PROPERTIES

OF

PURE SULPHUR DIOXIDE

AN INVESTIGATIONS OF THE PROPERTIES OF PURE SULPHUR DIOXIDE, AND ITS AQUEOUS SOLUTIONS.

Thesis

Submitted in Partial Fulfilment of the Requirements for the Degree of Doctor of Philosophy.

by

CAROL E. MAASS

McGill University, April,1927.

Acknowledgment is made to the Honorary Advisory Council for Scientific and Industrial Research, for a Bursary and Studentship, awarded during part of the period during which this work was in progress.

I N D E X

-oOo-

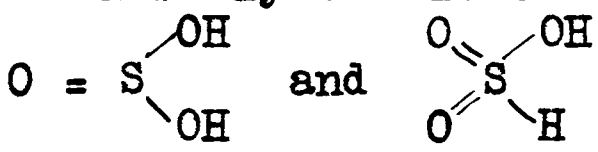
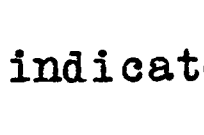
This thesis deals with certain physical constants of pure sulphur dioxide and its aqueous solutions. The results of experiments to determine these values are given, and are discussed both from the point of view of their theoretical significance and from their relation to one another.

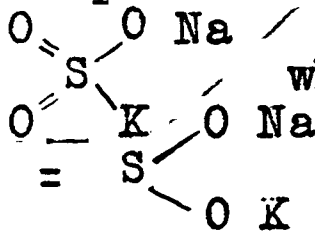
Sulphur dioxide has been known from a very early date. The ancients knew that the fumes evolved when sulphur was burnt in air exerted a purifying action, and they used it for fumigating and for bleaching cloth. The first recorded observations on a solution of sulphur dioxide in water, or sulphurous acid, were made by Libavius in about 1600. On burning sulphur with saltpetre,(sodium nitrate), a gas was evolved which formed the already known sulphuric acid on being passed into water. Libavius noticed that an acid was also formed, when fumes from sulphur, burnt in the absence of saltpetre, were passed into water. There was a good deal of confusion at first, between sulphuric and sulphurous acids. This is not surprising when one considers how easily sulphurous acid is oxidized to sulphuric. The difference between them was definitely settled by Stahl. Stahl distinguished between them by calling sulphuric acid the stronger, and sulphurous acid, the weaker acid. Further, he made the potassium salt of sulphurous acid, and showed

that it differed from the corresponding salt of sulphuric acid. Stahl was the great leader of the Phlogiston Theory, and he called sulphurous acid, "phlogistigated vitriolic acid". Even Cavendish referred to it by that name as late as 1765. It was left to Priestley in 1775 to prepare the pure gas, which was done by the reduction of sulphuric acid by mercury. A few years later, Lavoisier showed that sulphurous acid was an intermediate oxidation compound between sulphur and sulphuric acid.

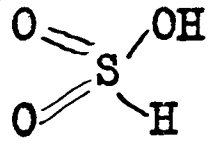
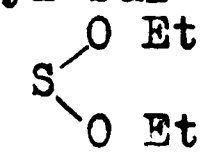
Since these times, sulphur dioxide and its aqueous solution have become more and more important. Little precision work, however, has been carried out on the measurement of its physical properties, and comparatively little has been done on it from a theoretical point of view. Three structures have been put forward for the gas, (1) O = S = O; (2) O = S - O; (3) $S\begin{smallmatrix}O\\|\\O\end{smallmatrix}$. The first formula is that most commonly accepted, and the direct formation of substances such as $O = S\begin{smallmatrix}Cl\\Cl\end{smallmatrix}$ from sulphur dioxide seems to support it very strongly. The second formula is that which is given by consideration of the sulphur dioxide from the point of view of Langmuir's theory of the atom. This indicates that one of the oxygen atoms is attached to the sulphur atom by one pair of electrons, while the other oxygen atom is bound by two pairs of electrons. The ring structure has been put forward as an analogy to the ring structure suggested for ozone, but there is not much evidence for its existence.

A paper has been published quite recently by C.P.Smyth[1], in which the author considers the structure of the molecule from the point of view of Langmuir. From calculations involving electric moments of the molecule, which had been determined experimentally, Smyth concludes that the Langmuir structure is the most probable.

The constitution of sulphurous acid, formed by the solution of sulphur dioxide in water, has not been definitely settled. The two formulae considered are:  and . The arguments in favour of each are based on the following. Thionyl sulphide is made directly from sulphur dioxide by treatment with phosphorous pentachloride. As there is no reason to suppose that the sulphur changes its valence during the reaction, the two chlorine atoms are considered to be directly attached to the sulphur atom. Hydrolysis causes thionyl sulphide to decompose to form sulphurous acid. That is, the two chlorine atoms have been replaced by hydroxyl groups, which are then attached directly to the sulphur atom. This would indicate that the structure for sulphurous acid is  . Whether the two hydroxyl groups occupy symmetrical positions in the molecule was investigated by preparing double salts. Acid sodium sulphite and acid potassium sulphite were treated with potassium hydroxide and sodium hydroxide respectively. The two salts obtained were apparently identical. These

salts were treated with methyl iodide, and in each case, the methyl group replaced the sodium atom. From this it would appear that the sodium atoms occupy equivalent positions in the two salts. This could only be so, apparently, if the two hydroxyl groups are symmetrically placed in the molecule. This evidence is not conclusive, however, as there is the possibility of the existence of an unstable compound  which changes over immediately into its isomer

The work just outlined, carried out by Godby[2] and later by Arbusoff[3], refuted the work of Schwicker[4] who had claimed to have found two different crystalline forms for potassium sodium sulphite, when prepared as indicated above. Similarly, the time variation of absorption spectra of bisulphites explained by Schaeffer[5] and others as being due to two isomeric forms, was questioned by the work of Baly and Bailey[6], as far as the necessity for the existence of two isomeric forms, is concerned.

On the other hand, a compound exists whose constitution is definitely known as being a derivative of sulphurous acid, written in the form  . This compound is unsymmetrical diethyl sulphite, and is obtained by the oxidation of ethyl mercaptan, in which the ethyl radicle is known to be attached directly to the sulphur. The action of ethyl alcohol on thionyl chloride, furnishes the isomer of the above compound, symmetrical ethyl sulphite having the following structural formula 

The distinct difference in boiling point of these two compounds establishes the fact that they are real isomers.

With the above conflicting evidence for the existence of both forms of the acid, the safest course at present is to regard it as a tautomeric substance. That the aqueous solution contains a large number of uncombined sulphur dioxide molecules, is indicated by the work of Wright[7], who showed that the absorption spectre of the aqueous solution is similar to that of sulphur dioxide gas, and it is this fact, of course, which probably prevents the separation of pure sulphurous acid.

As has been stated already, the number of theoretical papers on sulphur dioxide, has been small, as compared, for example, with carbon dioxide and its systems. This may, perhaps, be due in part to the importance which has been attached to sulphur dioxide, industrially. A great deal of research has been done on it, in connection with the manufacture of sulphuric acid, and in connection with the sulphite process in the Pulp and Paper industry. Up to the present, most of this research has been directed towards obtaining mechanical efficiency in commercial processes, Now, however, especially in the manufacture of Pulp and Paper, the need is being felt, of further theoretical knowledge of the processes used. For example, during the sulphite cooking of the pulp, it is known that polythionic acids are formed, but very little is known of the actual chemical processes involved. It may be of interest to

show the increasing importance of this work, to state, that even while this work has been under way, two papers dealing in part with the subject matter of this thesis, have been published. As a matter of fact, a demand has been made for a continuation of the work described below to cover higher temperature ranges, and the experimental technique which was evolved in the course of this work, will make it a simple matter to do this. The work will be continued next year at the instigation and with the financial assistance of the Pulp and Paper Association.

The above short historical review has been given in order to justify the undertaking of further research. And it is obvious that both from a theoretical and industrial point of view, that all exact data on physical constants will be of importance. The conductivities of aqueous solutions of sulphur dioxide may be taken as a good example of this. A knowledge of the conductivities gives the ionization constant of the acid. From this, the dissociation of sulphurous acid can be calculated, and from the variation of the dissociation constant with temperature, it is possible that some idea of the nature of the dissolved sulphur dioxide may be inferred. Furthermore, it should give a means of rapdily following some of the important reactions which sulphur dioxide undergoes in aqueous solution, and a study of whose dependence on catalysts is of peculiar interest. On

the other hand, electrical conductivity, if known, offers a convenient means of concentration control. Since the conductivity of an aqueous solution of sulphur dioxide varies considerably with concentration, this control is sensitive, and, what is important, it registers instantaneously. It should prove useful in industrial processes where sulphurous acid is manufactured.

Originally it was intended to limit the scope of this work to the determination of the electric conductivity of aqueous solutions of sulphur dioxide. The data found in the literature are very meagre. Ostwald and Barth[8] determined the conductivities of very dilute solutions, and the results of measurements made by Kerp and Bauer[9] and by Lindner[10], have not even been deemed worthy of inclusion in the Landolt Bornstein Tables[11].

The scarcity of conductivity data on sulphurous acid was readily understood when the first actual experiments were tried. Sulphur dioxide has a large partial vapour pressure in solution and is readily oxidised. Both factors give rise to changes in concentration and make quite impossible the investigation of the more concentrated solutions by means of the usual apparatus. Special methods were therefore devised by means of which sulphur dioxide could be added to the water by volume, and the apparatus was constructed so as to withstand pressures of the same

order as the vapour pressure of liquid sulphur dioxide, at room temperature. To calculate the conductivity, the vapour densities of sulphur dioxide, and partial vapour pressures of its aqueous solutions were required. Since insufficient data were available these had to be determined. Furthermore, analytical methods for sulphurous acid were found to be inadequate, and a modified method had to be devised.

The system, sulphur-dioxide-water, which has been investigated is one in which one of the components has a much higher vapour pressure than the other. It will be seen that new experimental technique has been developed for the examination of concentration, conductivities, and vapour pressures, etc., especially where the volatile component is present in large amounts, and where a second liquid phase appears. It may be pointed out that this technique is valuable as being applicable to systems, such as carbon-dioxide-water, presenting similar experimental difficulties.

At the outset, these investigations were looked upon as likely to be of subsidiary interest, and were undertaken solely as the means toward the end of determining the electric conductivities. However, some of the results obtained in the pre-investigations proved to be of at least as great an interest as the main one. Consequently, the description of the work is divided into sections dealing

with the following topics.

(1) Purification of Sulphur Dioxide.

(2) Analysis of Sulphurous Acid.

(3) Vapour Density determinations.

(4) Vapour Pressures of pure Sulphur Dioxide, and its aqueous solutions.

(5) Sulphur Dioxide Concentration in the two liquid phase system, sulphur dioxide-water.

(6) Water concentration in the two liquid phase system, water-sulphur dioxide.

(7) Conductivities of aqueous solutions of sulphur dioxide.

Each section will be treated more or less as a separate entity, and where data of other investigators are available a comparison will be made.

PURIFICATION OF SULPHUR DIOXIDE.

At first, sulphur dioxide was prepared by the action of concentrated sulphuric acid on copper, and an attempt then made, to purify the gas. This method was found to be cumbersome, and it was difficult to obtain the gas pure. This was confirmed by Cardoso[12]. He made many attempts to purify the gas, obtained by the above method, and found that practically the only way of eliminating the accompanying sulphur trioxide, was by passing the gas into ethyl alcohol. On heating, the alcohol retained the sulphur trioxide, while the dioxide was driven off. This process had

to be repeated twice, and the sulphur dioxide redistilled many times before a sample of the gas, having a constant vapour pressure, was obtained.

Fortunately, there was no need to carry out this long and involved purification. It was found that particularly pure liquid sulphur dioxide contained in six pound cylinders, could be purchased from the Ansul Chemical Company, of Marinette, Wis. Their product was carefully examined. In order to test the gas for sulphur trioxide, it was passed into an acid solution of barium chloride, in which air-free water had been used, and from which the air was excluded. No precipitate was formed. The only impurity found in the sulphur dioxide was a small trace of water. The gas from the cylinder E, (Fig.I.) was therefore passed over phosphorous pentoxide tubes F, and condensed in D by a carbon dioxide ether mixture. The liquid was then distilled a number of times in vacuo, the initial and final fractions being rejected. Cardoso mentioned a yellowish liquid left as residue in the vessel after some of his distillations. There was no sign of any such residue in the distillations carried out with the commercial gas. The distillation was carried out in an all-glass apparatus, bulbs C and R acting a receivers and tap H leading to a vacuum pump. The pressure was controlled by means of a manometer M, and tap A, glass sealed alternately to the various pieces of apparatus (described in the following

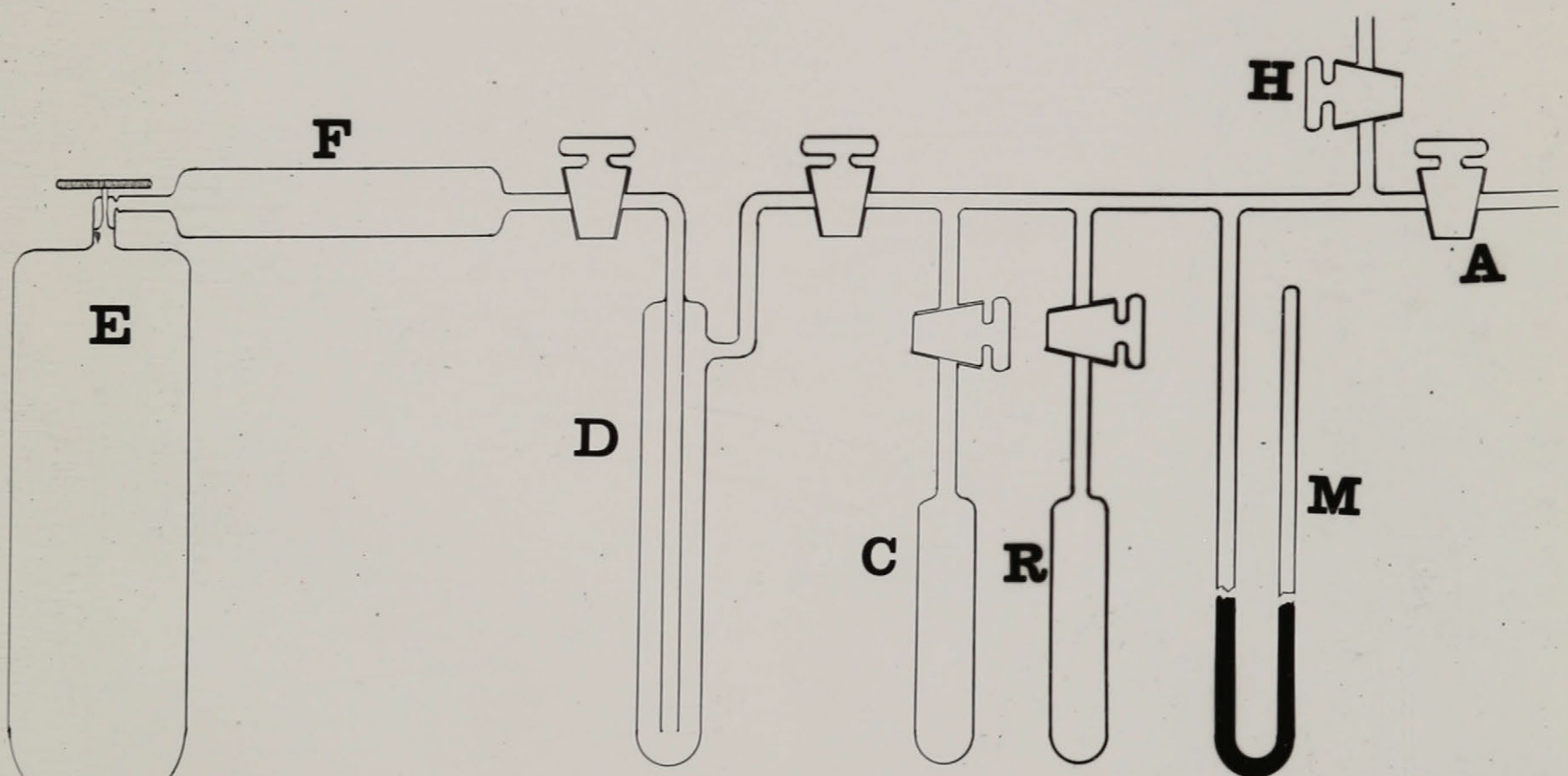


FIGURE I.

sections) where the experiments with the sulphur dioxide were to be carried out.

As a proof of the purity of the final fraction of sulphur dioxide, its vapour pressures were measured in the neighbourhood of the boiling point, and found to agree exactly with the values obtained by Hemming and Stock[13]. The vapour pressure determinations of these investigators were made with the greatest precision over the range -60° to -10°, and constituted one of the few physical constants of pure sulphur dioxide, which were accurately known when this work was started.

ANALYSIS OF SULPHUROUS ACID.

The estimation of sulphurous acid is described in most text-books on quantitative analysis, as being carried out very easily by means of a reaction with iodine, which depends on the reducing power of sulphurous acid.

$$H_2SO_3 + H_2O + 2I = 2HI + H_2SO_4$$

It was soon found that in practice the titration of sulphurous acid by iodine was not so simple as the text-books led one to believe. No consistent results were obtained, and two consecutive titrations of samples of the same sulphurous acid solution gave values differing by as much as twenty per cent.

A search in the literature soon disclosed that others had met with similar results, and various remedies had been suggested. Bunsen[14] recommended that before titration, solutions should be diluted below 4% sulphur dioxide content. Fordos and Gelis[15] believed that the inconsistencies were due in part, at least, to the volatility of the sulphur dioxide, and claimed that this could be obviated by the addition of $MgCO_3$ or $NaHCO_3$ to alkaline solution. Finkner[16], and later on, Volhard[17], suggested that good results could be obtained if the sulphurous acid be allowed to run into the iodine solution and not the reverse and usual way. An interesting and enlightening paper was published on this question by MacCauley[18]. MacCauley found that the low results obtained in the sulphurous acid titration are due nearly entirely to loss of sulphur dioxide from the solution. A solution of sulphurous acid was kept in a large vessel in an atmosphere of carbon dioxide. Oil was spread over the surface of the liquid in order to ensure that no sulphur dioxide escaped from the solution. The solution could be run into a burette from the bottom of the vessel, and titrated directly from the burette into the iodine solution. MacCauley obtained consistent results by this devise, and found that there was no difference when he ran the iodine into the sulphurous acid solution, if the latter was kept as explained above. That the volatility of the sulphur dioxide exerted a very appreciable influence in

the titration, was further shown by the following experiment. Iodine was run into a sulphurous acid solution contained in a flask, the flask being open to the air. When the end-point was reached, the flask was stoppered, and the contents well shaken. The colour disappeared at once. A comparatively large amount of iodine had to be added before the solution became permanently coloured. This proved conclusively that quite a sufficient amount of sulphur dioxide was present in the air above the solution, to cause appreciable errors in the results. MacCauley found that there was little or no oxidation during the titration of sulphurous acid. This, however, does not hold for solutions of alkali sulphites. Raschig[19] had earlier shown that sulphur dioxide solutions were more easily oxidized in the presence of alkali, and MacCauley's work confirmed this. In the case of these alkali solutions, the oxygen of the atmosphere appeared to have a considerable effect. Hudson[20], in investigating the solubility of sulphur dioxide in water and in various salt solutions, used two methods for the determination of the sulphur dioxide. The first method, a gravimetric one, consisted in the oxidation of sulphite to sulphate, and the precipitation of the sulphate by barium. This, of course, could only be used in cases where it was certain that there was no sulphate present originally in the solution. The volumetric method was the iodine-sulphurous acid titration,

with a modification based on a consideration of MacCauley's work. Hudson transferred his sulphurous acid solution to a sufficiently large amount of water to ensure that no sulphur dioxide escaped. This method gave good results, but unfortunately, it is not applicable to all solutions of sulphur dioxide. For example, a 25% sulphur dioxide solution, such as is dealt with in the section on "Sulphur dioxide concentration in the two-liquid phase system", would not lend itself to such a dilution without loss of sulphur dioxide.

After considerable time had been lost in attempting to obtain dependable results, in following some of the methods given above, a modification of them was worked out which gives accurate and reproducible results. This is true to such an extent that sulphur dioxide itself was used to calibrate the iodine solution. This method should be a valuable contribution since it can be generally applied to sulphur dioxide estimation, and an account of it will now be given in such a way that the development and details of the sulphurous acid analysis will be made clear.

A glass bulb B (Fig.II) of two or three c.c. capacity ending in a capillary tube bent in the manner shown was attached to a glass tube connected through tap A to the sulphur dioxide purification apparatus and through tap D to a vacuum pump. After evacuation about one c.c. of liquid sulphur dioxide was condensed in the bulb and then the

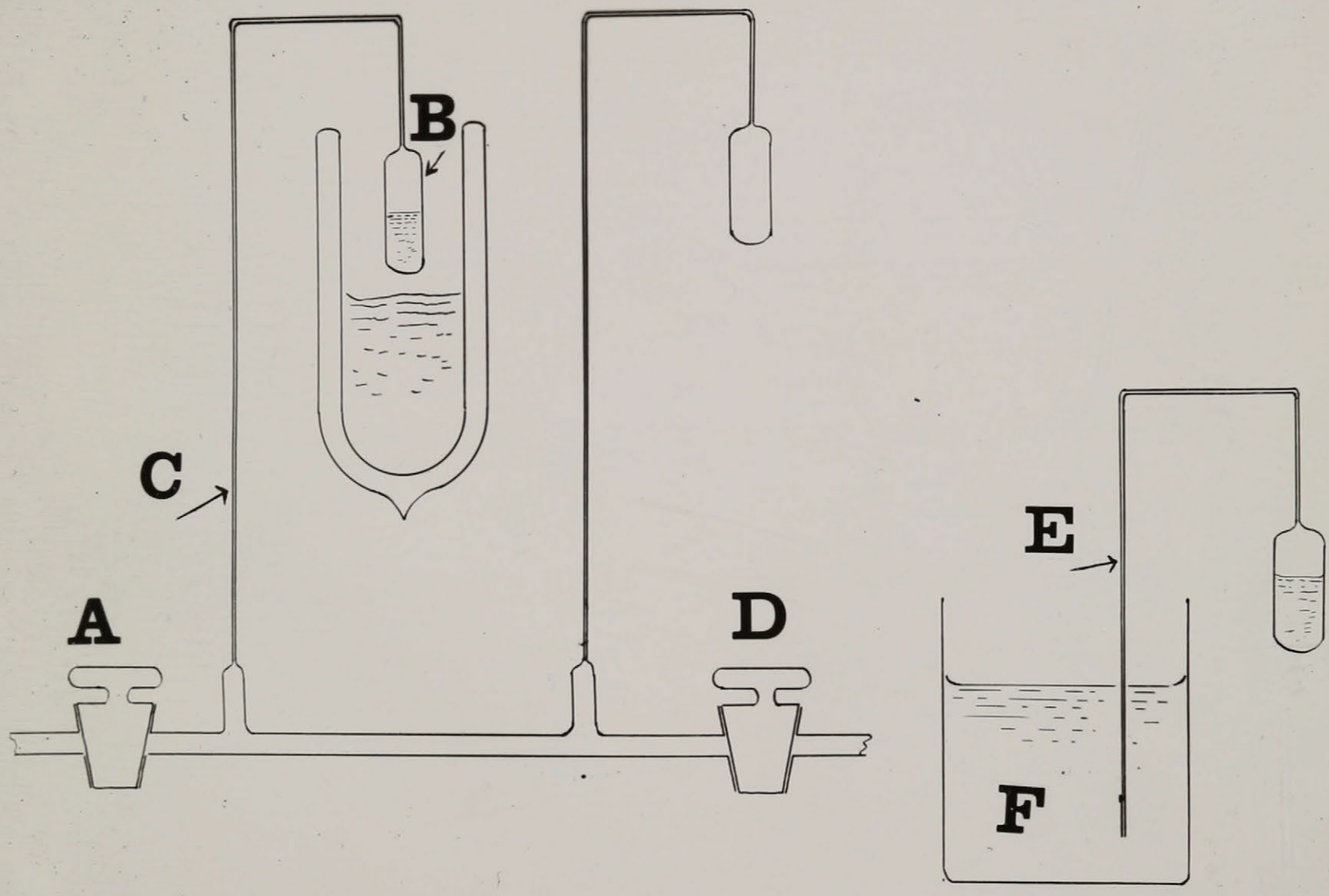


FIGURE II.

capillary sealed off with a hand blow pipe at the point marked C. The bulb was allowed to warm up to room temperature and then weighed. The bulb was then again cooled down by a carbon dioxide ether mixture (so as to lower the vapour pressure) and the capillary broken off near the sealed end. By having a thin capillary but one whose walls were thick relative to its diameter and furthermore by using a new file to scratch the glass, no splintering occurred so that the two broken parts represented the total weight of glass. The bulb is then allowed to warm up after the capillary is immersed into 50 c.c. of a 2 normal NaOH solution F as shown in Fig.II. The liquid sulphur dioxide which boils off is completely absorbed in the NaOH solution which then rises in the capillary as soon as all the liquid sulphur dioxide has evaporated. The moment this happens the capillary is sealed off at E. This bit of capillary is cleaned, dried and, together with the sealed off bulb and piece of capillary first broken off, is carefully weighed. The difference in weight between this and the first mentioned weighing gives the weight of sulphur dioxide absorbed by the NaOH solution to an accuracy of 1/10 of a milligram.

The essential feature governing the accuracy of the subsequent analysis depended on the solution of .1 gm. of sugar in the 50 c.c. of NaOH solution before the sulphur

dioxide was absorbed. The 50 c.c. was then made up to 250 c.c. in a graduate flask, care being taken to wash all the sulphur dioxide into the latter. This solution was then placed in a burette, 25 c.c. of an iodine solution to be standardised was measured out from a pipette into an Erlenmeyer flask. This was diluted with an equal volume of water and 2 c.c. of concentrated HCl added. The iodine solution was vigorously swished round in the Erlenmeyer flask and the sulphite solution was run in until the iodine colour disappeared, a very sharp and final end point being obtained. Obviously the above procedure can be used for any H_2SO_3 solution by making the solution strongly alkaline, adding a small amount of sugar and then following the above directions.

The reasons for some of the steps in the procedure are explained by the following considerations. Only a strong alkalinity insures that no loss of sulphur dioxide takes place due to evaporation. Sulphite solutions oxidise in an inconsistent and most exasperating manner. Evidently the rate of oxidation is greatly increased by catalysts present in the form of small traces of impurities. In Ostwald's Inorganic Chemistry[21] it is mentioned that the oxidation of sulphite is inhibited by the presence of a small amount of sugar which Ostwald calls an anticatalyst. Of course the probable action of the sugar is that it inhibits the action of the catalysts. The iodine solution

is made strongly acidic just before titration to neutralise the alkalinity of the sulphite solution.

As has already been indicated at first no consistent results whatever could be obtained in the titration even when the solutions were first treated with $NaHCO_3$. The method outlined above in the absence of sugar gave at least consistent results. This as well as the importance of sugar for uniformity and consistent results is shown by the following table:

TABLE I

Series	Gms. SO_2 dissolved in 250 cc.	Time in Minutes after solution complete	C.C.of sulphite solution required per c.c. of iodine solution.	Gms.SO_2 per c.c. of iodine solution.
A	.9470	30	.735	.002760 as given by first titration.
		50	.760	
		240	.900	
		2160	1.610	
				.00604 as given by last.
B	1.022	30	.665	.002718
		50	.660	"
		240	.665	"
		2180	.665	"
C	1.095	30	.620	.002716
		50	.614	"
		2180	.620	"

The results A were obtained with a sulphite solution to which no sugar has been added. B and C illustrate the constancy of the sulphite solution in the presence of sugar, and also the accuracy with which titrations can be repeated. It

may be of interest to record the results obtained from an experiment in which this effect of sugar on oxidation was tested out. Sulphur dioxide was passed into an acid solution of barium chloride, made up from water through which air had been passed. The solution was divided into two parts, one of which contained a trace of sugar. It was found that the oxidation of the sulphur dioxide, as indicated by the formation of the white precipitate of barium sulphate, proceeded very much more slowly in the beaker which contained the sugar. The accuracy of the analytical method warrants it being employed as a means of calibrating iodine solutions even when these are not to be used for titrating sulphite. Small bulbs of sulphur dioxide can be readily stored up indefinitely, the sulphur dioxide remaining unchanged and, on account of the relatively low vapour pressures of liquid sulphur dioxide, they can be handled conveniently. These bulbs can be filled up with known volumes of gaseous sulphur dioxide so that the weighing when filled and when empty can be dispensed with. This however requires an accurate knowledge of the vapour densities of sulphur dioxide the determination of which is described in the next section.

VAPOUR DENSITIES OF SULPHUR DIOXIDE

Reliable values for the vapour densities of sulphur dioxide are known at only one temperature, namely, at 0°C. as determined by Baume[22] and by Jaquerod[23]. The nature of the experiments to be described in the following sections requires an accurate knowledge of the vapour densities at other temperatures and therefore measurements were carried out over the range -6° to 32°.

The method employed was similar to that described by Maass and Russell[24]. The apparatus shown in Fig.III was connected to the sulphur dioxide purification apparatus through tap A. A flask B whose volume was calibrated to an accuracy of .05 cc. up to stopcock C. was sealed on in series with a manometer M and a number of small bulbs 0,0,0 at the end of capillaries. Tap F led to a vacuum pump by means of which the whole apparatus could be exhausted to less than .01 mm. Tap E opened to the atmosphere. The procedure was then as follows. After evacuation the whole apparatus was filled with sulphur dioxide to a pressure slightly greater than atmospheric. The flask B was kept at any desired temperature being surrounded by a salt solution which was kept vigorously stirred and whose temperature was maintained constant to 1/20°C by the addition of small quantities of hot or cold water or finely crushed ice, depending on the temperature desired. The thermometer

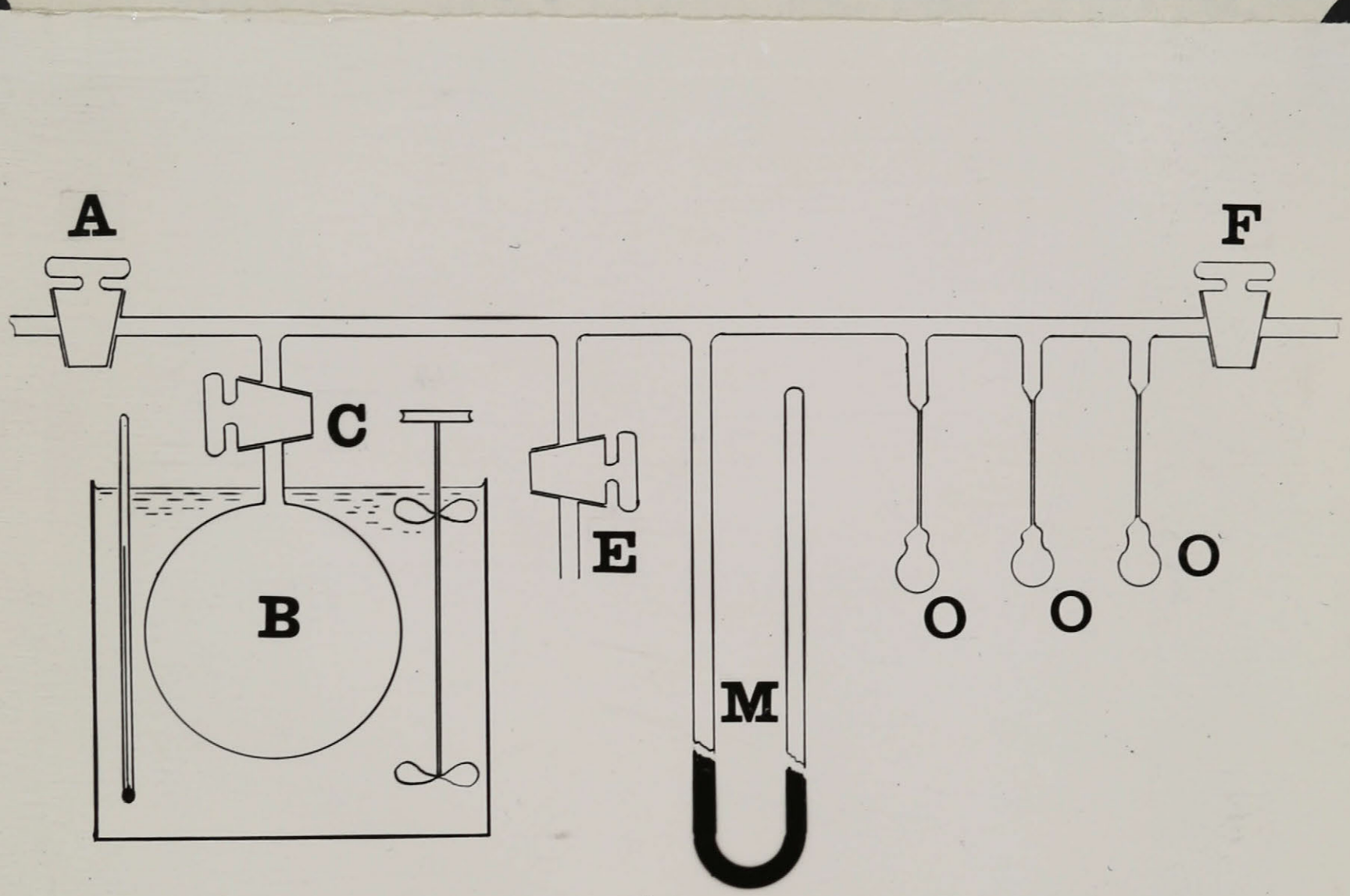


FIGURE III.

used, was one which had been calibrated by the Reichsanstalt. After temperature equilibrium had been established tap E leading to the atmosphere was opened and atmospheric pressure read at the same time on a special barometer reading to better than 1/10 mm. mercury pressure. The flask B therefore contained a known volume of sulphur dioxide at known pressure and temperature; tap C was closed and the rest of the apparatus completely evacuated. Since the vapour pressure of solid sulphur dioxide at -183° is immeasurably small all the gas contained in flask B could then be condensed in one of the bulbs O by immersing it in liquid air and opening tap O. Bulb D was then sealed off, allowed to warm to room temperature, weighed, emptied and reweighed, this time filled with air, the procedure being similar to that described in the case of the sulphur dioxide bulb mentioned in the preceding section. This method, as outlined, makes possible the weighing of a large volume of gas compressed into a small bulb of a few cc. capacity and in a way so that no dead space correction is required. Accurate results are obtained with far less trouble then the "ballon method" of Guye with all the errors inherent to the weighing of large glass surfaces.

A number of preliminary experiments all carried out at room temperature showed that results could be reproduced to better than 1/20 per cent. A sample calculation will show the factors upon which the accuracy depends. The apparent molecular weight is calculated at 76 cms. of Hg at 0° as this

gives the most convenient form in which the data can be used for calculating the mass of any volume of gas.

Barometer pressure 75.65 cms.at room temperature of 23°.

Corrected pressure to 0°C. 75.33 cms.

Temperature of gas in flask B 34.05°C. or 307.15°A.

Volume of flask B at 34.05°C. 315.65 c.c.

Weight of sulphur dioxide corrected for weighing in vacuo .8091 gms.

$$M = \frac{mRT}{pv} = \frac{.8091 \quad .08209 \quad 307.15 \quad 76}{75.33 \quad .315 \times 65} = 65.20$$

The values for M, the apparent molecular weight, are given in Table II and represented graphically in Fig.IV.

TABLE II

t° C.	p cms.	M
34.05	75.33	65.20
22.9	75.93	65.27
10.35	75.50	65.42
1.4	75.54	65.60
0.8	75.59	65.61
-6.55	75.53	65.76

From the graph the value for M at 0°C is found to be 65.62 which gives the weight of one liter under standard conditions as $\frac{65.62}{.08209} \quad \frac{}{273.1} = 2.927$ gms. which agrees exactly with the figure obtained by Baume[22]. As was mentioned above the zero degree value was the only one which had hitherto been determined accurately.

It may be of interest to show that the apparent molecular weight is the most convenient way of tabulating

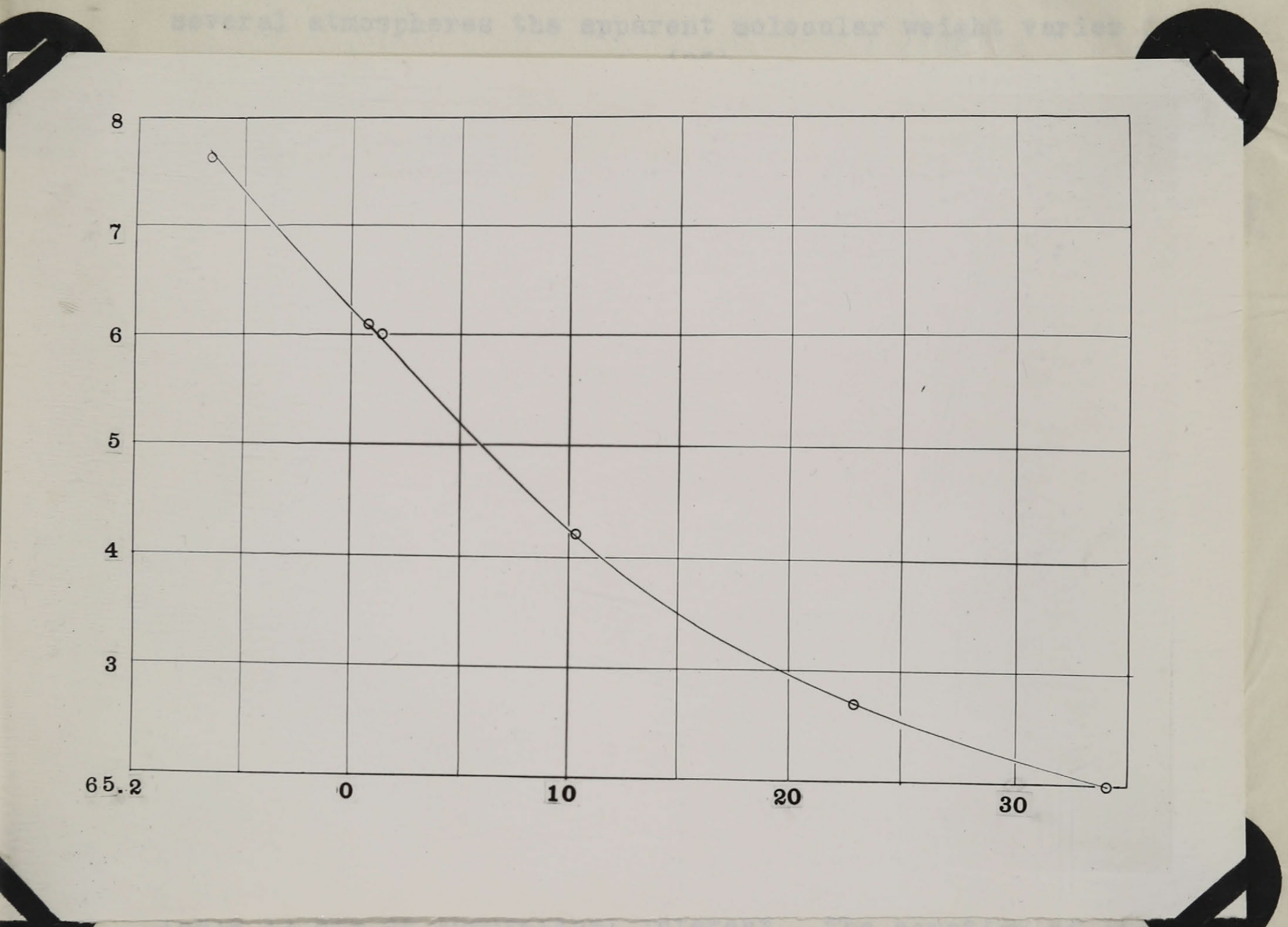


FIGURE IV.

p, V, T data for a gas from the point of view of calculating the weight of any quantity of gas taken out of a given volume. Use is made of the fact that at a definite temperature up to several atmospheres the apparent molecular weight varies in a linear way with the pressure[25] so that in the case of sulphur dioxide whose theoretical molecular weight is 64.06, the apparent molecular weight at any pressure p is $64.06+(M-64.06)\frac{p}{76}$. Hence the weight of gas contained in a volume V at pressure p, and temperature T°A is $(64.06+(M-64.06)\frac{p}{76})\frac{p'V}{76R\ T}$. It follows (without going through the algebraic steps) that the amount of sulphur dioxide taken out between pressures p_1 and p_2 is given by

$$\frac{p_1 - p_2}{76}\left\{64.06+\frac{M-64.06}{76}(p_1+p_2)\right\}\frac{V}{RT}$$

which is a more exact and general equation than that deduced by Maass and Boomer[26] and will in future find many applications. The above formula was used in all subsequent work, the values of M being read off from the graph of Fig.IV.

Apart from the practical side the values given in Table II are of theoretical interest. The equation of state which is being developed in the laboratory[27] where this work was carried out will represent the results obtained above.

VAPOUR PRESSURES OF PURE SULPHUR DIOXIDE AND OF ITS AQUEOUS SOLUTIONS.

In the following section, measurements of the vapour pressures of pure sulphur dioxide and its aqueous

solutions, are described. The tables containing the results are grouped together at the end of the description of the experimental details, and the results of other investigators are placed beside them, so that comparisons may be made more easily. Discussions of the solubilities of sulphur dioxide in water, and water in sulphur dioxide, in the two-phase system, sulphur-dioxide-water, are included.

The apparatus which was devised for the measurement of vapour pressures is shown in Fig.V. Tap A led to the sulphur dioxide purification apparatus (see Fig.I) and tap E to a vacuum pump. B was a flask separated from a small bulb L by a Morrison pressure tap C[28]. Another pressure tap D led to the bulb F containing the solution and stirred by a glass stirrer H in which an iron nail was sealed. This stirrer was operated by a solenoid I in series with an automatic current breaker[29].

The usual form of manometer M served to measure the pressures in the apparatus from A to D and a pressure manometer P on which pressures up to twenty atmospheres could be read was employed to measure the vapour pressures of the solutions. The closed arm R of manometer P instead of being evacuated was filled with air at atmospheric pressure when the mercury was level in both arms of the manometer. Before the manometer was put together the volumes of R were carefully measured for various positions of the mercury in this arm and these results plotted on a graph. A glass

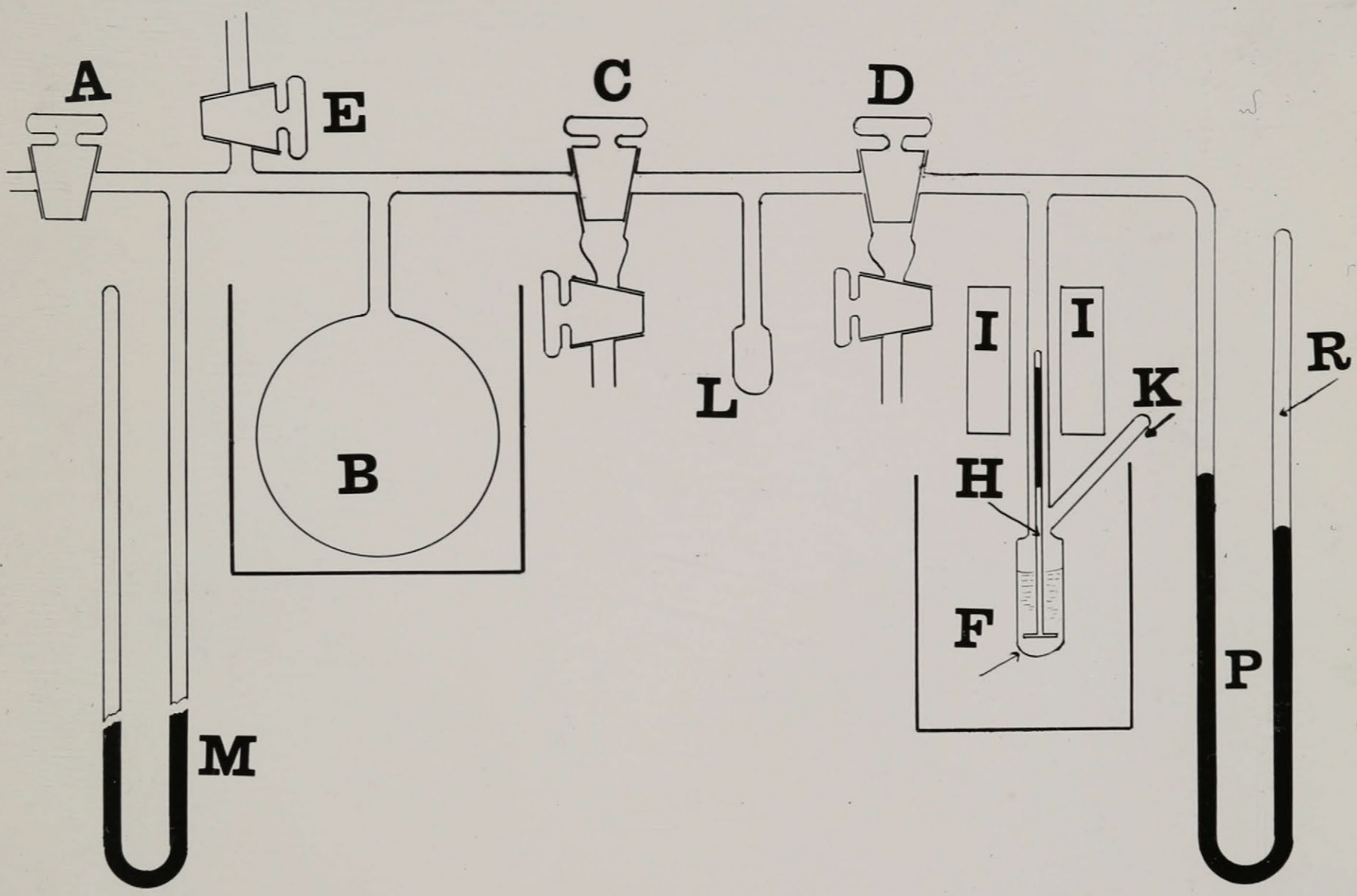


FIGURE V.

mirror scale made it possible to read the mercury levels to 1/10 mm. and a thermometer placed beside R gave the temperature T°A of the enclosed air. If l and r are the readings on the left and right arms of the manometer when the pressure was p then

$$p = r-l + \frac{kT}{V}$$ where V is the volume of the enclosed air. By applying a known pressure the constant k could be evaluated.

The procedure followed in the vapour pressure measurements was then as follows. Through side arm K a known weight of water was placed in bulb F by means of a specially constructed weight pipette. K was then sealed off and the water frozen by surrounding bulb F with liquid air. All taps except A were then opened so that the apparatus could be completely evacuated through tap E.

Tap D was then closed, and the water in F was allowed to melt. Any air occluded in the ice bubbled into the evacuated space above the water. The water was frozen again, and the space once more evacuated. The freezing of the water expelled all the air, and at the low pressure, none of this redissolved, as can be shown by repeating the process, when no occluded bubbles could be observed in the ice. This process, then, ensured that the water was quite free from dissolved air.

Taps E and D were then closed and the rest of the

apparatus filled (through A) with sulphur dioxide to a pressure p, as registered by manometer M. The volume from A to D including tubing, flask B, bulb L, etc., was accurately known having been previously determined. By means of a carbon dioxide-ether mixture a small amount of sulphur dioxide was condensed in bulb L and then tap C closed. After the sulphur dioxide had been allowed to warm up to room temperature tap D was opened so that the sulphur dioxide from bulb L distilled into the solution, the stirrer being started at this time. Tap D was then closed, Tap C opened and the pressure p_2 read on the manometer. The amount of sulphur dioxide which had passed through D could therefore be calculated with great accuracy by means of the equation developed in the preceding section and by making use of the data given there.

The sulphur dioxide which had passed through tap D may be divided into two portions, that which enters into the water and the quite appreciable amount which fills the tubing above leading to manometer P. The pressure registered was practically all due to the partial vapour pressure of the sulphur dioxide as the vapour pressure of water over the temperature range where experiments were carried out is relatively very small. The volume of bulb F and the tubing leading to the left arm of the manometer P was accurately known and hence the

amount of sulphur dioxide above the liquid in bulb F could be calculated. Hence the concentration of the solution formed in bulb F could be evaluated with great precision.

A few words are now in place with regard to the function of the magnetic stirrer. Naturally it takes time for equilibrium to be established between a liquid and a gaseous phase but it was found that without "a stirring" which both broke the surface of the liquid and circulated the gas above its surface true equilibrium was not established for several hours. As it was, even with the splendid stirring of the magnetic stirrer which moved through the whole body of the liquid and right out of the surface in each stroke, it required five minutes for complete equilibrium to be established. Once this was established the vapour pressure registered had a definite value which remained unaltered. After reading the pressure for a given temperature and then altering the pressure by changing the temperature, it was found that on returning to the original temperature the original pressure was again registered exactly. The temperatures of the solutions were governed by a well stirred bath surrounding bulb F, the temperature being read by a Reichsanstalt thermometer. In some of the solutions a trace of sugar was added for reasons which are apparent from the section on analysis of H_2SO_3. It was found that a trace of sugar did

not alter the pressures.

Now again a sample calculation will be given in order that from the quantities involved the accuracy of the results may be judged. All pressures are given in cms. Hg corrected to 0°C. The weight of water placed in bulb L as given by weight pipette and corrected for vacuo was 5.472 gms. Initial pressure p 75.41, final pressure p_2 56.65, volume of flask B, bulb L and tubing up to manometer .3891 liters. Temperature of gas 25.8°C. Apparent molecular weight of sulphur dioxide at 25.8°, 65.23.

Weight of sulphur dioxide.

$$\frac{(75.41 - 56.65)}{76}\left\{64.06 + \left(\frac{65.23 - 64.06}{76}\right)(75.41+56.65)\right\}\frac{.3891 \; .2989}{.08209}$$

$$= .2587 \text{ gms.}$$

Upward movement of manometer M during pressure change caused displacement of sulphur dioxide calculated from volume of tubing to be .0173 gms. Weight of sulphur dioxide passing tap D .276 gms. Pressure registered by manometer P was calculated to be 24.3 cms. giving .014 gms as the amount of sulphur dioxide above the solution, when the volume of the tubing and the temperature was taken into account. Hence the percent sulphur dioxide in the solution is given by

$$\frac{.262}{5.472 + .252} = 4.57\% .$$ The pressure 24.3 cms. being

registered when the solution was kept at 10°C.

In this way, the values of the vapour pressures of solutions at various concentrations and pressures, were measured. When the solution of sulphur dioxide in water, reached a certain concentration, a second liquid phase separated out, the solution of water in sulphur dioxide. The pressure registered by this two-phase system is, of course, independent of the relative amounts of water and sulphur dioxide present, and its pressures were measured over a temperature range, 10° - 27°. The vapour pressures of pure sulphur dioxide, were also determined, over the same temperature range. For this, bulb F was first carefully dried in vacuo, and then filled with pure sulphur dioxide. An attempt was made to measure vapour pressures of various percentages of water dissolved in sulphur dioxide. The pressure changes occurring in the course of this experiment were small, and the high pressure manometer was not quite sensitive enough for their accurate registration. The description and results of this particular experiment belong to the section on "Water Concentration in the two-liquid phase system, water-sulphur dioxide". Suffice it to say here that as a result of this attempt, a new manometer was designed, by means of which small changes in pressures could be more accurately detected.

A diagram of this manometer is shown in Fig.VI.

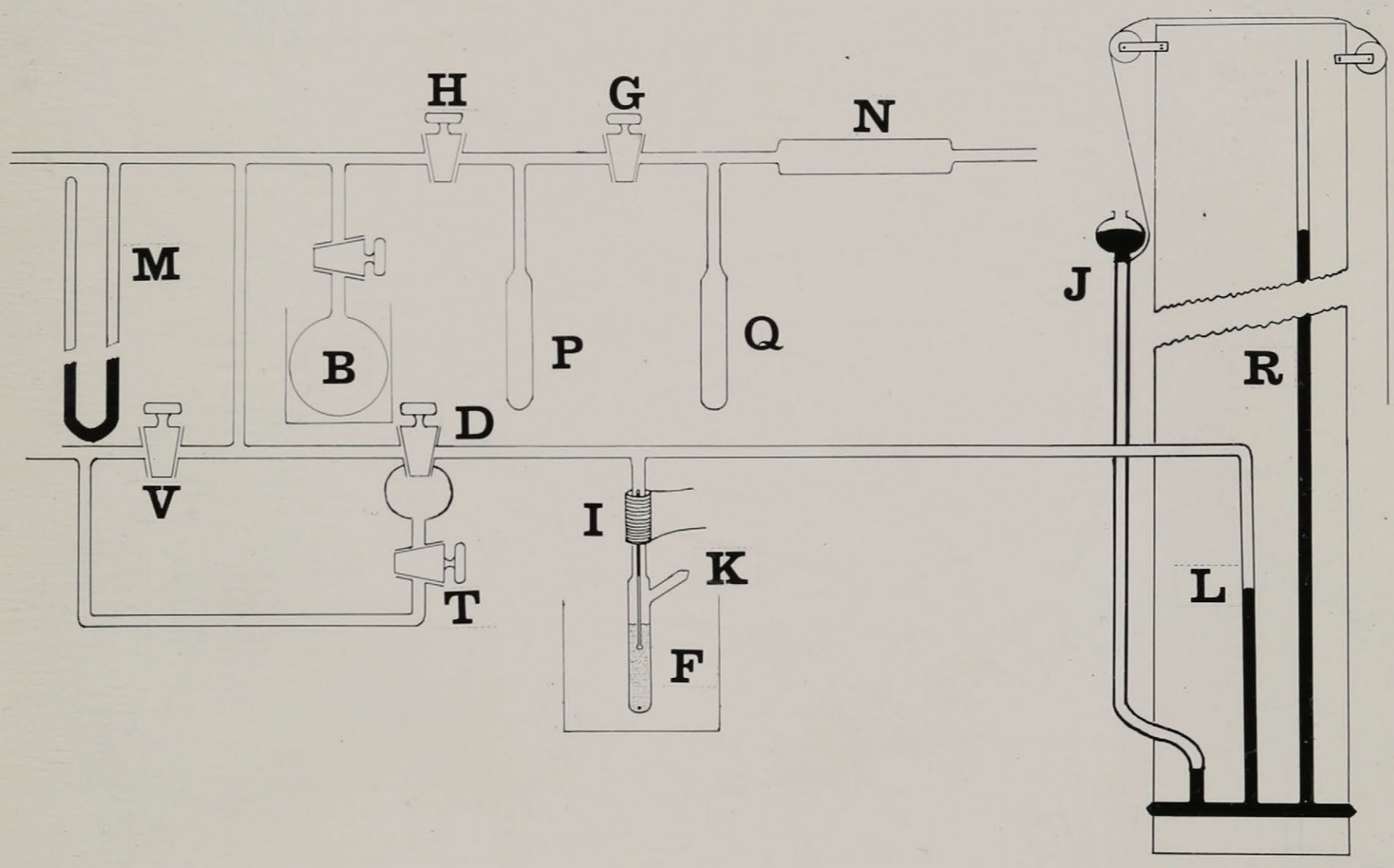


FIGURE VI.

The manometer consisted of two arms, R and L, one of which was 4 metres long, fastened to a scale, attached to a wooden framework. A ladder placed a foot away, in front of the scale, made it possible to read the position of the mercury column at any height. The long arm of the manometer was open at the top, so that atmospheric pressure had to be added to the pressure as read by the difference in level between the mercury columns in the two arms. Thermometers were placed at intervals along the mercury column, so that the temperature of the latter could be reduced to $0^{o}C$. J was a levelling bulb, connected to the bottom of the manometer (shown in Fig.VI) by a thick stout rubber tube. This levelling bulb was held by a rope, which passed over a pulley, at the top of the wooden framework. As the sulphur dioxide warmed up, the pressure in F rose and the levelling bulb was raised by means of the rope, to keep the mercury in the short arm at the same level.

When the sulphur dioxide in bulb F was at the temperature of carbon dioxide-ether, its pressure was only a few centimeters of mercury. This, combined with the fact, that the long arm was open to the atmosphere, made it necessary for the short arm to be at least 80 cms. long, to prevent the mercury from being forced into F, by atmospheric pressure. Each time that the bulb F was cooled down by carbon dioxide and ether, great care had to be taken

to lower the mercury.

The vapour pressures of pure sulphur dioxide, and of the two-phase system sulphur dioxide-water were redetermined, using this new manometer. The rest of the apparatus used,-for purification, addition of sulphur dioxide, and the stirring of the solution,-was identical with that shown in Fig.V. The same procedure was followed as was used in the previous experiments. The values found were slightly lower in both experiments than those obtained with the enclosed-air manometer previously used. These values obtained both with the old and new manometer, and are given below, and where it is possible, the values of other investigators are compared.

TABLE III.

Total Vapour Pressures of Sulphur Dioxide Solutions at Different Temperatures and Concentrations, measured on the Enclosed-air Manometer.

T. in Degrees Centigrade	Concentration in Per Cent.	Pressure in Cms. Hg0°C.
10.0°	4.57	24.3
	8.19	45.2
	11.64	67.4
	14.75	87.4
	18.91	124.5
	19.86	128.8
	23.10	154.3

Table III, Cont'd.

T. in Degrees Centigrade	Concentration in Per Cent.	Pressure in Cms. Hg0°C.
16.5°	4.48	31.0
	8.03	57.2
	11.42	84.4
	14.31	111.4
	18.57	151.9
	19.52	156.0
	22.71	188.4
22.0°		
	4.40	37.8
	7.88	69.3
	11.17	102.2
	14.04	132.6
	18.22	178.3
	19.14	186.1
	22.32	222.2
25.0°	6.9	66.2
	11.4	119.4
	16.9	184.7
	22.4	246.9
27.0°	4.32	44.8
	7.71	81.0
	10.95	118.3
	13.74	152.8
	17.85	206.9
	21.86	255.6

TABLE IV.

Vapour Pressures of Two-phase System, Sulphur Dioxide-Water, measured on the Enclosed air Manometer.

T. in Degrees Centigrade	Pressure in Cms.Hg 0°C.
10.0°	166.6
11.3°	175.2
16.5°	209.8
22.0°	254.1
22.7°	258.9
25.0°	277.4
27.0°	297.3

TABLE V.

Vapour Pressures of Pure Sulphur Dioxide, measured on the Enclosed air Manometer.

T. in Degrees Centigrade	Pressure in Cms.Hg 0°C.
1.3°	123.5
2.25°	127.6
10.0°	173.3
16.5°	218.8
22.0°	264.1
27.0°	314.2

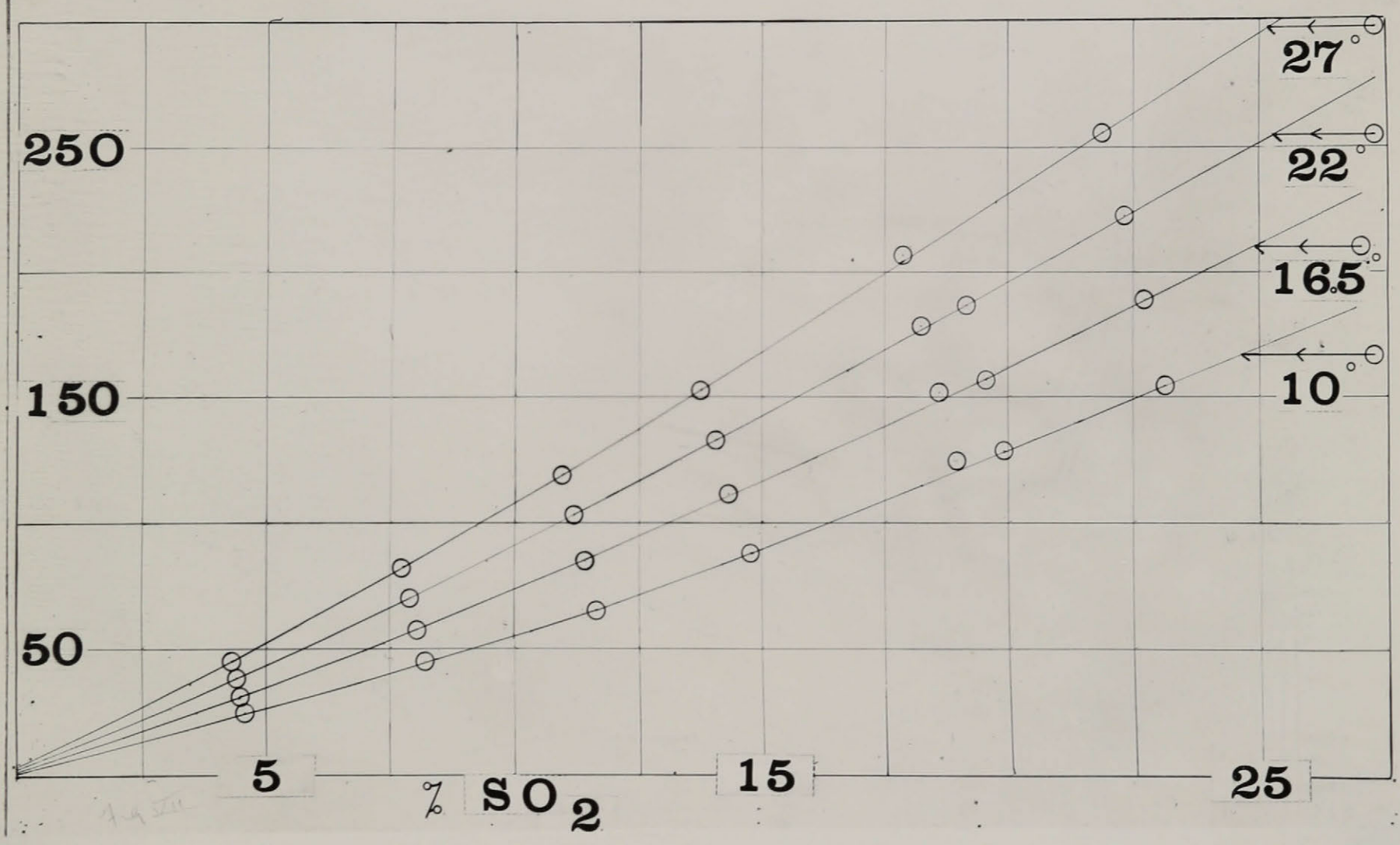


FIGURE VII.

TABLE VI.

Vapour Pressures of Two-phase System, Sulphur Dioxide-water, measured on the Open-end Manometer.

T.in Degrees Centigrade	Pressure in Cms. Hg 0°C.
11.0°	172.2
16.0°	204.4
18.0°	219.6
19.9o	234.8

TABLE VII.

Vapour Pressures of Pure Sulphur Dioxide, measured on the Open-end Manometer.

T. in degrees Centigrade	Pressure in Cms. Hg 0°C.
.2°	117.27
9.1°	168.17
15.0°	207.0
18.0°	230.5
22.6°	269.8

In Fig.VII, the values of the vapour pressures contained in Table III, are plotted against concentration, those determinations carried out at the same temperature, being connected by lines, which show that the pressures at first increase more gradually with concentration, to become finally nearly linear, at the higher concentrations.

The values in Table VI are plotted as horizontal lines, being independent of the concentration. Fig.VIII shows the relation of vapour pressure to temperature of pure sulphur dioxide (Curve I)and the two liquid-phase system (Curve II). The curves in this figure were drawn from the points marked with circles, which were taken from Tables VI and VII. The values found in Tables IV and V are marked in by crosses. It will be seen that in the case of the pure sulphur dioxide, these crosses lie on the curve. In Curve II, the crosses lie slightly above the curve. For purposes of comparison, it was found to be of great convenience to have the variation of concentration with temperature of solutions of definite percentage represented graphically. Values were taken from the curves in Fig.VII, for this purpose. They are given in table form below, and are represented graphically in Fig.IX.

The pressures are written in the vertical colums and are expressed in Cms. Hg.0°C. The headings written horizontally express the value of the percentage solutions of sulphur dioxide.

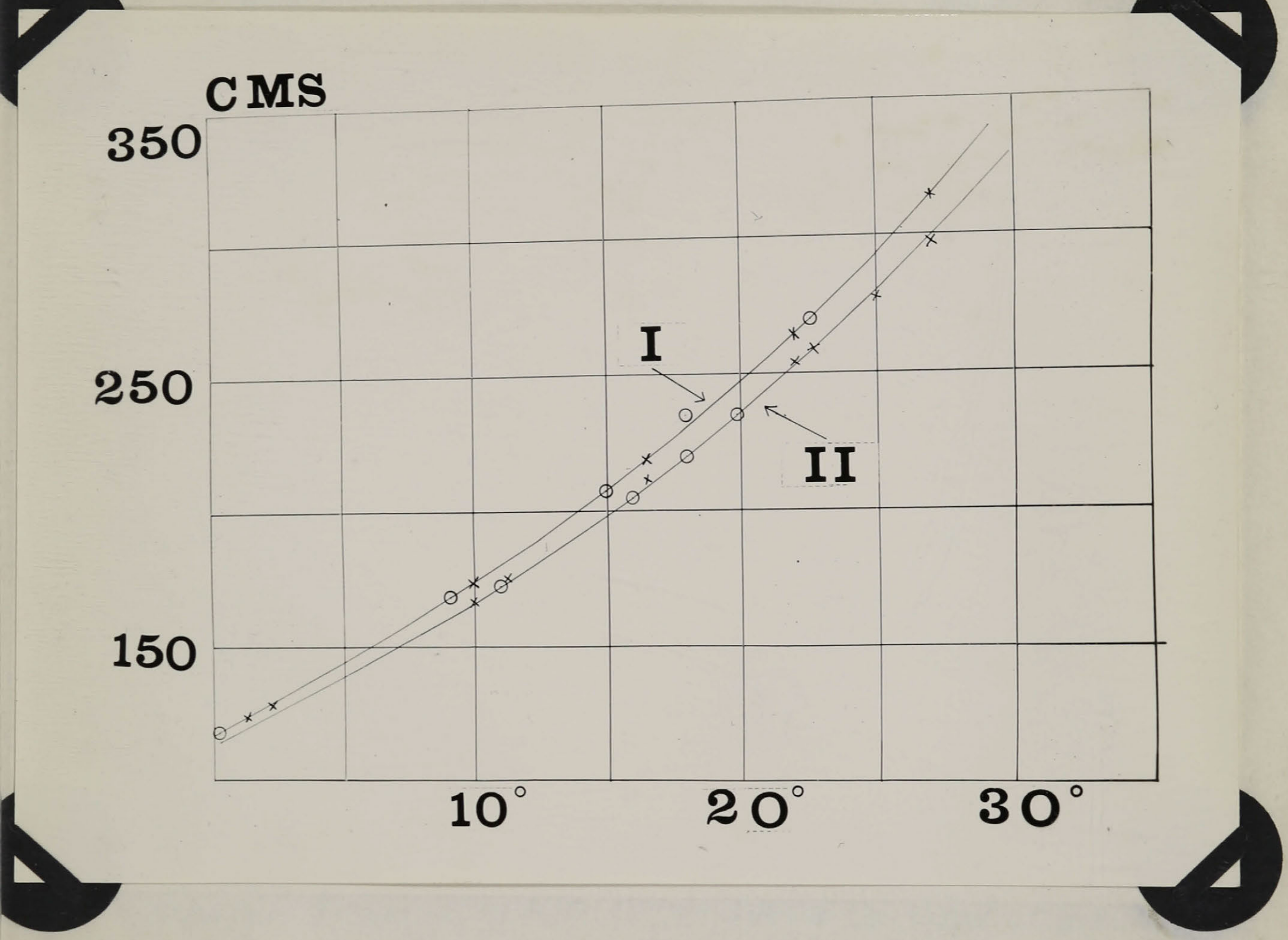


FIGURE VIII.

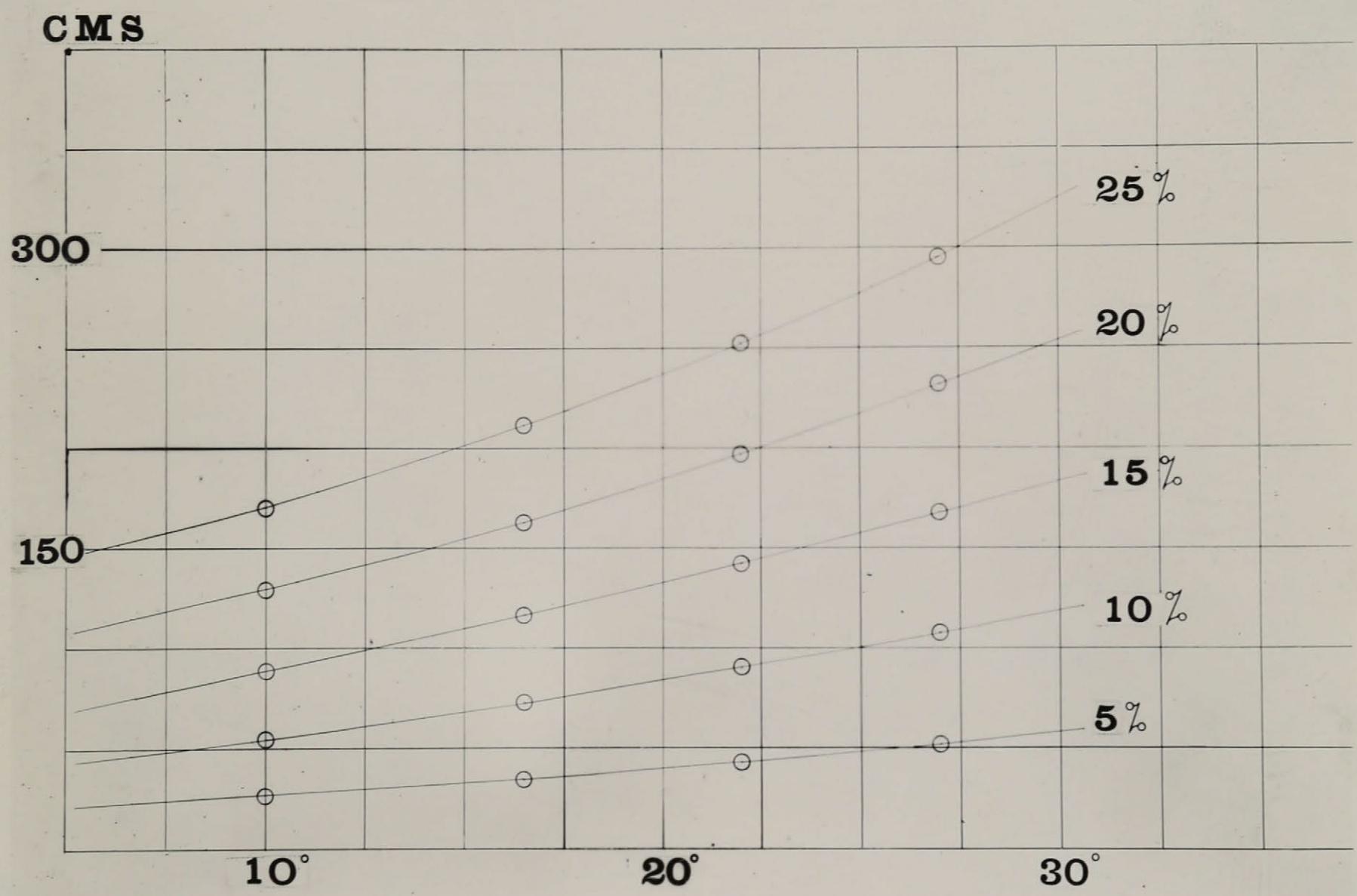


FIGURE IX.

T. in Degrees Centigrade	5%	10%	15%	20%	25%
10.0°	26.0 cm.	54.0	88.8	129.2	170
16.5°	34.1	72.8	116.3	162.4	211
22.0°	42.9	90.0	141.9	196.1	252
27.0°	51.8	107.2	167.8	231.3	295

COMPARISON OF DATA ON VAPOUR PRESSURES OF AQUEOUS SULPHUR DIOXIDE SOLUTIONS. The only investigations which have been carried out along these lines, have dealt with the determination of the solubility of sulphur dioxide in water. Schönfield[30] carried out the first investigation of this kind. Several serious sources of error, however, have been detected in his work, and his values for the solubility of the sulphur dioxide are now recognized as being too high, although they appear in the Landolt Börnstein Tables[31]. The values of Sims[32] and those of Hudson[33], as given in Hudson's paper, between 10° and 25° C. are compared below with the values found from the experiments described above. Sims and Hudson expressed their results in terms of grams of sulphur dioxide soluble in 100 grams of water at various temperatures when the partial pressure of the sulphur dioxide was 760 mm. For the sake of comparison, the solubilities were changed into percentage solutions, while the values of the writer, in which the pressure was expressed as the total pressure of the solution, were corrected

for the partial vapour pressure of the water.

Percentage solutions of sulphur dioxide in water, having a partial vapour pressure for the sulphur dioxide of 760 mm. at various temperatures.

Temp.	Sims	Hudson	Maass.
10°	13.35	13.32	13.35
15°	11.14	11.30	11.15
20°	9.42	9.623	9.45
25°	8.11	8.239	7.93

It will be seen that the values found in the present investigation agree closely with those of Sims and Hudson. Where differences occur the pressures as measured by the writer are slightly higher. This could be accounted for, if there was a trace of sulphur trioxide or air present in the sulphur dioxide used by Sims and Hudson. As Sims used the copper-sulphuric acid method for obtaining his sulphur dioxide, and as there is considerable difficulty in obtaining pure sulphur dioxide by this method, it is not impossible that there is a slight error due to this source.

Since the values of Sims are in such close agreement, the values interpolated from the writer's results are compared with values obtained by Sims over his whole pressure range. These values are given as the partial pressure of sulphur dioxide found for definite percentage

solutions at constant temperatures.

7°C.

Partial Pressure ~~in~~ of Sulphur Dioxide in mm. Hg 0°C.		Percentage Solutions of Sulphur Dioxide in Water.
Sims	Maass	
100	103	2.630
200	208	4.762
300	305	6.803
400	403	8.758
500	498	10.55
800	806	15.61
1000	1016	18.63
1300	1344	22.78

20°C.

100	105	1.575
200	205	2.913
300	314	4.215
400	422	5.572
600	602	7.665
800	804	9.910
1000	1009	12.05
1600	1600	17.90
1900	1882	20.57

In the present work, a larger range of concentration and pressure was covered, and the temperature range 10-27° more fully investigated. However, the values of Sims in the above table, like those mentioned before, agree fairly closely with those determined in this work, although the method used was entirely different.

COMPARISON OF DATA ON VAPOUR PRESSURES OF PURE SULPHUR DIOXIDE. Henning and Stock[13] measured these vapour pressures below the boiling point (-99°) with great accuracy. Using their vapour pressure equation, and extrapolating it to calculate some of the lower values obtained in this work, agreement was found to the extent which one would expect for an extrapolated equation of this kind.

The results listed in Tables V and VII had been completed when a paper by Cardoso[34] appeared, from which the following values are taken for comparison:

Vapour Pressure of Pure Sulphur Dioxide.

T. in Degrees Centigrade	Pressure in Cms. Hg 0°C.		
	Cardoso	Maass	Difference
0°	116.2	116.3	.1
8.3°	157.3	163.0	5.7
10.1°	176.3	174.2	-2.1
21.6°	256.1	261.0	4.9

Except for that at 0°, Cardoso's values differ in an irregular way from those determined by the writer. When Cardoso's interpolated values are taken, the agreement is better, as is evidenced, for example, by his value of 283.4 at 24°, as compared to 282.7 found. The conclusion is justified that over the temperature range where measurements were made, the writer's values can be considered the more accurate. It may be of interest to point out, that Regnault[35], one of the first workers in this field, obtained a value of 116.5 at 0°. His results at higher temperatures, however, differ from those of Cardoso, and the writer.

COMPARISON OF DATA ON TWO-LIQUID PHASE SYSTEM, SULPHUR DIOXIDE AND WATER. Roozeboom[36] measured a few pressures of the hydrate $SO_2.7\ H_2O$, when in equilibrium with the liquid phase. He found that the vapour pressure of this hydrate at the quadruple point 12.1° was 177.3 cms. This should correspond to the vapour pressure of the two liquid phase system at 12.1°. The curve in Fig.VIII gives a slightly higher value, 179.0 cm.s and this may be due to the fact that the quadruple point is really at a somewhat lower temperature.

The vapour pressures contained in Tables III and V can be used in connection with the determination of the

solubility of sulphur dioxide in the water phase of the two liquid phase system. This is made plain by a consideration of the curves in Fig. VII. As sulphur dioxide is added to the water the solution becomes increasingly stronger, and the pressure correspondingly higher. When the water phase reaches its saturation concentration, a second liquid phase separates out - a solution of water in sulphur dioxide. Further addition of sulphur dioxide results in a readjustment of the relative amounts of the two phases to a new equilibrium, but the percentage composition of both phases remains unaltered. That is, the percentage composition of the water phase does not change after its saturation concentration has been reached, and its pressure therefore remains constant. The constant pressure corresponds to the horizontal line on the graph. The percentage corresponding to the point where this line cuts the pressure concentration curve, gives the solubility of sulphur dioxide at that temperature. The next section contains the results obtained in this way, and deals with it more fully. The matter was mentioned here to point out the use of the vapour pressure curves in this connection.

An approximation of the water in the sulphur dioxide phase of the two phase system, can be derived by means of the vapour pressure curves shown in Fig.VIII. In the two-liquid phase system, the vapour pressure can be regarded

as due either to the water or to the sulphur dioxide phase, since these phases are in equilibrium. If the pressure is regarded as exerted by the sulphur dioxide phase, it follows from the proximity of the two curves that the vapour pressure of pure sulphur dioxide is only slightly lowered by the dissolved water, and that this can only be present in small amount in this phase. Since the solution is only a dilute one, calculations can be made to deduce the amount of water dissolved. This aspect will be treated in a separate section.

In conclusion of this section, it need only be stated that considerable new data have been added to the knowledge of pressure - concentration - temperature relations of sulphur dioxide and its aqueous solutions. These data give information with regard to the dissociation of sulphurous acid, and the existence of dissolved sulphur dioxide, which will be considered in connection with the conductivities.

SULPHUR DIOXIDE CONCENTRATION IN THE TWO LIQUID PHASE SYSTEM, SULPHUR DIOXIDE-WATER.

The concentration of the liquid water phase at the quadruple point as measured by Roozeboom is given as 31% sulphur dioxide[37]. This value is not in agreement with the results which can be deduced from the vapour pressure experiments given in the previous section. The concentrations at which the vapour pressures of the isothermal

concentration curves reach the corresponding vapour pressures of the two phase system is a very sensitive and novel method of estimating the concentrations of the aqueous liquid phases. In Table VIII these values (probably correct to 0.1%) are given.

TABLE VIII.

Temp. in degrees C.	% SO_2 in Aqueous phase
10.0°	24.60
16.5°	24.92
22.0°	25.24
27.0°	25.20

The concentrations of the aqueous phases are based on centainty. However the value at 12.1° is only 24.7% SO_2 which is quite a difference from the concentration of the liquid phase at the quadruple point as measured by Roozeboom[37]. It was therefore deemed advisable to check one of the concentrations by direct analysis.

On account of the high vapour pressure of the system, after true equilibrium has been established, it is a matter of great difficulty to remove one of the liquid phases without upsetting this equilibrium. This is a general experimental problem met with in the examination of systems of this type, for instance in the system H_2O-CO_2. The solving of this problem as described below is therefore of

some importance.

In Fig.X tap A leads to the sulphur dioxide purification apparatus, Tap E to a vacuum pump. A tube B is sealed on through a glass tube with a constriction. A side tube C on B leads through a capillary D to a smaller tube F of about two c.c. capacity the top of which ends in a closed capillary H. Ten c.c. of water had been placed in B before it was sealed on. This water was frozen and the apparatus evacuated through E. Approximately ten gms. of sulphur dioxide were then condensed on top of the ice in B and B sealed off at the constriction. It was then placed in a water bath and allowed to warm up to the desired temperature. The liquid layers which formed in the bottom of B were well shaken up, care being taken that no liquid entered C. The tube was then allowed to stand at constant temperature until the two layers were quite separate, and then the tube carefully tilted until some of the liquid in the upper layer ran into C filling it with some 4 c.c. of liquid which was held in place by the sulphur dioxide vapour in F. The tube B was then tilted back into a position as indicated in the second part of the diagram (Fig.X). On gradually immersing F in a cooling bath the contraction of the sulphur dioxide vapour in E caused some of the liquid in C to flow through the capillary. Before all the liquid from C had entered F,

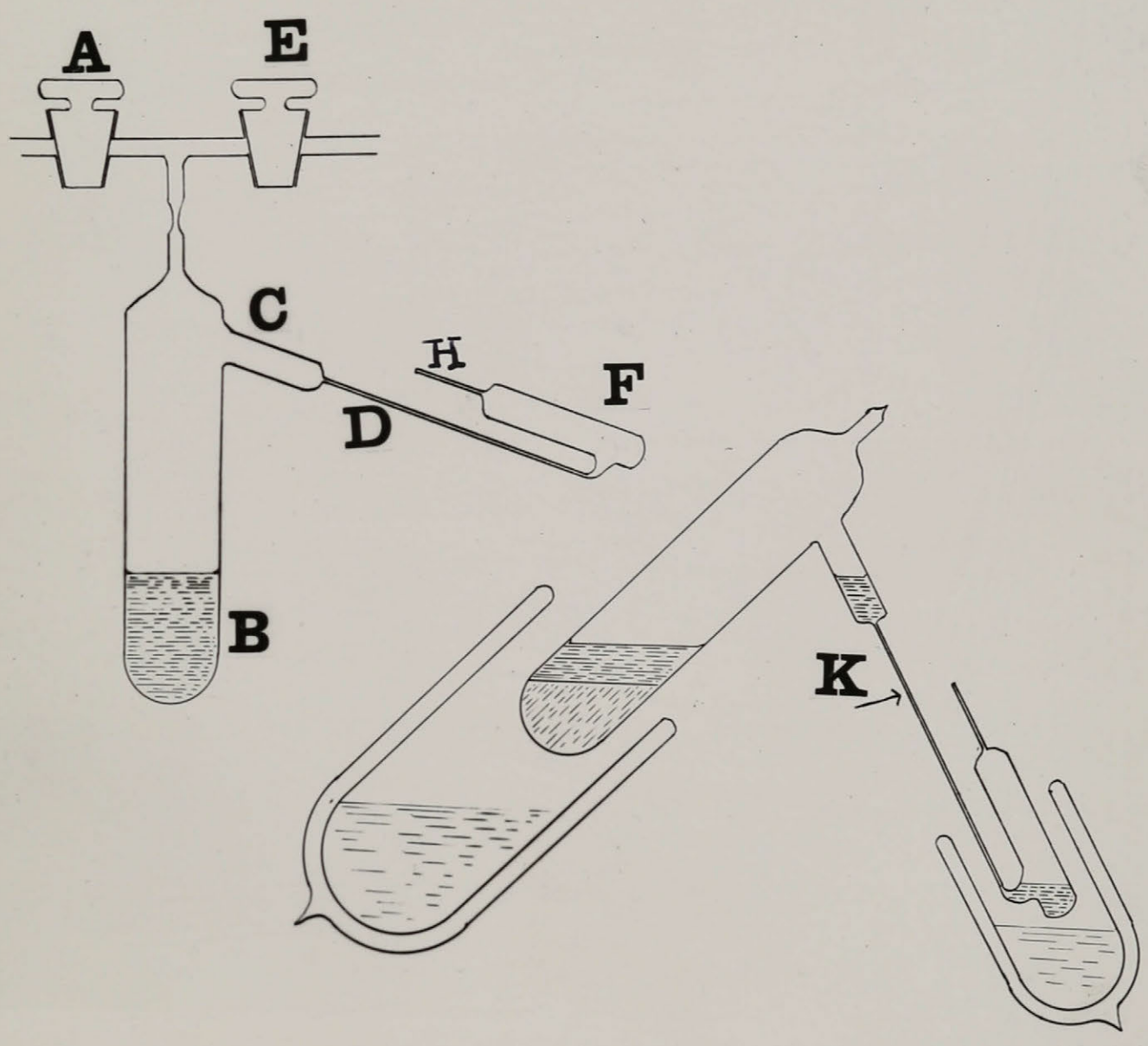


FIGURE X.

F was plunged quickly into a carbon dioxide ether mixture so that the liquid flowing through the capillary was frozen. That was the essential feature of the whole method because the liquid in F was trapped and represented the true equilibrium condition corresponding to the temperature of the water bath. The bottom of tube B was then immersed in a second carbon dioxide-ether bath the tube F being still kept in the first one. All the liquid remaining in tube C above the frozen part in the capillary distilled back into C. The capillary was then sealed off at K. Tube F was allowed to warm up, weighed, cooled again in a carbon dioxide-ether mixture and the capillary tube was broken off. The ends of the capillary was then placed beneath the surface of a NaOH sugar solution and the contents of F allowed to warm up and dissolve. The glass was then washed, dried and weighed. The analysis of the solution was then carried out as described in a former section. A sample calculation is given below.

Temperature of water bath 20^{o}

Weight of solution trapped in F 1.525 gms.

Solution in NaOH made up to 250 c.c.

1 c.c. of iodine equivalent to .002717 gms. SO_2

Oxidised 1.72 c.c. of the solution in NaOH

Total SO_2 was therefore .2951 gms.

SO_2 vapour trapped in F .0121 gms.

%SO_2 in aqueous phase 25.10%

Three other determinations carried out at the same temperature gave practically identical values, thus confirming the results given in Table VIII.

It is seen that saturation solubility of sulphur dioxide does not vary appreciably with the temperature. The critical temperature of sulphur dioxide is in the neighbourhood of 155°C., and it will be interesting to determine the rest of the solubility curve. There is a slight increase in solubility with temperature, about 1% per 30°, as evidenced by the results in Table VIII. Consequently there must be a rapid increase in solubility at some high temperature if complete mutual solubility takes place before the critical temperature is reached, or, the solubility of water in sulphur dioxide must increase very rapidly. This possibility will be treated in the next section.

WATER CONCENTRATION IN THE TWO-LIQUID-PHASE SYSTEM.

In the section on vapour pressures, the determination of the solubility of water in the sulphur dioxide phase, by means of vapour pressure measurements, was discussed. From the vapour pressures represented in Fig.VIII, the values of the percentage water in the sulphur dioxide phase, can be calculated by means of Raoult's Law(38).

$$\frac{n}{N} = \ln \frac{p}{p^1}$$

This can be written:

$$\frac{m}{M_{H_2O}} \quad \frac{M_{SO_2}}{W} = \ln \frac{p}{p^1}$$

Where m and W are the weights of the water and sulphur dioxide respectively.

Hence,

$$\% \ H_2O = \frac{m}{W+m} = \frac{\frac{18}{64} \ 2.3 \ \lg \frac{p}{p^1}}{1 + \frac{18}{64} \ 2.3 \ \lg \frac{p}{p^1}}$$

This equation is based on the assumption that water is not associated, when dissolved in liquid sulphur dioxide, and the percentages calculated in this way must, therefore, represent the minimum possible water concentration.

TABLE IX.

Percentage water in sulphur dioxide phase of two-liquid phase system, calculated from vapour pressure measurements taken from Fig.VIII.

Temperature in degrees centigrade.	Vapour Pressure of Pure Sulphur Dioxide in Cms.Hg 0°C.	Vapour Pressure of two-phase system in Cms Hg 0°C.	Percentage of water in solution.
5.0°	143.4	138.2	1.024
10.0°	173.9	165.7	1.333
18.0°	230.5	219.6	1.340
22.0°	264.3	251.8	1.340
25.0°	292.2	277.5	1.422
27.0°	314.2	297.2	1.529

Since the above values had been obtained only by calculation, some direct experimental method of determining them was sought. The method employed was based on the measurement of the vapour pressures of solutions of water in sulphur dioxide. Due to the slight solubility of water in liquid sulphur dioxide, the difficulty in this procedure lay in making up solutions of known concentrations. The following device was finally used. A piece of ordinary glass tubing was drawn out into a capillary, at the end of which, a small thin walled bulb of about 3 mm. diameter, was blown. The bulb and tubing were then accurately weighed. Water was introduced into the bulb, through the capillary by alternately heating and cooling the bulb, and thus driving out the air in it. In this way enough water to fill the bulb (about 50 milligrams) entered, and the capillary was then sealed off as close above the surface of water as possible. The piece of tubing was carefully dried, and weighed again with the filled bulb, from which the weight of water was definitely known. The little bulb was placed in tube F (see Fig.VI) through side arm K. The magnetic stirrer was kept down, while the small bulb slipped past it, down to the bottom of F. Side arm K was sealed off, tube F was evacuated, and surrounded with carbon dioxide-ether mixture. When the water was frozen, the bulb was broken by means of the magnetic stirrer,

which acted as a hammer. The freezing of the water was important, as was found by experience. If the water bulb is broken, in the evacuated space, the water will spatter all over the tube, and evaporate into the space. After the bulb was broken, measured quantities of sulphur dioxide were added to the tube, and the resulting pressure measured at 18°.

From the values contained in Table IX, it was known that the saturation concentration of the water in sulphur dioxide would be small, in the neighbourhood of 1 or 2%. The percentage solution calculated after the first addition of sulphur dioxide was about 5% H_2O. This, of course, did not exist, and the amount of water left over, above the amount required to form a saturated solution of water in the sulphur dioxide, separated out to form a small amount of second phase, a solution of sulphur dioxide in water. The pressure registered at this point, then, was that due to the two liquid phase system at that temperature, and agreed with the value found for this in Fig.VIII.

As further quantities of sulphur dioxide are added, the pressure remains constant, until a point is finally reached at which the amount of sulphur dioxide present is just sufficient to give the saturated solution of water. The second phase disappears, and the pressure

registered is due only to this saturated solution. Further addition of more sulphur dioxide raises the pressure, until it nearly reaches the pressure of pure sulphur dioxide. This value is never quite reached, however, as, no matter how much sulphur dioxide is present, the original amount of water remains. The values obtained are given in Table X.

TABLE X.

Vapour pressures for two-phase system, water-sulphur dioxide.

Temperature C°.	% H_2O in SO_2	Pressure in Cms. Hg 0°C.
18°	4.23	219.6
	2.16	219.7
	1.096	221.7
	.735	224.9
	.494	226.8
	(0%)	(230.5)

These results are shown graphically in Fig.XI. At 18°, the vapour pressure of pure sulphur dioxide was found to be 230.5 cms. and that of the two-liquid phase system was found to be 219.6 (see Fig.VIII). It will be seen from the figure that the three last valuesare in a straight line, which when produced in one direction, meets the zero percentage of water, ie., pure sulphur dioxide,

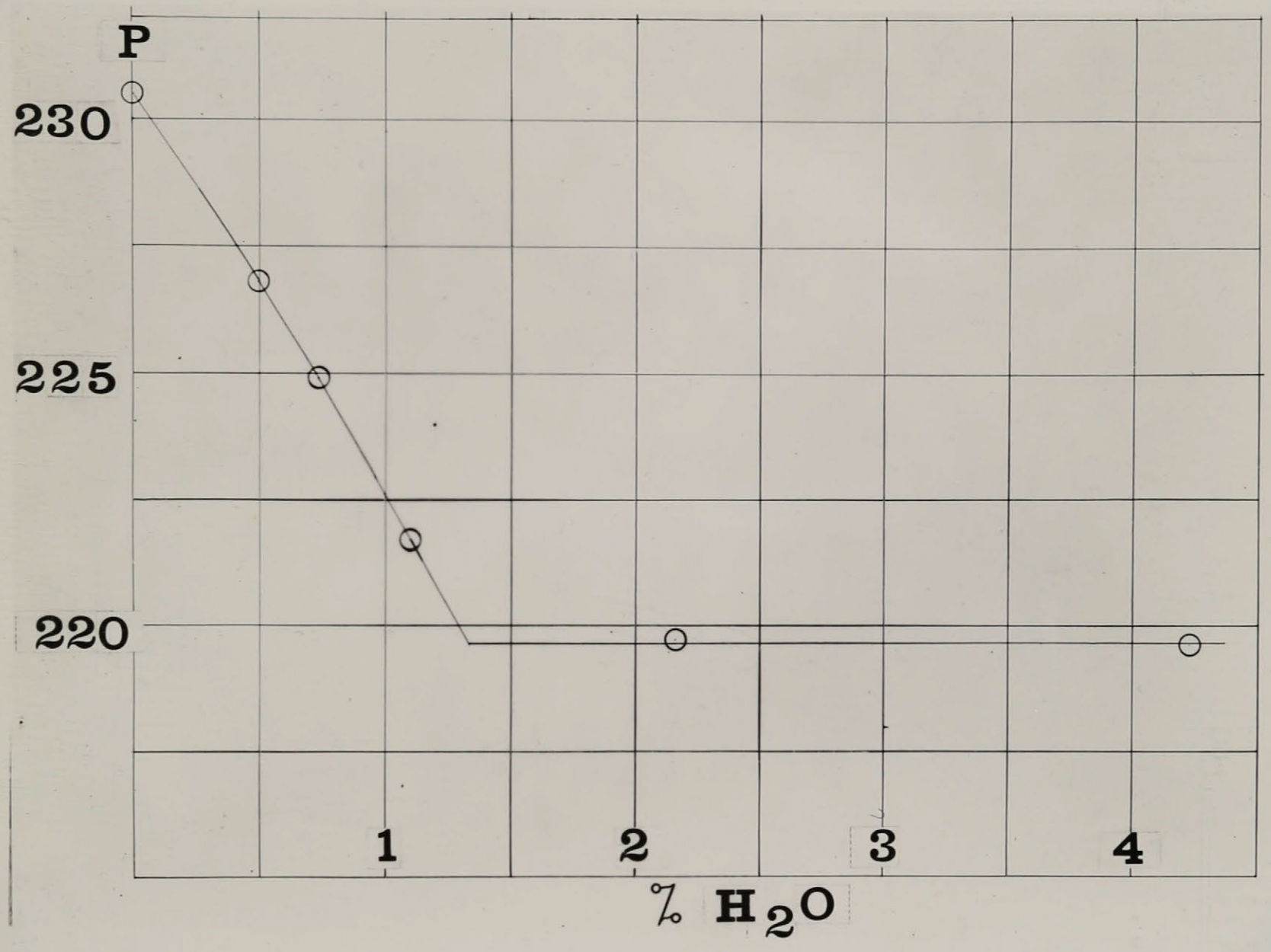


FIGURE XI.

at 230.5 cms, and cuts the 219.6 cm. iso bar at 1.331% water. 1.33% must therefore be the percentage of water dissolved in the liquid sulphur dioxide, that is, the saturated solution.

Raoult's equation as given is based on the assumption of unassociated molecules, and this is justified by the experimental results. The agreement of 1.34%, calculated from the equation, with 1.33% found experimentally, is better than the accuracy of the measurements.

This is confirmed further, by measurements made over a temperature range of the pressures of a 49% H_2O solution. Table XI contains the results obtained.

TABLE XI.

Temperature C°.	Vapour Pressure in Cms. Hg 0°C.
3.0°	130.2
7.0°	151.5
11.0°	175.9
18.0°	226.9
20.0°	243.7

In the measurements just given, the concentration was so low that the pressure differences were small, and the error correspondingly large. Using the pressures in Table XI in Raoult's equation, to determine

the percentage, a mean value of .51% was given, which agrees remarkably well with the value .49%.

Water is a substance which has a great tendency to associate. It does not do so in substances of similar nature.In these cases, however, there is far greater solubility than is shown by water in sulphur dioxide. Hence it is more probable that the water in the solution is combined with the sulphur dioxide to form sulphurous acid. The results obtained by Raoult's law, would be the same, within experimental accuracy, whether the water is present as unassociated water or as sulphurous acid. These are the only two possibilities of the condition of the water, and from what has been said above, the existence of the water as sulphurous acid, is the more probable.

The increase in solubility of the water in sulphur dioxide, with temperature is only of the order of 1% in 40°. This, taken in conjunction with what was said in the previous section, indicates that complete mutual solubility will probably not take place until a temperature is reached not far removed from the critical temperature of sulphur dioxide.

CONDUCTIVITIES OF AQUEOUS SOLUTIONS OF SULPHUR DIOXIDE

The two outstanding difficulties which have been met in dealing with solutions of sulphur dioxide, are: the ease with which these solutions oxidize and the tendency of the sulphur dioxide to volatilize. When the experiments on the conductivities were started, it was believed that the volatility factor would have little effect in the case of dilute solutions. As a result, ordinary Washburn conductivity cells of the closed type were used for dilute solutions. The cell was simply filled with a solution of appreximately the desired strength, the conductivity was measured and then the contents of the cell immediately analysed. It is not necessary to describe the details of the conductivity measurements since the usual procedure was followed and all the precautions necessary for accurate work were taken. A thermostat regulated to stay constant at 25.0 served as bath.

The effect of any oxidation of the sulphur dioxide, would show itself in changes of the conductivity with time. Such changes were found, and the effect of bubbling air, passage of current, temperature, etc. were examined. At 0°C. the changes were found to be very much less than at 25°C. The alternating current used for the measurements had a negligible effect but bubbling air had a very large effect on the conductivity. Hence the solutions were made up at 0°, measurements were made quickly and access of air was excluded. Sometimes as a check, the analysis was first made on a portion of the solution, then conductivity measurements extended over some time and by

extrapolation the conductivity calculated corresponding to the time the analysis had been made.

The values for the conductivities obtained as above, are now known to be too high. Sulphur dioxide is so volatile, that there was probably loss from even very dilute solutions, especially during the transference from the cell into the flask where it was analysed. In addition, there was a probable error due to the analysis itself, as these measurements were made before the improved method of analysis (see section on "Analysis of Sulphur Dioxide Solutions) was worked out. The values are not recorded but in order to give some idea of the magnitude of the error involved, the value of .001 for specific conductivity at 25° is given, as compared to a value .0007, as found by later work.

The next step in the measurements, was the construction of a special apparatus, by means of which the sulphur dioxide could be added to the water in known volumes, thus avoiding the necessity of analysis. The electrolyte cell was constructed so as to be able to withstand 5 atmospheres of pressure and also to allow the solution to be well mixed.

The conductivity cell D had the form shown in Fig.XII. Two platinum wires, I,I, with electrodes at the end were sealed into two tubes connected at bottom by a glass tube of smaller diameter and connected at the top by a glass tube with a T leading to the rest of the apparatus. An amount of water sufficient to cover the electrodes in D was first of all placed in a tube F. The water was added from a weight pipette before F

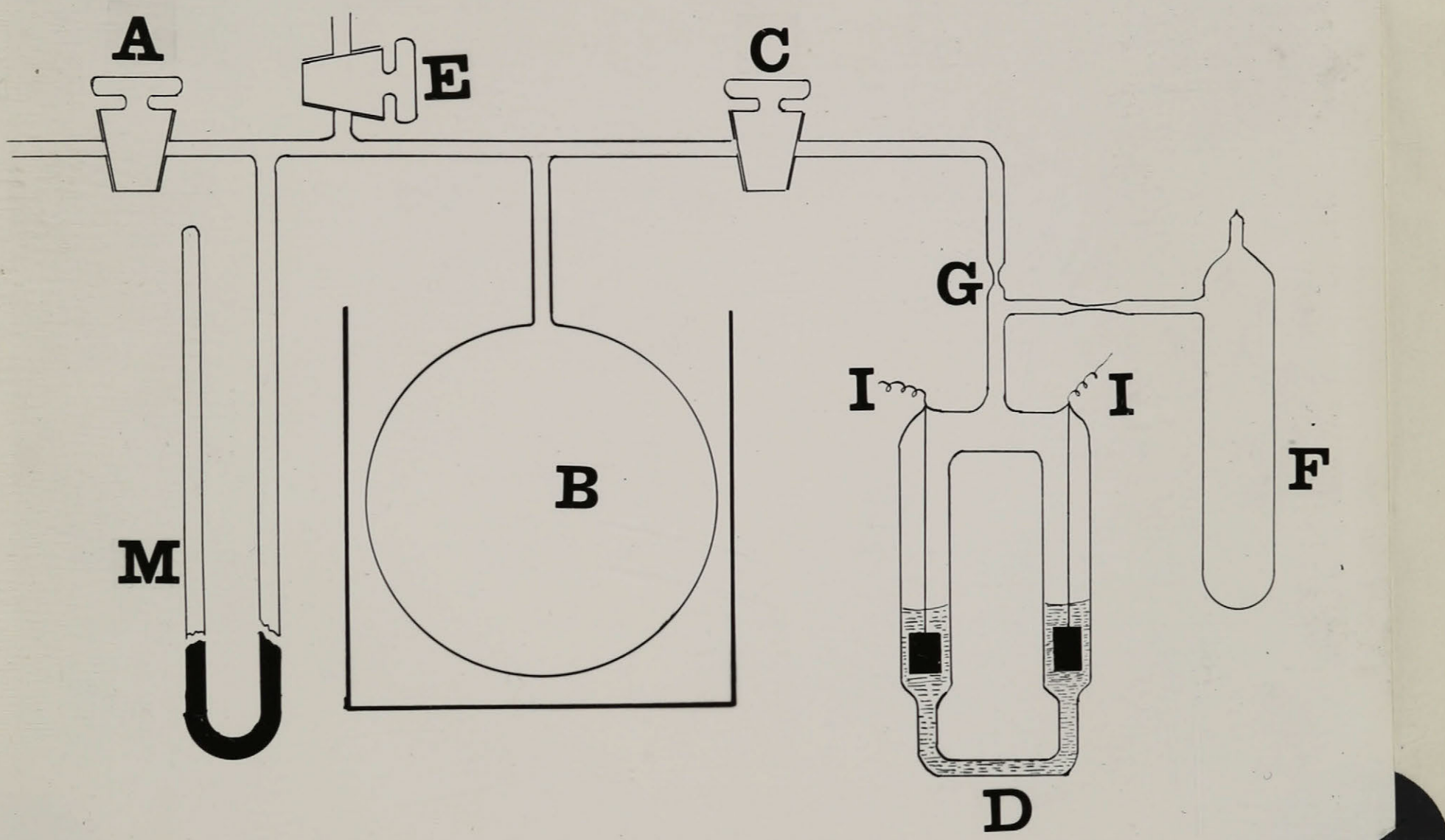


FIGURE XII.

was sealed off. The water was frozen by means of a carbon dioxide ether mixture and then the whole apparatus thoroughly evacuated. The water was then distilled into D, being frozen there out of the vapour. If directly placed in the cell and then frozen it was feared that the electrodes might be permanently displaced altering the cell constant. Tube F was then sealed off. Tap A led to the sulphur dioxide purification apparatus. The portion of the apparatus between taps A and C is the same as the corresponding portion in Fig.V. and served to make possible the addition of a known amount of sulphur dioxide to the cell. The cell was then sealed off and allowed to warm up. The contents could be thoroughly stirred by rotating the cell. The volume of the cell had been measured, the volume of the water was known and therefore the volume of gas above the solution could be estimated and thus the concentration of sulphur dioxide was accurately calculated from the vapour density and vapour pressure data. The conductivity of the solution was then determined. In every instance the cell was opened immediately after the measurements had been made and the cell constant was redetermined.

This cell was used only for solutions of high concentration, as the values obtained for lower concentrations, as obtained by means of the Washburn cell, were, at that time, considered reliable. Table XII contains the conductivity data obtained at 25°, by means of the pressure cell just described.

TABLE XII

Percentage Sulphur Dioxide	Specific Conductivity
5.44	.0543
8.69	.0641
13.00	.0735
19.29	.0781
20.10	.0831
20.95	.0851
22.24	.0794

The above values are somewhat erratic, as shown for instance, by the decrease in conductivity of the last solution. These irregularities could be partly accounted for by variation in the cell constant. Nor is this an unlikely source of error. After the conductivity was measured, the cell was cut off, and the cell constant immediately redetermined, as has been described already. Before the cell was cut off, however, the solution had to be frozen in order to reduce its vapour pressure, and it is possible that the cell constant was slightly changed during the freezing and melting of the solution by the displacement of the electrodes. Another factor which was considered, was that of obtaining true equilibrium between the gaseous sulphur dioxide and the solution. In the cell described, the volume occupied by the gaseous phase was relatively large and thorough stirring was difficult. The rotation of the cell served as stirring. This was not

satisfactory, as the cell was placed in a thermostat after rotation, and time had to be allowed for it to come to the temperature of the bath. Thus, true equilibrium was not assured, by the time the conductivity was measured.

It was also realized that the whole series of values might be too high, due to traces of air contained in the water used, since at that time, the water was only frozen once.

A trace of air, if present, has a marked effect on the conductivity by causing oxidation of sulphurous acid to sulphuric acid.

With these possible sources of error in mind, a new apparatus was devised, in which these were eliminated. A decided advantage of the new method was that a series of measurements at various concentrations could be made without opening the cell.

Sulphur-dioxide-water is not the only system in which the conductivities at high concentrations are difficult to measure. Other systems, such as carbon dioxide-water, hydrochloric acid-water, etc., can be thoroughly examined by means of the apparatus to be described.

Fig.XIIIrepresents diagramatically, the apparatus, in which the various parts, for purposes of convenience, are not drawn to scale. Bulbs A and B serve in the process of the purification of the volatile component. C is a pentoxide tube used in the process. This purification system is connected through tap O to the main apparatus, in which tap E leads to a mercury vacuum pump. This pump can therefore

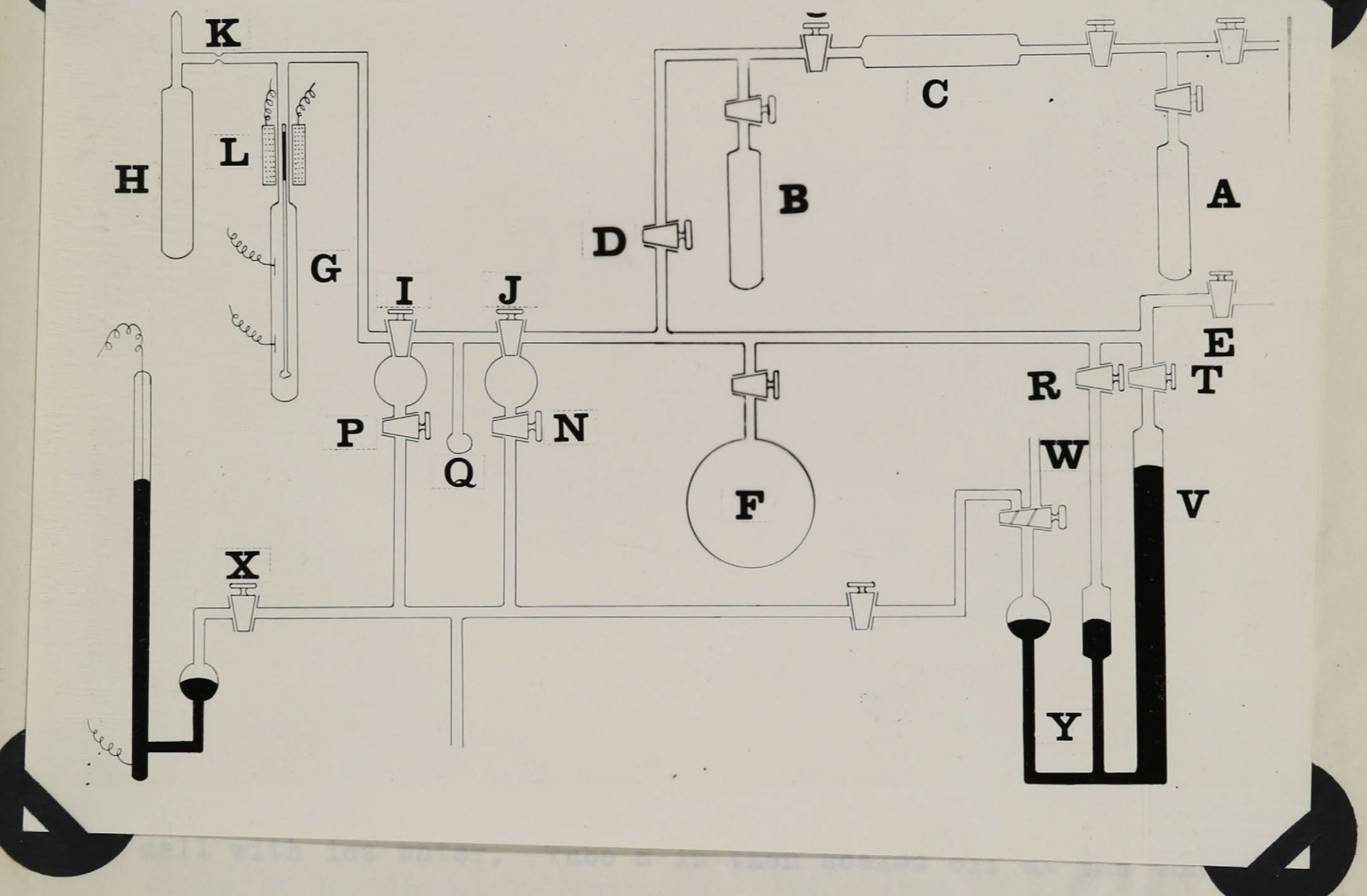
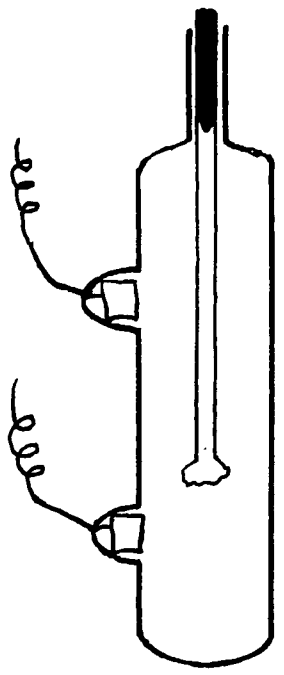


FIGURE XIII.

be used in the process of purification. A flask F , kept in a constant temperature bath, serves in the addition of known quantities of the volatile component to the electrolytic cell, G . The water was transferred into the cell from bulb H. The requisite amount of water to fill the cell, and cover the upper electrode is dropped into bulb H, from a weight pipette, which gives the weight of the water accurately. The opening to H is then glass sealed off, and the water within frozen, first by a salt-ice mixture, and finally by CO_2 - ether mixture at -78°. The bulb and cell are then evacuated by opening taps I and J and E to the mercury pump. I is then closed, and the ice in H is allowed to melt. A small amount of dissolved air, occluded during the freezing of the ice (sufficient to hinder the establishment of true equilibrium between sulphur dioxide and water, later on), is freed during the melting process. The water is therefore frozen again, and the space above once more evacuated. The ice is again allowed to melt, and the water condensed in the cell by heating up tube H and surrounding the cell with ice water. Tube H is then sealed off at the constriction marked K. The cell has two platinum electrodes sealed in its side, with room enough below the lower for the presence of a small amount of a second liquid phase, and room enough above the upper electrode for the increase in volume caused by the addition of sulphur dioxide.

The actual position of the electrodes in the cell is not quite correctly represented in the diagram. Two glass

pockets were blown in the side of the cell, into which the electrodes were drawn, as shown in the accompanying sketch, thus preventing the knocking of the electrodes by the stirrer.



The electrodes were pulled tight against the glass, to prevent changes in the cell constant due to their movement, and the wires were glass-sealed through the end of the glass pockets.

A glass stirrer with a nail sealed in the upper end can be moved up and down by means of the solenoid L, thus bringing about thorough stirring. During the actual conductivity determination, the stirrer is drawn above the liquid so that the cell constant is not interfered with. The addition of the sulphur dioxide is carried out without the necessity of cooling the water in the cell more than a few degrees below room temperature. I and J are pressure taps. The ends of the glass stoppers in these taps are connected, through taps P and N, to a suction pump running continuously. Between the pressure taps, there is a small glass tube Q, in which the sulphur dioxide to be added, is condensed. The volume of this tube, and the glass tubing between taps I, D, R, T and E, is very small, but is accurately known, and is added to the volume of the large flask F, for purposes of calculation. All this tubing and flask F are filled with sulphur dioxide, whose pressure is accurately known by means of the manometer to be described later on. Some of this is condensed in Q. Tap J is closed, the condensed sulphur dioxide is allowed to warm up to room

temperature, and tap I is opened. The sulphur dioxide distils over into the cell which is a few degrees below room temperature. Tap I is then closed. It is true that some sulphur dioxide at a high pressure remains in Q, but on opening tap J this runs back into the tubing and flask F. The amount of sulphur dioxide which has passed from flask F and the small connecting tubing, into the cell, is then given with an accuracy depending on the accuracy with which the change in pressure can be measured. A special manometer was constructed which allows the reading of pressures of one atmosphere and less with an accuracy of one tenth of a millimetre. This manometer is represented in the lower right-hand side of the diagram. The large arm V, and the small arm W, are connected at the bottom to a mercury reservoir, which in turn is closed by a two-way tap, one tube leading to the suction system, the other tube open to the air. At the start, taps R, T, are opened to the mercury pump through tap E, and the tubing is completely evacuated. Tap J is then permanently closed. Tap R is opened when the pressure in flask F and connecting tubing is to be measured. The mercury level is brought to the wide portion of manometer arm W, by applying suction or pressure to reservoir,Y. A calibrated glass scale was used to read the mercury levels. Arm V, and that part of arm W, at which the level was read were 2 cm. wide, thus making possible very accurate pressure reading. The apparent excessive length of arms V and W, below the level of reservoir Y, is necessary to

take care of sudden changes in pressure during the adjustment of the manometer during a pressure reading.

The lower left-hand portion of the diagram is connected with the electric apparatus used in the conductivity determination, and is shown here because it was connected through tap X to the suction system which was used at the same time for pressure taps P and N, and for the manometer regulation.

Since the apparatus used in the measurement of the resistance of the electrolytic cell was somewhat different from the ordinary bridge-wire method, it is worth devoting a little space to a description of it.

Figure XIV. shows diagramatically the electric lay-out used in the measurement of the cell resistance. A and B are the ratio arms, 100 ohms each, of the Wheatstone Bridge. D + F is the variable resistance which is then balanced against the cell resistance E. The part D consists of a resistance box with decade dials of thousands hundreds tens and units of ohms. The part F is the special resistance which was represented in Fig.XIII., since it was regulated by varying pressures. F consists of a platinum wire, sealed in an evacuated tube, the lower portion of which is connected to a mercury reservoir. By turning tap X, the mercury column can be made to rise or fall in the tube. Since the resistance of the wide mercury column is exceedingly small compared to the resistance of the platinum wire, rise of the mercury column decreases the resistance, lowering of the mercury column - by suction - increases the resistance. This resistance was

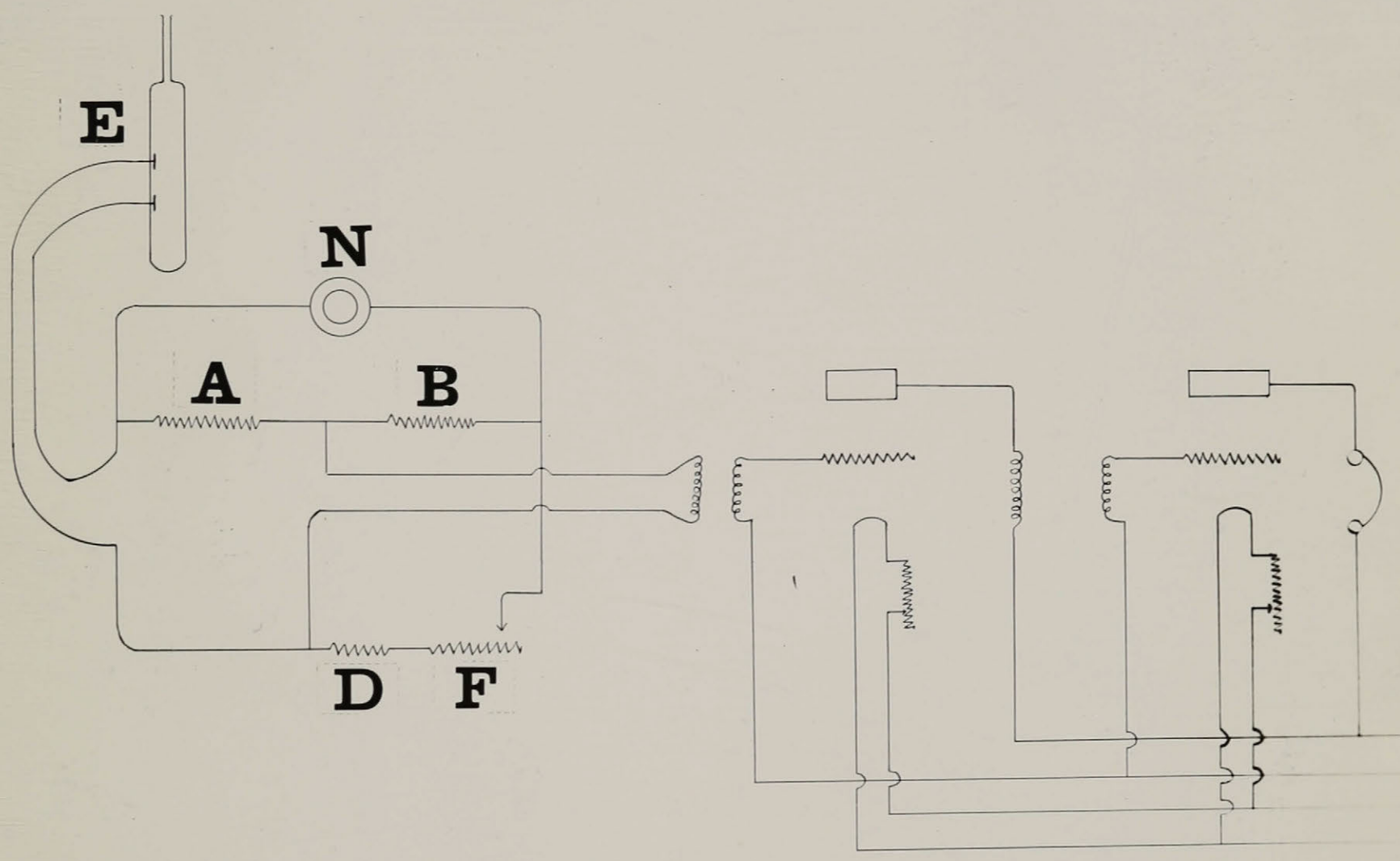


FIGURE XIV.

calibrated for each portion of the mercury column in the tube, and at its lowest level, corresponded to about 1.5 ohms. Thus F makes possible the measurement of fractions of an ohm. The source of current used is a Vreeland Oscillator (N in Fig.XIV) which gives a perfect sine curve. Instead of attaching a telephone directly, a two-stage amplifier is used. The connections are shown in Fig.XIV., the same diagramatic representation used in radio hook-ups being used. The electrodes of the cell were well electro-plated with platinum black so that a good minimum could be established, the amplifier making it possible to discern it easily, in spite of the noise of the suction pumps. The cell constant was obtained by measuring the conductivity of a standard KCl solution, under identical conditions as those under which the sulphur dioxide solutions were measured. This eliminates all need for correcting for capacity, since the resistances in absolute value were all of the same order and the accuracy desired was of the order of .5%. Perhaps the simplest way of indicating the manner in which the percentages of the liquid phase in the cell were obtained, is to give a sample calculation below.

Weight of water in cell	4.906 gms.
Initial pressure of sulphur dioxide volume	330.2
Final pressure of sulphur dioxide volume	120.8
Pressure change in sulphur dioxide volume	209.4
Temperature of sulphur dioxide	25°

Amount added to cell		.231 gms.
Amount previously added		.587 "
Total amount of sulphur dioxide in cell		.818
Apparent percentage sulphur dioxide	= =	14.29 %
Vapour pressure of sulphur dioxide at 15° for a concentration of	14.29 %	110 cms.
Volume of space above liquid		10.7 c.c.
Weight of sulphur dioxide in space above		.041 gms.
True percentage sulphur dioxide in liquid	= =	13.68 percentage sulphur dioxide.

In this calculation it is seen that the amount of sulphur dioxide transferred into the cell is obtained with great exactness. If all the sulphur dioxide were dissolved the calculation of the percentage would be a simple matter. But part of the sulphur dioxide is above the liquid, the amount depending on the vapour pressure which in turn is dependent on the concentration of the solution. The concentration of the solution is therefore first calculated on the basis of complete absorption. The vapour pressure of such a solution is then obtained from vapour pressure determinations given in a previous section. The volume of the space above the liquid being known, it is possible to calculate the amount of sulphur

dioxide in the gaseous phase. On subtracting this from the total amount of sulphur dioxide added, the concentration of the solution is obtained. The difference in vapour pressure between the two percentages is too small to cause any appreciable error, since in every case, the vast bulk of the sulphur dioxide is dissolved. The sample calculation chosen is one in which the correction had the greatest magnitude.

Below are given the results obtained with the first cell of the type described above.

TABLE XIII.

Temperature in degrees Centigrade	Percentage Sulphur Dioxide	Specific Conductivity
15°	2.74	.02732
	6.34	.04355
	10.26	.05586
	13.68	.06579
	17.30	.07101
	19.18	.07350
	20.45	.07496
	22.01	.07660
	23.62	.07731
	25.13	.07850
	27.26	.07875
	28.18	.07875
25°	2.74	.02848
	6.27	.04476
	10.13	.05724
	13.50	.06651
	17.04	.07186
	18.98	.07415
	20.19	.07536
	21.80	.07660
	23.41	.07731
		.07762

During a second experiment to check up the values obtained, the cell was broken, which necessitated the making of a new one. Advantage was taken of experience gained with the first cell, and several minor points were improved. For example, more room was left above the upper electrode for the addition of sulphur. Furthermore, glass tubes were sealed on to the cell through which the wires from the electrodes could be led out of the thermostat ensuring complete electric insulation.

Results obtained with the new cell, using KCl solution for its standardization, gave very good agreement with those in Table XIII.

TABLE XIV.

Temperature in Degrees Centigrade	Percentage Sulphur Dioxide	Specific Conductivity
15.0°	.1981	.004232
	.5187	.009497
	.8746	.01306
	1.524	.01866
	2.379	.02445
	5.403	.03945
	7.984	.04864
	10.94	.05703
	13.64	.06311
	15.98	.06759
	19.54	.07276
	21.98	.07548
	24.65	.07734
	26.86	.07841

The results obtained in another experiment at the same temperature with the same cell as used above, are given to show how accurately the work may be repeated.

These values are only given from 0.14% to 8.9%, as the stirrer broke at this point, and the experiment was discontinued.

TABLE XV.

Temperature in Degrees Centigrade	Percentage Sulphur Dioxide	Specific Conductivity
15.0°	.1479	.003787
	.2917	.006189
	.5924	.01011
	.8728	.01305
	1.811	.02054
	2.927	.02757
	3.741	.03145
	4.447	.03510
	6.383	.04271
	8.980	.05142

TABLE XVI.

Temperature in Degrees Centigrade	Percentage Sulphur Dioxide	Specific Conductivity
23.0°	.1689	.004355
	.4257	.009908
	.7820	.01352
	1.151	.01663
	3.126	.03004
	4.347	.03649
	6.457	.04526
	7.838	.05001
	12.28	.06203
	14.49	.06628
	17.69	.07168
	20.53	.07491
	23.75	.07739
	25.78	.07807
	28.52	.07803

The conductivities contained in Tables XIV and XVI are plotted against percentage in Fig.X.

Both at 15° and at 23° the specific conductivity eventually reached a constant value independent of the further

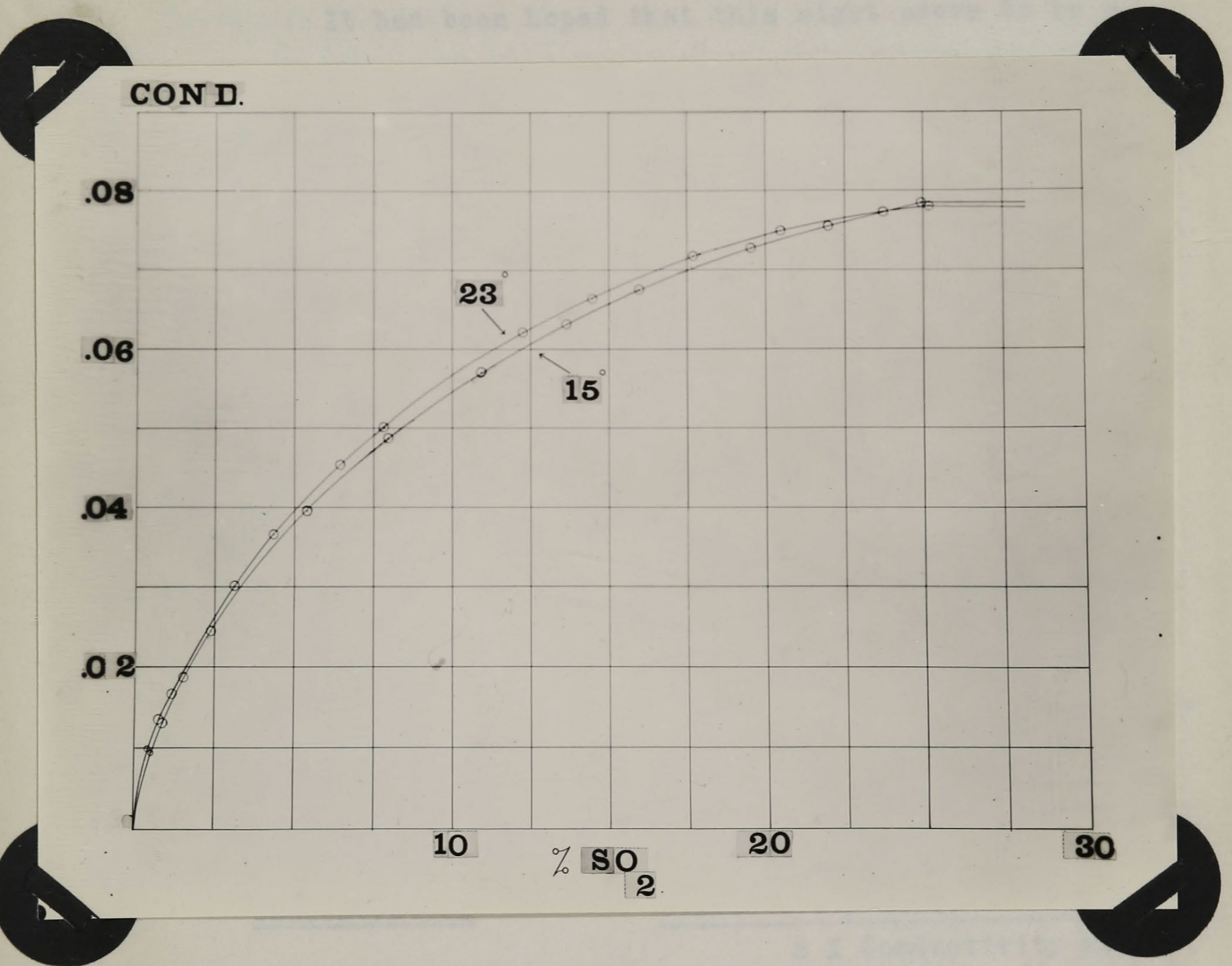


FIGURE XV.

addition of sulphur dioxide. This of course is to be expected in view of the appearance of the second phase, after which the concentration of the conducting phase cannot vary.

It had been hoped that this might prove to be a sensitive method for estimating the percentage compositions of the water phase. But, unfortunately, for that purpose, the variation of specific conductivity becomes exceedingly small around the higher concentrations. Nevertheless, it can be seen from the diagram that the straight line signifying constant conductivity cuts the curves at the 25% concentration, which is in agreement with the values deduced, both in the sections on "Vapour Pressure" and "The Two-phase Systems". Furthermore, it is of interest to note that the temperature coefficient of the specific conductivity decreases with rise in temperature, and apparently has a small negative value above 23% concentration, as indicated by the following table.

TABLE XVII.

Temperature Coefficients of Specific Conductivities.

Concentration	$\frac{\text{Conductivity at } 23^\circ - \text{Conductivity at } 15^\circ}{8 \times \text{Conductivity at } 15^\circ}$
5%	+.0056
10%	+.0050
15%	+.0029
20%	+.0020
23%	+.0010
24%	+.00016
25%	-.0010

A comparison of Tables XIII and XIV shows that the measurements have been repeated with an accuracy of 1%, although they were made with different cells, and at long intervals of time.

Very little is to be found in the literature on the conductivity of sulphurous acid solutions. Of the three investigations that were carried out, none of them included measurements of solutions with a higher concentration than 6%; that is, the range was about one fourth of that covered in the present investigation. Values taken from these three papers are given below, and compared with the values found in the present experiments. Where the concentrations were given in terms of volume of solution containing 1 gram. molecule, they were changed into percentages, so that corresponding values could be read off from the curves in Fig.X.

Temperature in Degrees Centigrade.	Percentage Sulphur Dioxide	Specific Conductivity Kerp & Bauer	Maass.
25°	6.437	.04919	.0496
	3.299	.03419	.0315
	1.640	.02280	.0208
	.6334	.01335	.01225
	.3178	.008426	.0083
	.1599	.005067	.0043

Temperature in Degrees Centigrade	Percentage Sulphur Dioxide	Specific Conductivity Lindner	Maass.
15°	6.20	.04627	.0425
	3.24	.03296	.0295
	.343	.008185	.0070
23°	6.20	.04831	.0444
	3.24	.03430	.0309
	.343	.008720	.0084

Temperature in Degrees Centigrade.	Percentage Sulphur Dioxide	Specific Conductivity	
		Barth	Maass
25°	.200	.00591	.0051
	.100	.00358	.0027

Kerp and Bauer's[39] values agree very well at higher percentages, but on the average, are about 10% higher than the writer's results. Lindner's work shows a disagreement of about 9%, while Barth's values differ by about 12%.

All three of the experimenters referred to above, used titration methods for determining the strength of the sulphur dioxide solutions. As has been shown, there is considerable chance for error in even the most careful analytical work, when dealing with so volatile, and easily oxidizable a substance as sulphur dioxide. Both these effects tend to increase the conductivity. The early values obtained by the writer where concentrations were determined by titration, were in every case found to be too high, and are in much closer agreement with the results obtained by Barth and Lindner (low concentrations).

In all the measurements made with the new procedure, the time factor was completely eliminated. After an interval of many hours, no change in conductivity of a sulphurous acid solution obtained in the manner outlined, could be detected.

The conclusion is justified that the values obtained by the writer can be accepted as being more accurate

than any previously determined.

In order to calculate the molecular conductivities, it was first necessary to change percentages of solutions into the volume containing one gram molecule of sulphur dioxide. The densities of the solutions were needed for this. Giles and Schearer[42] determined the densities over a short range. Their values were plotted, and the densities taken from the curve. At higher percentages where no values were given, the values were extrapolated. The molecular conductivities were then obtained by multiplying the specific conductivity by the volume of solution in c.c. containing one gram molecule of sulphur dioxide.

The dissociation constant α is the ratio of the molecular conductivity at any one concentration, divided by the molecular conductivity at infinite dilution. The molecular conductivity at infinite dilution cannot be obtained by extrapolation because of the secondary ionization,

$$HSO_3' \rightleftharpoons SO_3' + H^+$$

which occurs at greater dilution. Hence this has to be estimated from the sum of the limiting conductances of the H^+ and HSO_3' ions. These conductances can be obtained from the work of Kohlrauch[43] and Drucker.[44] Theyvare 299 and 337 at15° and 23° respectively for the H^+ ion, and 42, and 49.5 at 15° and 23°, for the HSO_3' ion. The sum of these values gives 341, and 388.6 as the molecular conductivity at infinite dilution at 15° and 23°.

In Table XVIII, the molecular conductivity corresponding to the specific conductivities contained in Tables XIV and XVI, are given. The fourth column gives the amount of dissociation, and the last column gives Ostwald's dilution law constant.

TABLE XVIII

15.0°C.

Percentage Sulphur Dioxide	Number of Gm. Mols.per litre	Molecular Conductivity.	Dissociation (M_∞ = 341)	K
.1981	.03098	136.6	.4005	.008318
.5187	.08119	116.9	.3430	.01454
.8746	.1372	95.17	.2790	.01481
1.524	.2397	77.82	.2282	.01614
2.379	.3758	65.07	.1908	.01694
5.403	.8668	45.51	.1335	.01797
7.984	1.296	37.54	.1101	.01762
10.94	1.845	30.91	.09065	.01669
13.64	2.274	27.75	.08137	.01641
15.98	2.692	25.11	.07364	.01574
19.54	3.346	21.75	.06377	.01455
21.98	3.803	19.86	.05821	.01368
24.65	4.318	17.91	.05252	.01256
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
		23.0°C.	(M_∞ = 388.6)	
.1689	.02638	165.1	.4271	.008395
.4257	.06664	148.6	.3845	.01606
.7820	.1227	110.3	.2852	.01393
1.1510	.1809	91.94	.2379	.01345
3.126	.4957	60.60	.1568	.01450
4.347	.6653	54.86	.1419	.01563
6.457	1.041	43.48	.1125	.01499
7.838	1.271	39.36	.1018	.01472
12.28	1.989	31.18	.08067	.01409
14.49	2.424	27.35	.07074	.01304
17.69	3.005	23.85	.06172	.01200
20.53	3.533	21.20	.05486	.01126
23.75	4.144	18.67	.04832	.01015
25.78	4.536	17.21	.04452	.009396
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

K varies in the same way at both temperatures, reaching a maximum value at a concentration corresponding to 8 grams moles per litre. Over the large range, .06 to 4 grams moles, the variation is remarkably small, from the point of view of the variation usually met with in the dissociation constant of electrolytes. The dissociation constant decreases considerably with the temperature, an 8° change causing a decrease of 22%.

The values obtained by Kerp and Bauer, and Lindner are 15% higher, This is due in part to the higher values for conductivity obtained by these investigators. A discussion of the true significance of the dissociation constant, in this particular case, and the deductions that can be made in regard to it, from vapour pressure data of sulphur dioxide solutions will be given in the next section.

It may be of interest to mention in conclusion of this section that the sulphur dioxide phase which has been shown to contain more than 1% of water, has an exceedingly small conductivity, less than that of tap water.

THEORETICAL DISCUSSION

As has already been stated in the introduction, the exact composition of a solution of sulphur dioxide in water, is not known. There is some experimental evidence[7] for the existence of sulphur dioxide molecules, as such, in these solutions, but nothing is known of the percentage of these molecules existing uncombined. It is of great interest to know the exact distribution of the sulphur dioxide molecules. Sulphurous acid is considered a weak acid, from the point of view of its conductivity. Calculations of conductivity, however, have always been based on the assumption that all the sulphur dioxide in solution existed as sulphurous acid. Hence, if very little of the sulphur dioxide forms sulphurous acid then this acid may be much stronger than has been thought.

Solutions of sulphur dioxide do not obey Henry's Law, as indicated by the early work of Sims[32] on solubilities. Attempts have been made by Fulda[45], and later on by Lindner[40] to account for the discrepancy by taking into account the sulphur dioxide used up in the dissociation of sulphurous acid. This factor is, of course, not sufficient to make possible exact correlation of experimental results and theory, as was pointed out by Lindner, both with regard to his own and Fulda's calculations.

In the following discussion, this is first of all confirmed, and then an attempt is made to deduce an exact

relationship between partial vapour pressure of sulphur dioxide and the concentrations of sulphur dioxide, sulphurous acid, and HSO_3' ions. This relationship was found to represent accurately the experimental results, and makes possible a reliable estimate of the true strength of sulphurous acid, and of the equilibrium existing between uncombined sulphur dioxide molecules and sulphurous acid.

Let C_{SO_2} be the total concentration of the sulphur dioxide dissolved in the solution, expressed in gram molecules per litre. Now, this sulphur dioxide exists as sulphur dioxide molecules, as sulphurous acid molecules, and as HSO_3' ions. Hence -

$$C_{SO_2} = (SO_2) + (H_2SO_3) + (HSO_3') \qquad (1)$$

where the brackets indicate the concentrations of the various substances. The following are the equilibria to be considered;

(a) $H_2SO_3 \rightleftharpoons H_2O + SO_2$

This equilibrium can be expressed as follows:

where k is the mass law constant,

$$\frac{(H_2O)\ (SO_2)}{(H_2SO_3)} = k \qquad (2)$$

(b) $H_2SO_3 \rightleftharpoons H^+ + HSO_3'$

which can be expressed

$$\frac{(H^+)(HSO_3')}{(H_2SO_3)} = K_0 \qquad (3)$$

where K_0 is the true ionization constant as defined by

Ostwald. The ionization constant K, which has been calculated from values of α and V, the dilution, is not the true constant K_0. V represents the volume in litres containing one gram molecule of sulphurous acid. If all the sulphur dioxide does not form sulphurous acid, then V is really the volume containing one gram molecule of sulphurous acid and sulphur dioxide. The equilibrium, then, must be written:

$$\frac{(H^+)(HSO_3')}{\{(H_2SO_3)+(SO_2)\}} = K \qquad (4)$$

where K is the ionization constant actually measured and tabulated in Table XVIII. Furthermore, the partial vapour pressure of the sulphur dioxide above the solution is proportional to the real concentration of sulphur dioxide, so that,

$$(SO_2) = hp \qquad (5)$$

where (SO_2) is the sulphur dioxide present, as such, in the solution, h is Henry's constant, and p the pressure of sulphur dioxide gas. Now, in equation (1), (H_2SO_3) can be replaced by $\frac{(SO_2)(H_2O)}{k}$ (from 2), and (HSO_3') by $\sqrt{K\{(H_2SO_3)+(SO_2)\}}$ (from 4) since the concentration of hydrogen ion is the same as that of HSO_3'. This gives,

$$C_{SO_2} = (SO_2) + \frac{(SO_2)(H_2O)}{k} + \sqrt{K\{(H_2SO_3)+(SO_2)\}}$$

Substituting again for (H_2SO_3)

$$C_{SO_2} = (SO_2) + \frac{(SO_2)(H_2O)}{k} + \sqrt{K\left(\frac{(SO_2)(H_2O)}{k}+(SO_2)\right)}$$

But $(SO_2) = hp$, from equation (5),

$$C_{SO_2} = hp + \frac{hp(H_2O)}{k} + \sqrt{K\left\{\frac{hp(H_2O)}{k} + hp\right\}} \qquad (6)$$

If, in equation (6) the concentration of water is considered as constant, this becomes,

$$C_{SO_2} = ap + b\sqrt{p} \qquad (7)$$

where $a = h\left\{\frac{1+(H_2O)}{k}\right\}$ and $b = \sqrt{Kh\left\{\frac{1+(H_2O)}{k}\right\}}$

It follows that,

$$K = \frac{b^2}{a} \qquad (8)$$

The above equation takes into account only the effect of ionization on the aberration of Henry's Law, and in order to test this out, the values contained in the Table on p.44 are chosen. The percentages in this table are expressed in weight per cent., and have been recalculated as gram molecules per litre, taking into account the densities of the solutions. Table XIX contains the concentrations expressed in this way, together with the corresponding calculated concentrations of water.

TABLE XIX

% SO_2		5	10	15	20	25
Concentration	C_{SO_2}	.7984	1.631	2.499	3.400	4.335
"	C_{H_2O}	53.93	52.20	50.34	48.37	46.26
Temperature		Partial Vapour Pressure of SO_2				
10.0°		25.1	53.1	87.9	128.3	169.1
16.5°		32.7	71.4	114.9	161.0	209.6
22.0°		40.9	88.0	140.0	194.2	250.2
27.0°		49.1	104.5	165.2	228.7	292.5

Choosing the values for the vapour pressures of sulphur dioxide at 10°, for concentrations C_{SO_2} = .7984 and C_{SO_2} = 1.631, equation (7) gives for the values of a and b, .0283 and .0175 respectively. Substituting in equation (8), K is given as .0108. This value for K is not so far from that deduced from the conductivity experiments, namely .016* at that temperature. But using the above values for a and b, to calculate the C_{SO_2} values for the other 3 concentrations at 10°, these are found to diverge enormously from those given in the table, the last one corresponding to an error in pressure reading of 40 cm! If concentrations 1.631 and 2.499 are used in equation (7) to calculate a and b, the latter have values .0205 and .0741, giving the absurd value of .267 for K. It is obvious that equation (8) does not represent experimental conditions, and deviates widely at all concentrations above .8 . The assumption of the constancy of the water concentration is evidently not justified, and in the following,

* The value of K was chosen as follows. An examination of Table XVIII shows that K decreases with rising concentration. The average value above 5% of sulphur dioxide for 5% intervals was taken as .012 at 23° and .0145 at 15°, and .016 as the approximate extrapolated value at 10°.

it will be seen how this can be taken into account.

In equation (6), (H_2O), the real concentration of water in the solution, can be calculated as follows. Let C_{H_2O} be the calculated concentration of water in the solution, as if no water was used up in any of the equilibria. It follows, as in the case of C_{SO_2} that,

$$C_{H_2O} = (H_2O) + (H_2SO_3) + (HSO_3^-)$$

Then,

$$C_{H_2O} = (H_2O) + \frac{(H_2O)(SO_2)}{k} + \sqrt{K\left\{\frac{(H_2O)(SO_2)}{k} + (SO_2)\right\}}$$

$$C_{H_2O} = (H_2O) + \frac{hp\ (H_2O)}{k} + \sqrt{K\left\{\frac{hp\ (H_2O)}{k} + hp\right\}} \qquad (9)$$

By subtracting equation (6) from (9),

$$C_{H_2O} - C_{SO_2} = (H_2O) - hp$$

or

$$(H_2O) = C_{H_2O} + hp - C_{SO_2} \qquad (10)$$

as the last two terms in each equation are identical, and thus cancel out. (H_2O) is now expressed in terms of known values, and (H_2O) in equation (6) can be replaced by $(C_{H_2O} + hp - C_{SO_2})$, giving,

$$C_{SO_2} = hp + hp\ \frac{(C_{H_2O} + hp - C_{SO_2})}{k} + \sqrt{K\ hp\left\{1 + \frac{(C_{H_2O} + hp - C_{SO_2})}{k}\right\}} \qquad (11)$$

Equation (11) contains 2 unknown quantities, h and k, if the value for K found in the conductivity experiments is employed. By selecting two different values of C_{SO_2} from the conductivity tables, and using the corresponding pressures, h and k can be found. As can be seen, the solving for h and k from the above

equation, is a very complicated matter. The last term is comparatively small, and in order to facilitate the solution of the equation, can be neglected for the first approximation. The values for h and k determined in this way, can then be substituted in the last term of equation (11), and new values found for h and k, which completely satisfy the two equations employed. The values found for h and k at 10^{o} are .00624 and 15, respectively. With these values, and K = .016, the concentrations calculated are found to agree with every one of the concentrations in Table XIX, within .02 of the concentration, so that the pressures are represented within one centimetre. This close agreement, however, does not signify that the values of k and h are determined with anything like this accuracy, since a considerable increase in k and a corresponding increase in h, will represent the results within experimental accuracy. This is not surprising, since, after all, the variation in water concentration is small compared to the variation in sulphur dioxide concentration. In order to estimate the accuracy with which k has been determined, a number of values of k, differing widely from that found, were chosen, and by a series of approximations, corresponding values for h, (calculated to best represent experimental results), were deduced.

In the following table, the values of h and k, head the concentrations calculated for these particular values,

beside which are placed the differences from those actually found.

TABLE XX

k = 5.1 h = .00258		k = 10.15 h = .0046		k = 15 h = .00624		k = 22.1 h = .0081		k = 40.5 h = .01157	
.849	+.05	.842	+.042	.819	+.02	.799	0.0	.777	-.02
1.60	+.03	1.65	+.02	1.61	-.02	1.573	- .06	1.53	-.10
2.56	+.06	2.52	+.02	2.51	+.01	2.48	-.02	2.43	-.07
3.50	+.10	3.47	+.07	3.46	+.06	3.43	+.03	3.41	+.01
4.33	.00	4.31	-.02	4.33	.00	4.31	-.02	4.33	-.00
		Average							
	+.05		+.026		+.014		-.014		-.036

It is seen that the best value of k lies between 15 and 22.1 . For values less than 5, and greater than 40, the divergence becomes far greater than experimental error. The average of k chosen, is 15, but this may differ from the true value by -5 or $+10$. However, even the estimation of k, which is the first that has been made, is of considerable interest, because it makes possible the estimation of the real strength of sulphurous acid.

The constants K_0, K and k (see (a),(b), and (4)) are related as follows:

$$\frac{(H^+)\ (HSO_3^-)}{\{(H_2SO_3)+(SO_2)\}} = K = \frac{K_0\ (H_2SO_3)}{\{(H_2SO_3)+(SO_2)\}}$$

Substitute $\frac{(SO_2)(H_2O)}{k}$ for (H_2SO_3) and

$$K = \frac{K_0\ (SO_2)(H_2O)}{k\left\{\frac{(SO_2)(H_2O)}{k} + (SO_2)\right\}}$$

$$K = K_0\ \frac{(H_2O)}{(H_2O)+k} \qquad (12)$$

From the numerical values at 10°, it follows that K_0 = .023, as compared to K = .016, that is, at this temperature the dissociation constant has practically the same value as the constant given by the conductivity. In Table XVIII, it is noted that the value of K after a concentration of .8 moles decreases with rising concentration of sulphur dioxide and consequently, decreasing concentration of water. Equation (12) shows that this is to be expected even though the true ionization constant, K_0, remains constant, and a numerical calculation shows that the order of magnitude in the decrease of K is exactly that which has been found.

An examination of Table XVIII shows that there is a marked decrease in the value of K with temperature, corresponding to 2% per degree. The ionization constant of most electrolytes increases very slightly with rising temperature at ordinary temperatures, and only at high temperatures does a decrease occur. From that point of view, sulphurous acid would be quite anomalous, and the strength of sulphurous acid at about 140°, where it is used in pulp cooking, would be exceedingly small. The decrease, however, is only apparent, for K is not the true ionization constant.

Let K_{t_1} and K_{t_2} be the ionization constants as determined by the conductivity method at temperatures t_1 and t_2 respectively, where t_2 is greater than t_1. Then the change in K can be accounted for by a change in k. Let k_{t_2} and k_{t_1} be the

values of k corresponding to these temperatures. Then equation (12) gives:

$$\frac{K_{t_1}}{K_{t_2}} = \frac{(H_2O)+k_{t_2}}{(H_2O)+k_{t_1}}, \qquad K_0 = \text{constant} \qquad (13)$$

If k_{t_2} is greater than k_{t_1}, then K_{t_1} is greater than K_{t_2}. Hence the decrease in K can be accounted for by an increase in k. This is equivalent to assuming that the higher the temperature the greater will be the amount of uncombined sulphur dioxide in solution. When the values of the pressures and concentrations are examined at 22° (see Table XIX), then these values can be represented perfectly by a choice of k = 100 and h = .01138, whereas smaller values of k lead to large discrepancies.

Thus a simple calculation shows that at 10° the amount of uncombined sulphur dioxide in solution is approximately 20% of the total dissolved, whereas at the higher temperature, 50% is uncombined for a 5% sulphur dioxide solution.

It follows, also, that the higher the temperature, the greater will be the value of k, and the smaller will be the influence played by the water concentration, and hence, at higher temperatures, equation (7) will approximate more closely as a representation of the experimental results. Since K decreases with rise in temperature, eventually the pressure will be directly proportional to C_{SO_2}, the calculated

sulphur dioxide concentration. Experiments are in progress at higher temperatures which confirm the above.

It might be well to point out that the quantitative side in the relationships deduced above is not being unduly stressed. A number of assumptions have been made the validity of which might be the subject of discusion. For instance, the part played in the equilibrium between associated and unassociated water molecules, and the possible existence in the solution of hydrates of sulphur dioxide. The remarkable agreement between experimental results, and deduced values may be taken to indicate that the above mentioned assumptions were justified, and that the following conclusions are probably correct.

Sulphur dioxide dissolves in water and exists there only in part in the form of sulphurous acid. With rise in temperature, the amount of uncombined sulphur dioxide increases rapidly, the order of magnitude being about 20% at 10°, and 50% at 25°. The true dissociation constant of sulphur dioxide lies in the neighbourhood of .02, and with rise in temperature this does not decrease at all rapidly. The decrease of the conductivity dissociation constant with rise in temperature is due to a decrease in the amount of sulphurous acid which is in equilibrium with the sulphur dioxide.

SUMMARY

The following brief resumé is designed to bring out the salient features of the above investigation.

A short historical account of sulphur dioxide and sulphurous acid was given.

A procedure for accurately analysing solutions of sulphurous acid, and incidentally for the standardization of iodine solutions, was described.

The apparent molecular weights of sulphur dioxide were measured over the temperature range -5° to +35°C. An equation was developed in terms of apparent molecular weight which gives the most convenient and accurate evaluation of the weight of a gas taken out of a known volume when the initial and final pressures are measured.

A convenient method for measuring vapour pressures of solutions containing one volatile component was described. The vapour pressures of aqueous solutions of sulphur dioxide were measured over the temperature range 10° - 27°, and covering all possible concentrations. The vapour pressures of pure sulphur dioxide were measured over the range 1° - 27°. The vapour pressures of the two liquid phase system were measured over the range 10° - 27°. A comparison of values found by other investigators, is included. It was shown that the concentration of the volatile component in the water phase can be determined by means of the vapour pressure measurements, and the concentration of water in the sulphur dioxide phase, approximately

calculated by using Raoult's Law.

A method was designed for separating a portion of one liquid phase from any three phase system (liquid-liquid-gas) which is in equilibrium at pressures which are so great that other methods cannot be used to obtain accurate analysis of the equilibrium concentration. This method was employed for measuring the concentration of sulphur dioxide in the aqueous phase and the values deduced from the vapour pressure measurements for the range 10^{o} - 27^{o}C. were confirmed at the temperature where measurements were made.

A method was devised by means of which the concentration of water in the sulphur dioxide phase can be more exactly determined. This method consisted in the measurements of vapour pressures of solutions of water in sulphur dioxide, and gave values agreeing very closely with those calculated.

Methods used in the determination of conductivities of sulphurous acid, were described. An apparatus was designed suitable for conductivity measurements, in the case of all solutions in which the solute is a gas with a high partial vapour pressure. The results obtained over a concentration range of .1 - 25%, by means of this apparatus, are tabulated, and compared with values of other workers. The dissociation constand of sulphurous acid was calculated.

The theoretical conclusion with regard to the state of sulphur dioxide in solution can be best summed up as in the last section:

Sulphur dioxide dissolves in water and exists there, only in part, in the form of sulphurous acid. With rise in temperature the amount of uncombined sulphur dioxide increases rapidly, the order of magnitude being about 20% at 10° and 50% at 25°. The true dissociation constant of sulphur dioxide lies in the neighbourhood of .02, and with rise in temperature this does not decrease at all rapidly. The decrease of the conductivity dissociation constant with rise in temperature is due to a decrease in the amount of sulphurous acid which is in equilibrium with the sulphur dioxide.

REFERENCES

1. Smyth, Phil. Mag. 47, 530, 1924.
2. Godby, Chem.Soc.Proc., 241, 1907.
3. Arbusoff, Chem.Soc.Abstr., ii, 573, 1909.
4. Schwicker, Ber. 22, 1728, 1889
5. Schaeffer, Zeit.Elek.Chem. 21, 181, 1915.
   Zeit.Anorg.Chem. 104, 212, 1918.
6. Baly & Bailey, Jour.Chem.Soc. 121, 1813, 1922.
7. Wright, Chem. Soc. T. 105, 2909, 1914.
8. Ostwald & Barth, Zeit.Phys.Chem. 9, 176, 1892.
9. Kerp & Bauer, Kaiserliches Institut, 26, 297,1907.
10. Lindner, Monatsch. 33, 613, 1912.
11. Landolt Börnstein Tables, 5th Ed., 1068-1098, 1923.
12. Cardoso, Jour.Chimie Physique, 23, 829, 1926.
13. Henning and Stock, Zeit.Phys. 4, 226, 1921.
14. Bunsen, Ann. de Chimie et de Physique, 3, XLI, 339,1854
15. Fordes & Gelis, Comp. Rend. 20, 771, 1845.
16. Finkner, Quant.Analyse, 1871.
17. Volhard, Ann. de Chem.u.Pharm. 242, 94.
18. MacCauley, Jour.Chem.Soc. 121, 553, 1922.
19. Raschig, Zeit.Anorg.Chem.17, 577, 1904.
20. Hudson, Chem.Soc. 127, 1332, 1925.
21. Ostwald, Greindlinien der Anorg. Chem. 4th Ed. 323,1919.
22. Baume, Jour.Chim.Phys. 6, 1, 1908.
23. Jaquerod & Pintze, Minn.Geneve, 35, 589, 1908.
24. Maass & Russell, Jour.Amer.Chem.Soc.40, 1847,1918.

25. Maass & Mennie, Roy.Soc.Proc. A.110, 198, 1926.

26. Maass and Boomer, Jour.Amer.Chem.Soc. 44, 1727, 1922.

27. Unpublished, Contained in Ph.D.thesis of J.H.Mennie, C.Sivertz, and J.Russell, McGill University, 1925-26.

28. Maass & Morrison, Jour.Amer.Chem.Soc. 45, 1677, 1923.

29. Maass, Trans.Roy.Soc. Can., 11, 137, 1917.

30. Schonfield, Annalen, 95, 1, 1855.

31. Landolt Börnstein Tables, 5th Ed., 762, 1923.

32. Sims, Chem.Soc.Trans. 14, 1, 1862

33. Hudson, Chem.Soc. 127, 1332, 1925.

34. Cardoso, Jour.Chimie Physique, 23, 835, 1926.

35. Regnault, Relation des Experiences, II, 581.

36. Roozeboom, Rec.Pays Bas, 3, 44, 1884
4, 68, 1885

37. Roozeboom, Zeit. Phys.Chem. 1, 206, 1887

38. Raoult, Zeit.Phys.Chem. 2, 253, 1818

39. Kerp & Bauer, Chemische und Pharmakologische Unterruchungen, II, 68, 1913.

40. Lindner, Ber.K.Akad.Wiss.Wien. 121, 293, 1912.

41. Barth, Zeit.Phys.Chem. 9, 176, 1892

42. Giles & Schaerer, Jour.Soc.Ch.Ind. 4, 303.

43. Kohlrauch, Zeit.Phys.Chem. 43, 511, 1903.

44. Drucker, Zeit.für Elect.Chem. 13, 83, 1907.

45. FOLDA
Arb.a.d.Kais.Gesundheitsamt, 30, 81(1909)

cd. June '30 '37