxide low temperatures favour the formation of sulphurous acid, this ionizes to give bisulphite ion and hydrogen ion, the latter having a very high mobility. The presence of lime in the system tends to lower the hydrogen ion concentration, consequently at low temperatures it would be expected that the conductivities of Morgan and Maass would be greater than those of the present work, and this is found to be the case. At higher temperatures, since, in the system of Morgan and Maass, there was no lime present to act as a buffer, increased temperature tended to decompose the sulphurous acid, forming sulphur dioxide and water; this decomposition prevents the conductivity from reaching such values as would be expected if the only effect of temperature had been to increase the ionization, and mobility of the ions, of the sulphurous acid. Consequently, it is to be expected that at a given sulphur dioxide concentration the conductivities found in the present system would tend, at increased temperatures, to approach or even exceed the values obtained by Morgan and Maass This is found to be the case: at 25° and for the 1% lime run, the two sets of values are very nearly equal, while in the 2% lime run, the present values are considerably greater than those of Morgan and Maass; the 0^{o} values, on the other hand, in both runs are lower than those of Morgan and Maass.

An increase in the lime concentration causes an increase in the amount of calcium bisulphite and, consequently, of its ions. Therefore, at a given temperature, and sulphur dioxide concentration, the conductivities obtained in the 2% lime run are higher than those of the 1% run. This can be confirmed most easily by reference to the curves in figure 9, in which a high positive value represents a smaller conductivity relative to that of Morgan and Maass.

It is realized that this discussion of the equilibria existing between 1 and 2 moles of sulphur dioxide per mole of lime has been entirely qualitative, however it cannot be quantitative until certain other data are obtained. Of these, the most valuable would be determinations of the hydrogen ion concentration and of the total calcium concentrations of the solutions. However from the data presented it is believed that the following points have been established, or confirmed.

1. Calcium sulphite reacts with sulphurous acid to form calcium bisulphite.

2 The reaction for the formation of calcium bisulphite reaches an equilibrium which is considerably short of completion.

3. Optimum conditions for the formation of calcium bisulphite are low temperature and high lime concentration.

At sulphur dioxide concentrations of slightly more than 2 moles per mole the properties of the system undergo some rather interesting changes. Most noticeable of these is the fact that the suspended solid, which has been present in considerable amounts, disappears completely, and rather suddenly. Coinciding with this disappearance of solid, a break occurs in the partial pressure curve and also in the conductivity curve; each curve has an entirely different slope above this point. The break in the partial pressure curve is probably due to the reaction of sulphurous acid with the remaining calcium sulphite, and its removal in this way reduces the partial pressure of the sulphur dioxide. The break in the conductivity curve is due to the fact that up to that point, additions of sulphur dioxide have caused some of the solid to dissolve, while above that point sulphur dioxide is being added to the equilibria which exist in the solution in which all the solid is dissolved.

In what follows, reference will be made to the equilibrium chart given on page 89. This chart serves to represent the equilibria which may be expected as more sulphur dioxide is added to the solution.

It can be seen from the chart that adding sulphur dioxide to the system will cause the formation of more sulphurous acid and consequently more calcium bisulphite, to-

together with more of the ions of each. This increase in the number of ions causes the specific conductivity to increase. However, now that the solid calcium sulphite has all dissolved, the amount of calcium bisulphite formed by a given addition of sulphur dioxide will be greatly reduced, and the presence of HSO_3^- due to the ionization of the calcium bisulphite will tend to repress the ionization of the sulphurous acid. Consequently the slope of the conductivity curve would be expected to be less in this concentration range than between 1 and 2 moles per mole, and this is found to be the case.

At the same time the repression of the ionization of the sulphurous acid tends to shift the whole equilibrium towards the formation of free sulphur dioxide. For that reason we not only find that the partial pressure increases upon addition of sulphur dioxide, but also that the slope of the partial pressure-concentration curve is very much greater than it was between 1 and 2 moles per mole.

The properties of the system beyond the point where all the solid has dissolved can best be discussed, as were the properties of the system between 1 and 2 moles of sulphur dioxide per mole of lime, by comparing the data obtained in the present work with the data of Morgan and Maass(3), and noting the effect of changes in temperature and sulphur dioxide concentration, and of the addition of calcium oxide on the properties of the two systems and, from the differences observed, drawing conclusions as to the equilibria involved.

Comparison of the representations of the equilibria to be expected in the present system with those to be expected in the sulphur dioxide water system leads to the following generalizations regarding the effect of increasing sulphur dioxide content, increasing calcium oxide concentration, and increasing temperature.

The presence of calcium oxide leads to the formation of calcium bisulphite, as was pointed out in the section on the concentration range between 1 and 2 moles per mole. The presence of this bisulphite, which yields HSO_3^-, tends to repress the ionization of sulphurous acid, which shifts the equilibrium towards the formation of free sulphur dioxide. Consequently as sulphur dioxide is added it would be expected that the vapour pressures would be higher than in the corresponding system from which lime was absent. The presence of the lime removes hydrogen ion; consequently, as sulphur dioxide is added, lower conductivities are to be expected than when lime is absent.

If, instead of considering the effect of increased sulphur dioxide concentration at constant calcium oxide concentration, we consider the effect of increased calcium oxide concentration at constant sulphur dioxide concentration, it would be expected that the partial pressure of sulphur dioxide would be decreased by the removal of sulphur dioxide to form calcium bisulphite, hence the vapour pressure would be less than in a solution containing no lime. Also it might be expected that the larger amount of calcium bisulphite which would be formed would increase the conductivity relative to the conductivity of a sulphurous acid solution.

Increasing the temperature would be expected to cause a smaller increase in the partial pressure when lime is present than when it is not, because, when present, the amount of sulphurous acid is reduced. The sulphurous acid decomposes very readily at higher temperatures to form sulphur dioxide and water, hence that system which contains the larger amounts of it will have its partial pressure more noticeably increased by temperature increase. The effect of increased temperature on the conductivity will be minimized by the removal of hydrogen ion by the decomposition of sulphurous acid. Consequently, a system containing lime will have less free sulphurous acid and therefore its conductivity will be increased more by temperature than will a system containing no lime.

To sum up these generalizations: it is to be expected that the difference between the partial pressure of sulphur dioxide above a solution of sulphur dioxide and the partial pressure above a solution of sulphur dioxide containing calcium bisulphite, will be decreased by increasing the sulphur dioxide concentration, and will be increased by increasing the temperature and by increasing the calcium oxide concentration. The difference between the specific conductivity of a solution of sulphur dioxide, and the specific conductivity of a solution of sulphur dioxide containing calcium bisulphite, will be increased by increasing sulphur dioxide concentration and will be decreased by increasing the calcium oxide concentration and by increasing the temperature.

In order to test out these generalizations reference may be made to Table 16 and to figures 11 and 12 which are plotted from the data of Table 16. These data have been obtained in the same manner as the data of Table 15. In Figures 11 and 12 the portions of the curves represented by dotted lines are a re-plot of the data of Table 15.

Examination of these data and curves reveals that the generalizations given above fit the data obtained fairly satisfactorily.

TABLE 16.

1% CaO (Approx)

%	k Grieve x 10^2	k Morgan x 10^2	k Morgan -k Grieve	p_{so_2} Grieve	p_{so_2} Morgan	p_{so_2} Morgan $-p_{so_2}$ Grieve
			0°			
1.235	1.16	1.55	0.39	1.1	2.9	1.8
1.553	1.30	1.79	0.49	2.1	3.8	1.7
2.003	1.48	2.09	0.61	3.7	5.1	1.4
3.182	1.94	2,74	0.80	8.1	8.9	0.8
7.261	3.26	4.39	1.13	24.7	23.7	-1.0
			25°			
1.235	2.15	1.95	-0.20	2.3	8.9	6.6
1.553	2.31	2.23	-0.08	5.2	11.5	6.3
1.986	2.47	2.58	+0.11	9.8	15.1	5.3
3.157	2.93	3.38	+0.45	22.1	25.6	3.5
7.175	4.21	5.25	+1.04	67.4	65.0	-2.4

TABLE 16 (cont'd)

2% CaO (Approx)

%	k Grieve x 10^2	k Morgan x 10^2	k Morgan -k Grieve	p_{so_2} Grieve	p_{so_2} Morgan	p_{so_2}Morgan $-p_{so_2}$Grieve
			0°			
2.214	1.79	2.21	-0.42	1.8	5.8	4.0
2.714	2.00	2.49	0.49	3.2	7.4	4.2
4.084	2.36	3.19	0.83	9.1	11.9	2.8
5.627	2.73	3.81	1.08	16.1	17.4	1.2
8.10	3.26	4.65	1.39	27.9	27.0	-1.1
			25°			
2.214	3.29	2.74	-0.55	4.7	17.2	12.5
2.714	3.59	3.09	-0.50	8.4	21.7	13.3
4.055	3.91	3.88	-0.03	24.7	34.0	9.3
5.577	4.25	4.62	+0.37	43.5	48.9	5.4
8.02	4.71	5.53	+0.82	74.6	73.6	-1.0

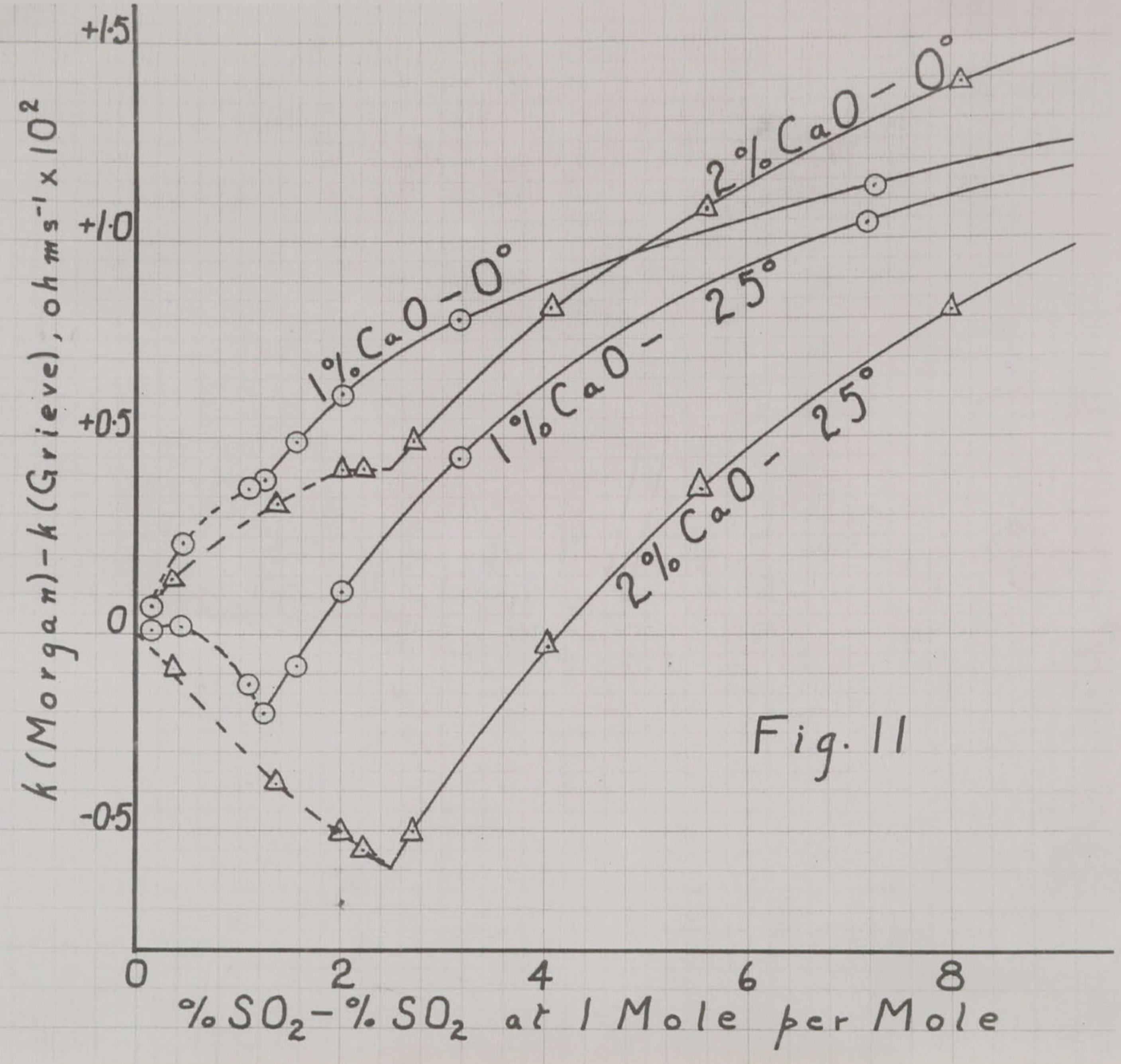

+1·5
+1·0
+0·5
0
-0·5
k (Morgan) - k (Grieve), ohms⁻¹ x 10²
0
2
4
6
8
% SO₂ - % SO₂ at 1 Mole per Mole
2% CaO - 0°
1% CaO - 0°
1% CaO - 25°
2% CaO - 25°

Fig. 11

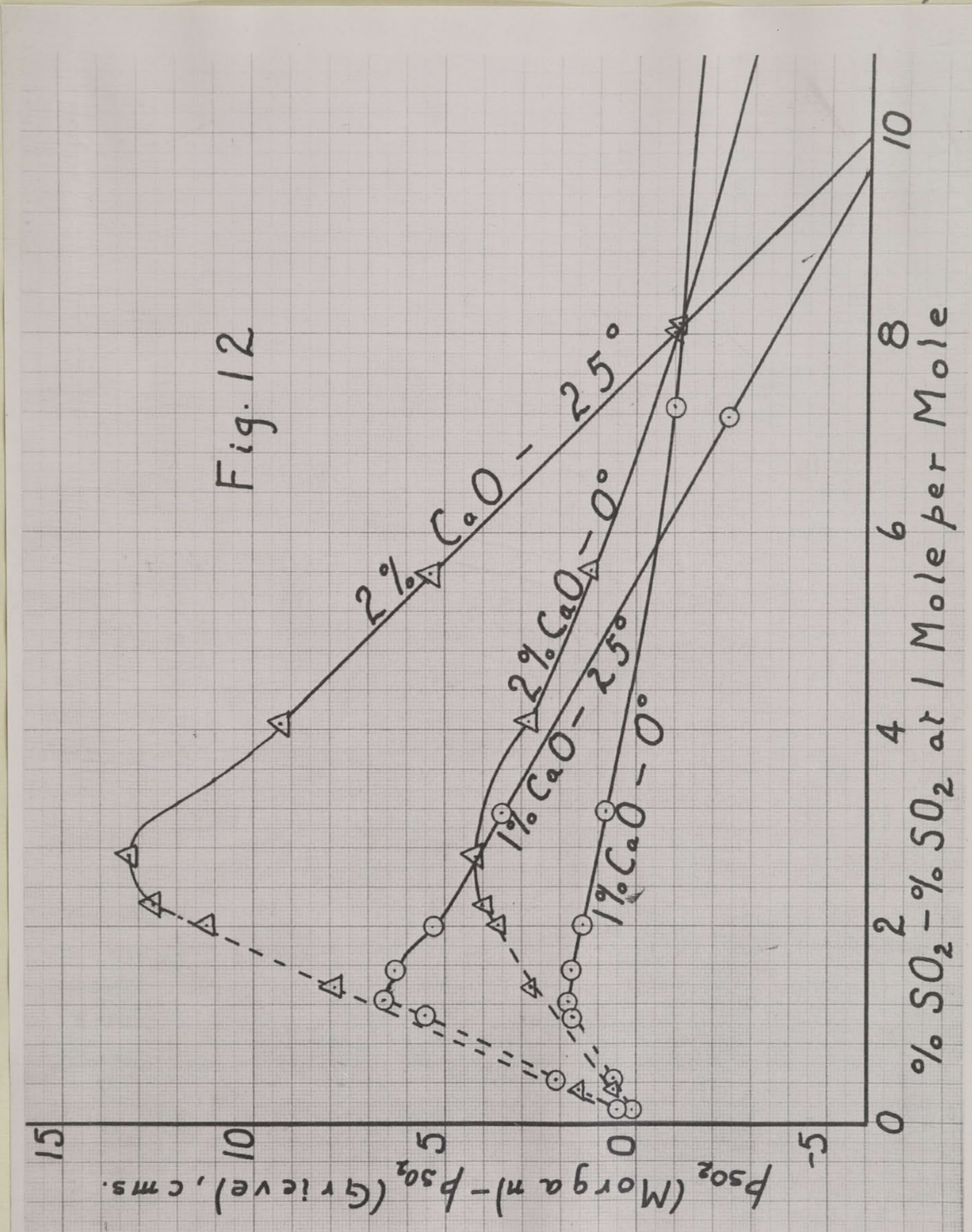


Fig. 12

2% CaO - 25°
2% CaO - 0°
1% CaO - 25°
1% CaO - 0°
15
10
5
0
-5
0
2
4
6
8
10
p_{SO_2} (Morgan) - p_{SO_2} (Grieve), cms.
% SO_2 - % SO_2 at 1 Mole per Mole

SUMMARY.

The specific electrical conductivity and the vapour pressure of saturated solutions of calcium hydroxide have been measured over a temperature range from 0° to 25°C. These solutions were prepared with greater precautions than have been taken before to ensure purity of materials From the data obtained the degree of dissociation, and dissociation constants for these solutions have been calculated. Analysis of these values has led to the conclusion that the available data on the solubility of calcium hydroxide in this temperature range is in error. Values for the solubility have been calculated which are believed to be more nearly correct, and evidence is offered to support these calculated values

The specific electrical conductivities and vapour pressures of the three component system calcium oxide - sulphur dioxide - water have been measured over a temperature range from 0° to 25°C, at calcium oxide concentrations of approximately 1% and 2%, and at sulphur dioxide concentrations of more than 5 moles of sulphur dioxide per mole of lime Special precautions were taken to ensure the purity of the components and the precise determination of their concentrations.

The partial pressure of sulphur dioxide of the solutions have been calculated from the vapour pressure data.

From the data obtained it has been concluded that:

As sulphur dioxide is added to a suspension of calcium hydroxide, calcium sulphite is formed but that the properties of the system are governed almost entirely by the calcium hydroxide, because of its greater solubility. Ultimately the addition of sulphur dioxide results in the neutralization of the calcium hydroxide, but this neutralization does not occur at equivalent amounts of sulphur dioxide and lime. It is believed that the calcium sulphite forms a complex with the calcium hydroxide.

When sulphur dioxide is added to the suspension of calcium sulphite, it reacts with it to form calcium bisulphite which is more soluble than the sulphite. The reaction for the formation of calcium bisulphite does not go to completion. Sulphurous acid and sulphur dioxide are present in the solution. At a point above 2 moles of sulphur dioxide per mole of lime, all the calcium sulphite dissolves. When sulphur dioxide is added to this solution which contains calcium bisulphite, the partial pressure of sulphur dioxide increases more rapidly than would be expected, the conductivity increases less rapidly than would be expected for a given addition of sulphur dioxide. Increasing the calcium oxide concentration decreases the partial pressure and increases the conductivity in relation to the values for a corresponding solution of sulphur dioxide which contains no lime. Similarly increasing the temperature decreases the partial pressure and increases the conductivity relative to a system containing no lime.

REFERENCES.

(1). Maass, C. E. and Maass, O.; J.A.C.S. 50, 1352 (1928).

(2). Campbell, W. B. and Maass, O.; Can. Jour. research; 2, 42 (1930).

(3). Morgan, O. M. and Maass, O.; Can. Jour. Research; 5, 162 (1931).

(4). Maass, C. E.; Thesis, McGill University, 1927.

(5). Ostwald, W.; Journal fur Praktische Chemie, 33, 357 (1886).

(6). Ostwald, W.; Journal fur Praktische Chemie, 32, 300 (1885).

(7). Miller, L. B. and Witt, J. C.; Journal of Physical Chemistry, 32, 285 (1929).

(8). Maben, Pharm. J. Trans.; (3) 14, 505 (1848).

(9). Lamy, Comptes Rendus; 86, 333 (1878).

(10). Herzfeld; Zeit. ver. Rubenzucher.- Ind. 1897, 818.

(11). Guthric; J. Soc.,Chem. Ind., 20, 223 (1901).

(12). Moody; J. Chem. Soc., 93, 1772 (1908).

(13). Haslam, Calingaert and Taylor; J.A.C.S., 46, 311 (1924).

(14). Cavazzi; Gazzetta Chimica Italiana; 45, I, 529 (1915).

(15. Robart; Bull. d. Assoc. des chim. d. Sucr. et Dist., 31, 108.

(16). van der Linden; Arch. Suikerind., 24, 1113 (1916).

(17). Weisberg; Bull. Soc. Chem. 15, 1247 (1896).

(18). Schwarz and Muller-Clemm; Zeit. fur Angew. Chemie, 34,272 (1921).

(19). Smith and Parkhurst; J.A.C.S. 44, 1918 (1922).

(20). Enckell; Papierfabrikant, 23, Tech.- Wiss. Teil, 633 (1925).

(21). Farnell; Jour. Soc. of Chem. Ind., 44, 530, 2T, (1925).

(22). Reilly, Joseph; Physico-Chemical Methods, 1925 ed.; pp.588-9.

(23). Landolt-Bornstein; Physikalish-Chemische Tabellen, 1923 ed., Vol II, p.1098.

(24). International Critical Tables, Vol. 1, p.69

(25). Cooper and Maass; Canadian Journal of Research, 4, 495, (1931)

(26). International Critical Tables, Vol. 1, p.75.

(27) Gurd, G.W.; Thesis, McGill University, 1932

(28). Landolt-Bornstein; Physikalish-Chemische Tabellen, 1923 ed., Vol II, p.1105.

(29). Bain, J.W.; Toronto University; private communication.

(30). Gurd, G.W.; private communication.

(31) Seubert & Elten; Zeit Anorg. Chemie, 4, 44, (1893).