EQUILIBRIA EXISTING

IN

GAS-WATER SYSTEMS

AN INVESTIGATION OF THE EQUILIBRIA
EXISTING IN GAS-WATER SYSTEMS
FORMING ELECTROLYTES.

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A

THESIS.

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Submitted in Partial Fulfillment

of the Requirements for the

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By

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INTRODUCTION

The data and theoretical treatment contained in this thesis is the continuation of a series of researches instituted to investigate the equilibria existing in certain gaseous-aqueous systems. In this work the vapor pressures and electrolytic conductivities of aqueous solutions of sulphur dioxide, carbon dioxide, and ammonia have been measured with greater precision than ever before over a temperature range from $0^{\circ}C$. to $25^{\circ}C$. and over a concentration range where their respective vapor pressures do not exceed one atmosphere. From the data thus derived, equilibria relations have been calculated and certain changes have been made in the mode of theoretical procedure involved in this type of calculation.

Sulphur dioxide, carbon dioxide, and ammonia are very common materials and are widely used in many industries. It is amazing, when a search is made in the literature, to find that the data, which is of such economic interest, is either lacking or inaccurate. Perhaps the sulphur dioxide-water system has been investigate more thoroughly than the other two.

The solubility of sulphur dioxide in water was determined by Hudson (1) working at approximately

atmospheric pressure and temperatures up to $90°C$. Sims (2), working at pressures up to 200cms. and temperatures up to $50°C$., measured the vapor pressures with a considerable amount of accuracy. Enckell (3) and Oman (4) measured solubilities up to $90°C$., Enckell using less exact methods than Oman. Enckell also measured the solubility of sulphur dioxide in other solutions such as calcium bisulphite, sodium sulphate plus hydrochloric acid, and sulphuric acid. Vapor pressure measurements of solutions of sulphur dioxide in water, and in water plus various amounts of bases were made by Smith and Parkhurst (5).

Ostwald (6) and Barth (7) carried out investigations on the conductivity of SO_2 solutions. McRae and Wilson (8) determined partition coefficients of sulphur dioxide between water and chloroform. Walden and Centnerszwer (9) made freezing point determinations. Drucker (10) combined the results of the four previous investigations to calculate the so called dissociation constant. Kerp and Bauer (11) measured freezing points and conductivities. Fulda (12) gives figures for the dissociation constant at temperatures from $2°C$. to $50°C$. These he has calculated from the heat of dissociation data of Thomsen (13) and Berthelot (14). Lindner (15)

reviews and discusses these papers and has also
made determinations of vapor pressure at $0^{\circ}C.$,
$25^{\circ}C.$, and $50^{\circ}C.$ on four solutions ranging in
concentration from 0.05% to 3.8%. He also made
conductivity measurements of the following sol-
utions:- 6.20% at temperatures from $0^{\circ}C.$ to
$39.9^{\circ}C.$; 3.24% at temperatures from $12.7^{\circ}C.$ to
$56.7^{\circ}C.$; 0.34% at temperatures from $9.5^{\circ}C.$ to
$69.9^{\circ}C.$; 0.05% at temperatures from $0^{\circ}C.$ to
$70.5^{\circ}C.$

Any other available data on sulphur dioxide has
been obtained in this laboratory. C. Maass (16) made
vapor pressure and conductivity measurements over
all possible concentrations below $27^{\circ}C.$

The range of most interest to those concerned
with the sulphite process of cooking wood pulp is
that between 0% and 6% concentration and at $100^{\circ}C.$
or slightly above. This range has been covered by
W.B. Campbell and O. Maass (17) in this laboratory.
The apparatus used by these investigators was
designed to measure pressures up to four atmospheres
and hence did not give precise measurements at the
lower pressures. Their reaction chamber was small
which also tended to cut down the precision and the
maximum concentration attained was only 8%.

In order to obtain a true measure of the equilibria, as will be seen later, it is necessary to have a comparatively large variation in the water concentration. In the present work concentrations as high as 14% sulphur dioxide were attained which gave approximately twice the variation in the water concentration that was reached by Campbell. Campbell and Maass admit that the values of their equilibria constants are only approximate. The aim of this work was to arrive at a true evaluation of these constants and to investigate the type of equilibria existing at the lower temperatures.

Considerable data is available for carbon dioxide. Bohr (26) working over a temperature range of 0° to 60^oC. and over a vapor pressure range of 27 to 140 cms. has determined the Henry's Law constants. Findlay and Creighton (27) measured the solubility of CO_2 in water and the effect of fine suspensions on the solubility. Findlay and Williams (28) determined the solubility of CO_2 in water at pressures lower than one atmosphere. Findlay and Shen (29) investigated the effect of colloids and fine suspensions on the solubility of CO_2 in water. The results were in harmony with Henry's Law. Findlay and Howell (30) measured the vapor pressures of CO_2 in pure water and in starch solutions at 25^oC. for pressures from 272 to 960 m.m.

Buch (31) determined the solubility of CO_2 in water
at temperatures between 17° and $20^\circ C$. and calculated
the absorption coefficients. Just (32) working at
$25^\circ C$. determined Henry's Law constant and obtained
a value which agreed well with that of Bohr (26)
but differed from the rest.

Conductivity data for carbon dioxide is not
quite so plentiful. Data due to Knox (34), Pfeiffer
(35) and Walker and Cormack (36) is reviewed in a
concise manner by Kendall (33) who also supplies
considerable data. The above experimenters worked
at temperatures from 0° to $25^\circ C$. and concentrations
up to 0.08 gram mols per litre. The data due to
Kendall (33) agrees very well with that due to
Walker and Cormack (36) but does not compare favor-
ably with that of Pfeiffer (35) or Knox (34).
Wilke (37) attempts to explain the equilibria of
CO_2 in water solutions. He determined the dissoc-
iation constants by conductivity measurements at
various temperatures and showed H_2CO_3 to be a very
weak acid. Carbonic acid is shown to be a sensitive
compound and is decomposed by slight influences such
as the current used for measurement.

Vapor pressures of solutions of ammonia at 0°;
20° and $40^\circ C$. and up to 3640 m.m. have been measured
by Neuhausen and Patrick (43). Foote and Brinkley(42),
working at 10° and $20^\circ C$., determined the vapor pressures

up to 1500 m.m. As a side issue they investigated the equilibrium in the system ammonia: ammonium nitrate; and ammonium thiocyanate with the object of discovering what proportions of these substances were most efficient in absorbing ammonia from gas mixtures Perman (22) has also covered the lower range of vapor pressures.

Kanolt (38) determined the ionization constant of ammonium hydroxide at 0°, 18°, and $25^{\circ}C$. Lunden (39) has measured the affinity coefficients of ammonia solutions between 15° and $40^{\circ}C$. and conductivities between 10° and $50^{\circ}C$. in dilute solutions. Noyes and Kato (40) measured the conductivity and determined the ionization up to $156^{\circ}C$. using a steel bomb lined with platinum electrodes which were insulated away from the walls. Burke (41) investigated the ionization of aqueous solutions of ammonia in the presence of urea to find if an ammonia-urea complex were formed. The results showed that such appeared to be the case. Specific conductivity data is also provided by Kohlrausch (21).

The density of ammonia solutions up to 40% concentration and between -15° and $25^{\circ}C$. have been determined by Nichols and Wheeler (19) and Baud and Gay (20).

A general summary of the work carried out by other investigators on all three systems shows con-

siderable lack of agreement apart from the total
lack of data in certain concentration and temperature
regions. One special source of controversy is to be
found, not in the accuracy of actual pressure or
conductivity measurements, but rather in the determin-
ation of the concentration factor. Special emphasis
is laid, in the experimental work to be described, on
the elimination of all doubt as to the true concentrat-
ions, and of true equilibria having been reached bet-
ween the gaseous and liquid phase. This may have been
another source of discrepancies obtained by other
investigators.

It would lead too far afield to give a detailed
account of all theories that have been put forward
in connection with the equilibria existing in the
various systems investigated. Due to the fact that
the work herein contained is a continuation of the
work begun by C. Maass (16) and Campbell and Maass
(17), as far as sulphur dioxide is concerned, it is
convenient to overlap their work as far as it was
carried out. On the experimental side this will be
done by the comparision of refinements and improve-
ments that have been made. The need for the extreme
precision is brought out by the following review of
the theoretical considerations as they have been

developed so far. It will be seen that previous data is not adequate in testing it out.

In this theoretical discussion, terms peculiar to solutions of sulphur dioxide will be used. This discussion will contain the major number of steps necessary in dealing with gaseous-aqueous equilibria and all the steps necessary for sulphur dioxide as evolved by the above experimenters. However, certain characteristics, depending on the gas under consideration, necessitate minor changes in the mathematical treatment. These peculiarities will be dealt with in discussing the respective systems in later sections.

In aqueous solutions of sulphur dioxide there are three major and one minor equilibria existing. The partial pressure of the sulphur dioxide above the solution is in equilibrium with the uncombined gas in the solution,

$$[SO_2]_{soln.} = H[SO_2]_{gas} \tag{1}$$
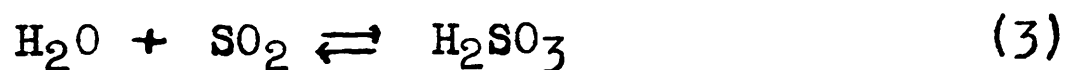
and since the partial pressure of the gas above the solution is a measure of the concentration of the gas in the vapor

$$[SO_2]_{soln.} = Hp \tag{2}$$

where p is the partial pressure of the gaseous sulphur dioxide and H is a constant (Henry's constant).

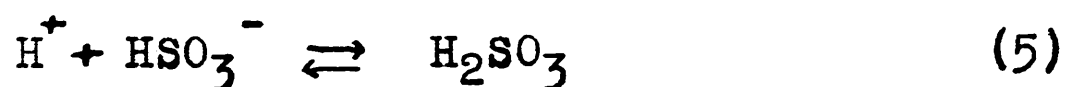The sulphur dioxide molecules in the solution are

in equilibrium with sulphurous acid and may be represented

$$H_2O + SO_2 \rightleftharpoons H_2SO_3 \tag{3}$$

and applying the mass law

$$[H_2O][SO_2] = K_1[H_2SO_3] \tag{4}$$

The sulphurous acid in solution is ionized to a certain extent and is in equilibrium with its ions

$$H^+ + HSO_3^- \rightleftharpoons H_2SO_3 \tag{5}$$

and assuming that the Ostwald dilution law holds in this case

$$[H^+][HSO_3^-] = K_2[H_2SO_3] \tag{6}$$

A further ionization is possible according to the equation

$$H^+ + HSO_3^- \rightleftharpoons 2H^+ + SO_3^= \tag{7}$$
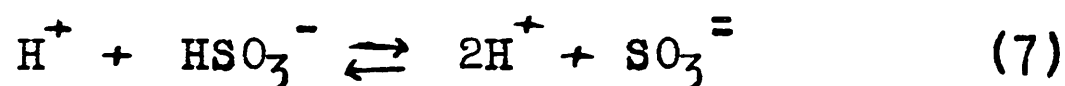
but this ionization is so small it may be safely neglected.

The problem now presented is the evaluation of the constants H, K_1, and K_2. Previous investigators have merely calculated the apparent dissociation constant obtained by the assumption that all the sulphur dioxide in the solution is combined with water to form H_2SO_3. That is

$$[H^+][HSO_3^-] = K_a\left([H_2SO_3] + [SO_2]\right)$$

$$= K_a\left(\frac{[SO_2][H_2O]}{K_1} + [SO_2]\right)$$

$$= K_a \left[SO_2\right] \left(\frac{\left[H_2O\right]}{K_1} + 1\right) \qquad (8)$$

then since

$$\left[H^+\right]\left[HSO_3^-\right] = K_2 \left[H_2SO_3\right]$$

$$= K_2 \frac{\left[SO_2\right]\left[H_2O\right]}{K_1}$$

the relation between K_1, K_2, and K_a is

$$K_a = \frac{K_2 \left[H_2O\right]}{K_1 + \left[H_2O\right]} \qquad (9)$$

The first attempt at the actual evaluation of the constants was made by C. Maass (16) as follows:-

$$C_{H_2O} = \left[H_2O\right] + \left[H_2SO_3\right] + \left[HSO_3^-\right] \qquad (10)$$

$$C_{SO_2} = \left[SO_2\right] + \left[H_2SO_3\right] + \left[HSO_3^-\right] \qquad (11)$$

On subtracting (10) from (11)

$$\left[H_2O\right] = C_{H_2O} - C_{SO_2} + \left[SO_2\right]$$

$$= C_{H_2O} - C_{SO_2} + Hp \qquad (12)$$

$$C_{SO_2} = \left[SO_2\right] + \frac{\left[SO_2\right]\left[H_2O\right]}{K_1} + \sqrt{K_a\left[SO_2\right]\left(\frac{\left[H_2O\right]}{K_1} + 1\right)}$$

$$= Hp\left(1 + \frac{\left[H_2O\right]}{K_1}\right) + \sqrt{K_a\, Hp\left(1 + \frac{\left[H_2O\right]}{K_1}\right)}$$

and substituting (12)

$$C_{SO_2} = Hp\left(1 + \frac{C_{H_2O} - C_{SO_2} + Hp}{K_1}\right) + \sqrt{K_a Hp\left(1 + \frac{C_{H_2O} - C_{SO_2} + Hp}{K_1}\right)} \qquad (13)$$

This equation contains two unknowns H and K_1. The value of K_a was obtained from conductivity measurements. By taking two values of C_{SO_2} at any one temperature and the corresponding pressures it is possible to arrive at the value of H and K_1, and hence K_2, the true dissociation constant. It must be remembered at this point, however, that to get an accurate evaluation of the constants there must be considerable variation in the water concentration, as was mentioned previously. Vapor pressures must also be measured very accurately. For the above reasons C. Maass (16) was only able to arrive at approximate values of the constants. It was found from the calculations that at $15^{\circ}C$. the amount of uncombined SO_2 in the solution amounted to about 20% of the total amount dissolved, whereas at $23^{\circ}C$. the amount of uncombined SO_2 was about 50% of the total, that is, K_1 increased rapidly with temperature. This was for a solution of 5% concentration in each case. The value of the true dissociation constant was found to be approximately 0.02 and did not change much with temperature. It will be shown later from this work that all previous data below $12^{\circ}C$. has been at fault.

Campbell and Maass (17) made a somewhat different use of their data. H_2SO_3 may be assumed to behave

as a strong acid. This is reasonable because the organic sulphonic acids are strong acids. They assume that H_2SO_3 is almost completely ionized. Then instead of considering that water and sulphur dioxide combine to form H_2SO_3 which in turn dissociates into its ions, the mechanism may be considered analogous to the formation of NH_4^+ from $NH_3 + H^+$ and the reaction written thus:

$$SO_2 + OH^- + H^+ \rightleftharpoons HSO_3^- + H^+$$
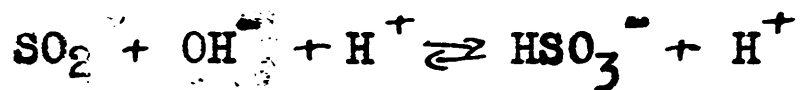
The extent of the reaction will be determined by the equilibrium expressed as follows:

$$[SO_2][OH^-] = K_3[HSO_3^-]$$

and

$$[H^+][OH^-] = K_w[H_2O]$$

Combining these

$$[SO_2][OH^-] = \frac{[SO_2]K_w[H_2O]}{[H^+]} = K_3[HSO_3^-]$$

or

$$[H^+][HSO_3^-] = \frac{K_w}{K_3}[SO_2][H_2O]$$

$$= K_b \left(c_{SO_2} - [HSO_3^-] \right)[H_2O] \qquad (14)$$

also

$$[SO_2] = c_{SO_2} - [HSO_3^-] = Hp \qquad (15)$$

Equation (15) may be derived from (13) as follows:-

Equation (13) may be written

$$c_{SO_2} = Hp \left(1 + \frac{[H_2O]}{K_1} \right) + [HSO_3^-] \qquad (13a)$$

If in the first place K_1 is large, or secondly $[H_2O]$

considered to be constant, (13) then becomes

$$c_{SO_2} = Hp + \left[HSO_3^-\right]$$

or

$$c_{SO_2} - \left[HSO_3^-\right] = Hp$$

At high temperatures the first is true and at low concentrations the second is true, so that the data obtained by Campbell and Maass (17) is not adequate to distinguish between equation (13) and (15).

When the data of Campbell and Maass was used and p, the partial pressure of SO_2, was plotted against the values of $c_{SO_2} - \left[HSO_3^-\right]$ a straight line was obtained as was required by equation (15). It must not be concluded though that no H_2SO_3 exists as such since the range of dilution in their work at high temperatures is not great enough to affect the proportionality of $\left[H_2SO_3\right]$ to $\left[SO_2\right]$ when $\left[H_2O\right]$ is constant. At any rate it would be too small to be evident in the plot. In this case two constants instead of three are used to express the equilibria, i. e, H and K_b. K_b, obtained in equation (14), bears a relation to the apparent dissociation constant through the following equations:

$$\left[H^+\right]\left[HSO_3^-\right] = K_a\left(c_{SO_2} - \left[HSO_3^-\right]\right)$$

$$= K_b\left(c_{SO_2} - \left[HSO_3^-\right]\right)\left[H_2O\right]$$

Hence $\qquad K_a = K_b\left[H_2O\right]$

It may be emphasized again that the measurements at high temperatures will be in accord with equation (15) because the equilibrium given by equation (4) is shifted to the left by rise in temperature as indicated by the data of C. Maass (16). Wright (23) and Baly and Bailley (24) showed by means of absorption spectra that free SO_2 exists in the solution which is in agreement with this idea.

From the above summary of previous work it is seen that measurements of greatest possible precision carried out at temperatures below $25^{\circ}C$. are essential in the determination of the true equilibria.

There is another reason for carrying out the work to be described apart from the use in the theory. All three systems investigated are of a particular interest from a commercial point of view. The importance of sulphur dioxide is emphasized in the sulphite cooking of wood pulp, in electrical refrigeration, as a disinfectant and preservative. Carbon dioxide is of importance to the manufacturers of carbonated beverages, while ammonia has a host of uses, the main one at the present time being that of a refrigerant.

The importance of this type of research has been proven since the publishing of the work carried out by Campbell and Maass (17). A paper company has informed the experimenters that by taking into account

their theoretical results it has been possible to get a 10% greater yield from their sulphite cook. An increased efficiency of this order is certainly worth while and establishes the value of this type of work.

The following section will contain a complete discussion of the apparatus and the experimental work with the exception of the respective purifications of each gas studied. Three sections will then be devoted to the presentation of the experimental results obtained for sulphur dioxide, carbon dioxide and ammonia respectively as well as the theoretical treatment, the corresponding theoretical data, and discussions of the intrinsic value of the data. In conclusion a summary of the entire research will be presented.

EXPERIMENTAL SECTION

The experimental part of this research may conveniently be divided into three sections for purposes of discussion. They are as follows:-

1. Explanation of apparatus

    (a) Evacuating system.

    (b) Gas purification apparatus.

    (c) Volume measuring apparatus and calibrations.

    (d) Thermostatic control and other electrical systems.

    (e) Type of conductivity cell used.

    (f) Conductivity apparatus.

    (g) Vapor pressure measurement.

2. Preparation of solutions.

3. Type calculation.

1. (a) Evacuating System.

It was possible to evacuate the system in three ways; by means of a Hyvac pump, a water pump, or a Langmuir diffusion pump backed by a Hyvac. At the time of drawing the accompanying diagram an automatic Toepler pump was being used but this was later replaced by the Langmuir diffusion pump. With the latter it was possible to evacuate the whole system to 1/1000 of a millimeter in half an hour.

The water pump was used mainly in altering the

FIGURE 1.

Diagram of Apparatus.
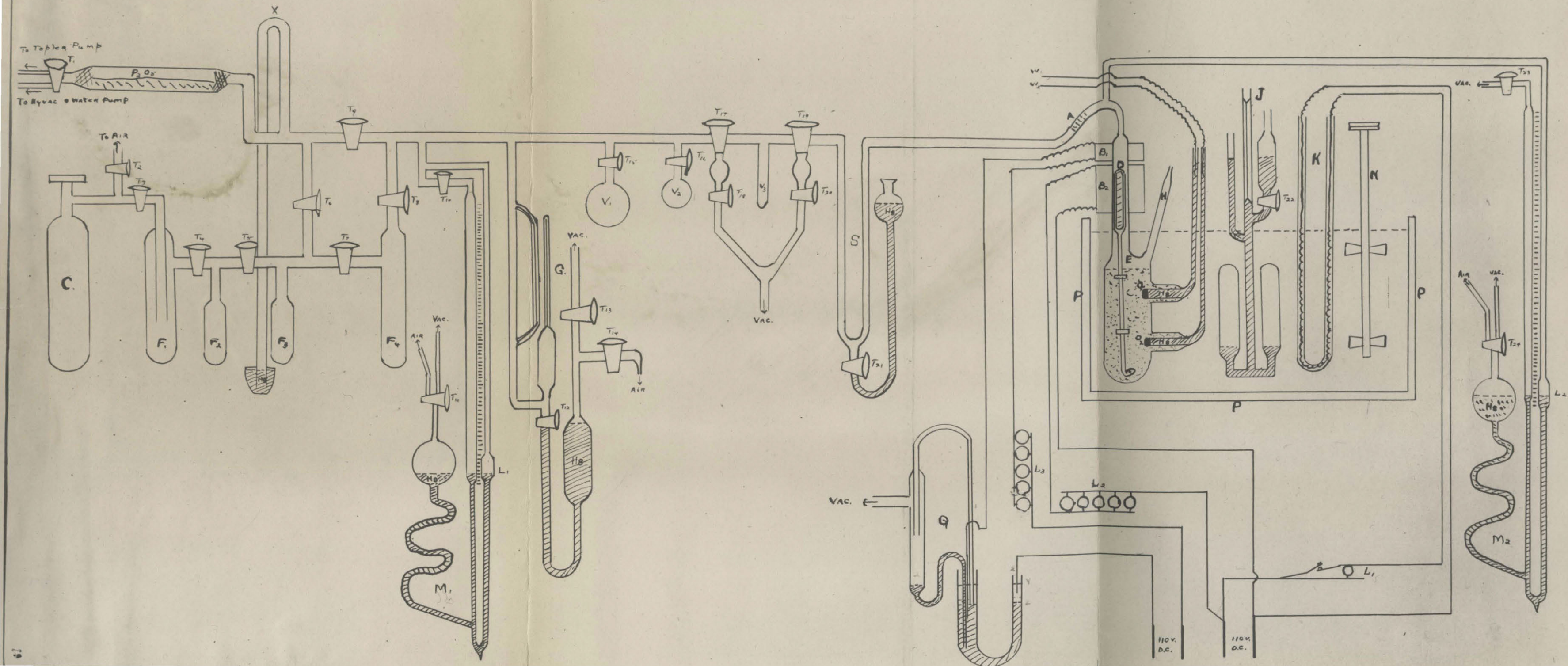
levels of the mercury in the manometers M_1 and M_2 as indicated in the diagram.

The Langmuir diffusion pump was found to be of exceedingly great value in obtaining and maintaining a good vacuum for the manometers M_1 and M_2, the left hand manometer arm being the evacuated one in each case. The McLeod Guage (G) was used for low pressure measurements.

(b)   Gas Purification Apparatus.

The gas to be used in this work in the case of sulphur dioxide and ammonia was obtained in liquid form in steel cylinders indicated by (C) in the diagram. The gas was transferred from the metal to the glass system by a "steel to glass" DeKhotinsky seal. The gas was allowed to pass through stopcock T_3 and was condensed by a carbon dioxide-ether mixture in F_1. From F_1 it was distilled into F_2, from F_2 to F_3 and from F_3 to F_4 rejecting "heads" and "tails" at each distillation. F_4 is the storage bulb in which the gas is held for future use. (X) is a rough manometer which served two purposes. It acted as a safety valve during the successive distillations of the gas.and also gave a measure of the vapor pressure of the gas which was a check on the rate of distillation.

(c) <u>Volume Measuring Apparatus and Calibrations.</u>

The volume measuring apparatus consisted of volumes V_1, V_2 and the connection tubing bounded by stopcocks T_8, T_9, T_{19} and the level L_1 on manometer M_1. The left arm of the manometer M_1 was evacuated and the right arm was always read at the level L_1. This was effected by alternately evacuating and compressing the air in the volume below the two-way stopcock T_{11} until the correct level was obtained. The pressure was then given by the difference of level of the two columns.

It was a simple matter to calibrate the volumes V_1 and V_2 by weighing them empty and then filled with water and applying the necessary corrections. To calibrate the connecting tubing was slightly more difficult and was done in two ways. The first method was by pressure changes. The volumes V_1 and V_2 having already been calibrated were filled with dry air to a known pressure. The connecting tubing was then completely evacuated and by opening T_{15} or T_{16} or both, a known volume of air at a known pressure was allowed to expand into the connecting tubing. The pressure in each case was read on manometer M_1. Then from the relation

$$p_1 V_1 = p_2(V_1 + X)$$

or $$X = \frac{p_1 V_1 - p_2 V_1}{p_2}$$

where p_1 = pressure in volume V_1 in cms. of Hg.

V_1 = volume of bulb V_1 in c.cms.

X = volume of connecting tubing.

p_2 = pressure in system after expansion.

it is possible to calculate X. In all of these

calibrations the temperature must be constant.

The other method of calibration of the connect-

ing tubing was as follows. The tubing was filled

with sulphur dioxide at a known temperature and

pressure. This gas was frozen out into a small

bulb using liquid air and the weight of the gas

was determined. In the relationship

$$pV = \frac{W}{M} RT$$

the only unknown is V and this may be calculated.

This method checked satisfactorily with the "pressure

change" method. The calibrations gave the following

values for the volumes

V_1 .... 587.82 c.c.

V_2 .... 175.69 c.c.

V_4 (.connecting tubing)   90.56 c.c.

The last figure in each of the above values is

doubtful.

The volumes V_1 and V_2 were immersed in a thermo-

stat in order to obtain accurate temperature readings

for the contained gas.

(d) Thermostatic Control and other Electrical Systems.

In working with aqueous solutions of gases temp-
erature control is an important factor. This is due
to the fact that the temperature coefficient of the
vapor pressures of such solutions is fairly high and
varies from gas to gas. A $10^{\circ}C$. change in an 11.5%
solution of sulphur dioxide changes the vapor press-
ure by 35%. A similar temperature change in an
aqueous solution of ammonia causes a 50% change in
the vapor pressure. For a 0.06% solution of carbon
dioxide a $10^{\circ}C$. change in temperature causes a 25%
change in vapor pressure. Hence it may be easily
concluded that the solution temperature must be
maintained accurately to $\pm .05^{\circ}C$.

In the diagram of the apparatus (P) represents
the thermostat. This contains a stirrer (N), an
electric heater (K), and a thermoregulator (J).
The heater consists of a coil of nichrome wire
immersed in glycoline in a pyrex tube.

The thermoregulator (J) is the "toluene over
mercury" type. Inside the two bulbs and fitting
closely against the walls are coils of copper gauze
to increase the heat conductivity and hence the
sensitivity. This regulator may be adjusted to any
temperature below the boiling point of toluene by
means of the mercury well on the right side. This

allows the mercury to have practically the same
level in the capillary at any temperature and obviates
the need of adding or withdrawing mercury when a diff-
erent temperature is desired. The temperature could
be regulated to $\pm 0.02^\circ$C. which was sufficiently
accurate for the purposes of this research.

The wiring arrangement with the thermoregulator
was of the usual type. The regulator operated a
relay which in turn made or broke the current through
the heater.

Due to the fact that it was necessary to work
through a closed system and also that it was very
essential to have adequate stirring maintained in the
conductivity cell an electromagnetic stirrer was used.
This was operated by two solenoids, a large one (B_2)
and a smaller one (B_1). (B_2) was kept permanently
in circuit thereby lifting the stirrer to the desired
distance from the bottom of the cell. The current
through (B_2) was regulated by the bank of lamps (L_2).
The current through (B_1) was regulated by the bank of
lamps (L_3). and was much greater than the current
through (B_2). This circuit was alternately made and
broken by the automatic mercury valve (Q). Thus
the stirrer moved up and down but never struck
bottom. This was a particularly good point since
the stirrer was large due to the large size of the

cell and a fairly heavy iron core was necessary to lift it. The fact that it did not strike bottom obviated the possibility of either breaking the stirrer or knocking the bottom out of the cell. When necessary the stirrer could be lowered gently to the bottom of the cell by gradually decreasing the current through (B_2).

The automatic mercury valve (Q) deserves a word of explanation, it being a very efficient part of the apparatus. The valve operates as follows:- Vacuum, as supplied by a water pump, is applied as indicated and mercury uses in (1) and (2) until the mercury in the U tube drops below the tip of (1). Air rushes in at the base of this tube and forces the mercury over into (2) from which it siphons back into the U tube and the cycle continues. At the beginning of the stroke the mercury level in the U tube is at (y) but during the stroke it drops to (Z) thereby breaking the circuit with the terminal (e). The mercury surface is covered to a good depth with water to prevent arcing. By regulating the vacuum and the depth to which the tube (1) dips into the mercury it is possible to obtain from 30 to 60 breaks per minute.

(e) TYPE OF CONDUCTIVITY CELLS USED.

It is quite obvious that in this work an ordinary type of conductivity cell would be useless. A cell had to be designed which was vacuum tight and which would have its electrodes so placed as to permit of continuous stirring without injury to the electrodes. It had to be strong, resistant to chemical action, and the temperature coefficient of its cell constant negligible.

A cell of the general type (E) (in the diagram) was constructed. (D) is the electromagnetic stirrer, (O_1) and (O_2) are platinized platinum electrodes, connection being made to the conductivity apparatus by means of mercury wells. (H) is an outlet through which the conductivity water is distilled into the cell. The distillation will be discussed later.

The conductivity cell was made of pyrex glass, it being the most resistant to chemical action. The body of the cell had a diameter of 3.5 cms. with a 1.5 m.m. wall, and was 12 cms. high. In order that the stirrer (D) would not interfere with the electrodes they were set in "bay windows" as is illustrated in the diagram. The platinum parts projected slightly inside the main wall of the cell but were at a safe distance from the stirrer.

Until about five years ago much difficulty had been experienced in making gas tight seals with glass

and the base metals. However the technique of this was developed by W. G. Housekeeper(47) of the Western Electric Research Laboratories. His technique was used by Campbell and Maass (17), previous workers in this laboratory, and this research benefited by their experiences.

The electrodes for this work were made by fusing very thin platinum foil, of about 0.00007 cms. thickness, into a pyrex tube, of about 0.75 cms. diameter, until it was molten. The two walls were then pressed together with the platinum foil sandwiched between them. Easily 50% of the electrodes made in this way were satisfactory. Each electrode was tested out separately before it was placed in the cell to see that it was vacuum tight.

The electrodes were carefully platinized and the cell constant was determined using tenth and hundredth normal potassium chloride which was re-crystallized three times before being used.

In the manufacture of the cell the glass blowers did not follow the specifications rigorously and an insufficient distance was left between the upper electrode O_1 and the neck of the cell. For this reason the cell constant varied depending on the height of the solution in the cell. After this was noted five etchings were made on the wall of the cell at regular intervals above the top electrode

and a cell constant was determined for each of these
levels. The amount of the liquid was regulated so
that it never rose above level #5.

In the calculation of the cell constant the data
due to Noyes (25) and his co-workers was taken as a
standard. This is considered to be the most accurate
measurement of the specific conductance of potassium
chloride. The cell constant values are given below:-

Level	Cell Constant
1	0.9759
2	0.9738
3	0.9718
4	0.9714
5	0.9714

It will be noted that beyond level #4 the cell constant
does not change. This level is about 2.5 cms. above
the upper electrode. The cell constant had no measur-
able temperature coefficient over the temperature
range at which this work was carried out, i.e.,
between $0^{o}C.$ and $25^{o}C.$

Due to the fact that very thin platinum foil
was used in the electrodes it was easily predicted
that the lead resistance would be appreciable. This
was calculated from the cell constant data as follows:-

$$\frac{K}{C_{s_1}} + r = R_{m_1}$$

$$\frac{K}{C_{s_2}} + r = R_{m_2}$$

where K = cell constant

C_{s_1} = specific conductivity of 0.1N KCL

C_{s_2} = "   "   " 0.01N KCL

R_{m_1} = measured resistance of 0.1N KCL

R_{m_2} = "   "   " 0.01N KCL

r = lead resistance

Since there are two equations with two unknowns, and since K is the same in each case, r may be calculated. It was found to be 0.418 ohms.

The cell mentioned above and illustrated in the apparatus diagram was used for carbon dioxide and sulphur dioxide. However it could not be used for ammonia as there was insufficient room for expansion, ammonia being much more soluble in water than sulphur dioxide or carbon dioxide. It was necessary to design a new cell to accommodate a large volume expansion, and this was done maintaining as far as possible the design of the original cell which had been found to be very satisfactory. This cell was made by the writer and the dimensions were such that one cell constant held for all levels attained by the solutions in the cell. The initial amount of water used in this latter cell was 21 c.c. and the maximum volume was 44 c.c. In the original cell the amount of water used was 119 c.c. and the

maximum volume was 130 c. c.

In the sulphur dioxide measurements the utmost
precision possible was required. This was facilitated
by using a conductivity cell with a large volume there-
by diminishing the percentage error in the preparation
of the solutions. The cell used in this work (volume
120 to 130 c. c.) was six or seven times larger than
any used by previous experimenters.

The cell constant of the ammonia cell was 9.716.
The cell was designed to have a large cell constant
in order that it might be used to measure the
conductivity of aqueous solutions of hydrogen chloride
at a future date. At the higher concentrations low
resistances will be measured and this large cell
constant will increase the accuracy of the measurement.

(f) Conductivity Apparatus.

The apparatus for the measurement of the electro-
lytic conductivities of the solutions in question con-
sisted of a Leeds and Northrup Kohlrausch slide wire,
two banks of Curtiss-wound resistance coils one read-
ing in steps of 1 ohm from 1 ohm to 1000 ohms, and
the other in banks of thousands reading up to 40,000
ohms. These resistances were checked against standard
coils and were found to be satisfactory. The slide
wire was also calibrated and gave satisfactory results.

A condenser with a maximum capacity of 0.00012 M.F.

was shunted across the resistance terminals in order to balance out any capacity that might exist in the cell at low concentrations when the water was more of a dielectric than a conductor. This aided in giving better end-points.

A Vreeland oscillator operating on a frequency of 1000 cycles was used as the source of current. This oscillator gives a pure sine wave with no harmonics.

One end of the slide wire was grounded to the plumbing in the laboratory. At no time were any body capacity effects noted. A two stage radio amplifier was used in the phone circuit. This gave much more sensitive end-points and increased the accuracy of the conductivity measurements.

(g) Vapor Pressure Measurement.

It will be shown in the discussion of the results that in order to obtain an accurate mathematical expression of the equilibria existing in gaseous-aqueous solutions the vapor pressures must be measured with the greatest possible accuracy. It is for this reason mainly that this research has not accomplished all that was desired of it. With the means at our disposal it was possible to measure vapor pressures to within 0.02 cms. It would have been much better to have measured them to 0.01 cms. or even 0.005 cms.

The pressure guage (M_2), was equipped with a

glass mirror scale. This was standardized against
an invar scale and found to be exceedingly accurate.
The vapor pressure was always read at a constant
level (L_2), the guage being manipulated similarly to (M_1).

In calculating the concentrations of the solut-
ions in the cell it was necessary to know the volume
of the dead space bounded by the surface of the sol-
ution in the cell, (T_{19}), and the level (L_2). This
volume varied with the level of the liquid in the
cell. The volume of the dead space was calibrated
by sealing the dry, empty cell into the system and
arriving at its volume by pressure changes as was
done in the calibration of the connecting tubing in
section (c). The volume of the cell was obtained by
running water into the cell from a burette. This
volume could be checked to 0.1 c.c. The volume of
the dead space was then obtained by subtracting the
volume of water in the cell from the total dead space
volume. The results are given below:-

Level	Vol. of Cell	Vol. of Dead Space
1	118.7 c.c.	109.5 c.c.
2	121.6 "	106.6 "
3	124.9 "	103.6 "
4	127.3 "	100.7 "
5	130.1 "	97.6 "

2. Preparation of Solutions.

The accurate preparation of aqueous solutions of gases involves many difficulties and very careful technique. In the case of sulphur dioxide which is easily oxidizable the solution must be absolutely free of air. Care must be taken to prevent water vapor from entering the gas measuring system. The system must be absolutely vacuum tight in order to prevent errors in vapor pressure measurement occasioned by small quantities of air leaking in. Also the apparatus must be such that it will withstand internal pressures of greater than one atmosphere which are met with during the injection of the gas into the conductivity cell.

The first step in the preparation of the solutions was to obtain good conductivity water and get it into the cell in as pure a state as possible. To do this a pyrex distillation cell, which had previously been thoroughly cleaned and dried, was sealed on to the arm (H) of the conductivity cell. Distilled water was injected into this cell from a weight pipette, the cell was sealed and the water frozen with a dry ice-ether mixture. The system was then evacuated by opening (T_{19}) which connected the two cells to the evacuating system. The ice was allowed to melt, (T_{19}) being closed after evacuation, and any residual air was extracted from the water.

The water was frozen again and evacuation was continued. This process was twice repeated to insure the complete removal of any residual air. Finally the conductivity cell was surrounded by an ice pack and the water was distilled into it very slowly, the process taking at least twelve hours. The distillation cell was then removed by sealing it off at the constriction above (H), at the same time sealing the cell. During the distillation the U tube (S) was filled with mercury. In this way the distillation was carried out in a system free from stopcocks.

At the beginning of each run the conductivity of the water, as prepared above, was carefully determined . As a rule it was of the order of 1.0 to 1.5 x 10^{-6} reciprocal ohms. A correction was made for this in all conductivity values. In the case of sulphur dioxide this correction was generally negligible but in the cases of ammonia and carbon dioxide it was an important factor.

The next step was the injection of the gas into the cell. After the volumes had been completely evacuated they were flushed out with the gas to be used. Finally they were filled with the gas, which was stored in (F_4), to approximately atmospheric pressure, the pressure being read on the manometer (M_1). Room temperature and the temperature of the bath containing the volumes V_1 and V_2 were read on

accurately calibrated thermometers. Room temperature was taken as the mean of the readings taken from four thermometers distributed at regular intervals along the connecting tubing.

The gas was then condensed into the small tube (V_3) using a dry ice-ether mixture. (V_3) is bounded by two pressure stopcocks (T_{17}) and (T_{19}). After the gas was condensed into (V_3), (T_{17}) was closed and (V_3) was gently warmed. Consequently a considerable pressure was built up in this small volume, (T_{19}) was opened slowly and the gas rushed into the cell with such violence that there was no possibility of water vapor penetrating through (T_{19}). This procedure was continued until all possible gas was driven out of (V_3). Then, (T_{19}) being closed, (T_{17}) was re-opened and the residual pressure was read on (M_1). During the course of the injection the contents of the cell were stirred vigorously. Knowing the original and final pressures, volumes, and temperatures it was possible to calculate the amount of gas injected into the cell.

3.   Sample Calculation.

The working principles of the apparatus have just been discussed. It might be well at this point to give a sample calculation showing the method of arriving at the concentration of the solution in the cell.

As a beginning, all pressures as read during the course of an experiment were reduced to centimeters of mercury at 0°C. using the data found in Beilstein's Chemical Tables for this correction.

Molecular weight isothermals were plotted using the data due to Carpenter (46). The molecular weight of the gas at each pressure and temperature could be picked off these curves.

The weight of gas injected each time was calculated as follows:-

$$m_1 = \frac{p_1 V_3 M_1}{RT_3} \qquad \frac{p_1 V_4 M_2}{RT_4}$$

$$m_2 = \frac{p_1' V_3' M_1'}{RT_3'} \qquad \frac{p_1' V_4 M_2'}{RT_4'}$$

From this

$$W = m_1 - m_2$$

where

p_1 = pressure of gas before injection.

p_1' = " " " after "

V_3 = volume of connecting tubing.

V_4 = " " measuring bulbs used

i.e., (V_1) and (V_2) in the diagram.

T_3 = room temperature before injection.

T_3' = " " after injection.

T_4 = temperature of the immersed bulbs before injection.

T_4' = temperature of the immersed bulbs after injection.

M_1 = molecular weight of gas at T_3 and p_1

M_2 =   "   "   "   "   " T_4 and p_1

M_1' =   "   "   "   "   " T_3' and p_1'

M_2' =   "   "   "   "   " T_4' and p_1'

m_1 = weight of gas in the system before injection.

m_2 =   "   "   " "   "   "   after   "

W = weight of gas injected.

R = the gas constant.

In order to arrive at the correct concentration in the liquid phase it was necessary to know the amount of gas present in the vapor phase when the system was at equilibrium. This was derived as follows:-

$$W_1 = \frac{(p - p_{H_2O})\, V_1 M_v}{R T_1}$$

where

p = total vapor pressure.

p_{H_2O} = partial pressure of water vapor.

V_1 = volume of dead space.

M_v = molecular weight of gas at T_1 and $(p - p_{H_2O})$

T_1 = temperature of vapor.

R = gas constant.

W_1 = weight of gas in dead space.

From these two calculations the weight of gas

in solution was given by

$$W_2 = W - W_1$$

The percentage of gas in the solution was given by

$$\% \ Gas = \frac{W_2 \ x \ 100}{W_2 + Weight \ of \ Water \ in \ Cell.}$$

This may easily be transformed into gram mols per

litre as follows:

$$Gm.Mols/l. = \frac{\% \ Gas \ x \ 1000 \ x \ d}{100 \ x \ M}$$

where d = the density of the solution

M = the theoretical molecular weight of the gas

The specific conductivity was calculated in

the ordinary way.

$$Spec. \ Cond. = \frac{1}{R_1 - r} - \frac{1}{R_2} \ K$$

where R_1 = measured resistance of the solution

r = lead resistance

K = cell constant

R_2 = resistance of the conductivity water.

It will be noted that the preliminary calc-

ulations were not difficult theoretically but they

were very lengthy. As a rule it took three days

to make a run and three or four days to calculate

it. Further calculations with respect to equilibria

occurring in these solutions will be discussed later.

SULPHUR DIOXIDE.

As was indicated in the introduction very accurate data has to be obtained for sulphur dioxide in order to obtain a true insight into the equilibria. For this reason particular care was taken and more time was spent on this system than on the other two.

A cylinder of liquid sulphur dioxide was obtained from the Ansul Chemical Co. in Marinette, Wisconsin. Analysis showed this gas to be very pure but in order to insure the greatest purity possible it was subjected to three consecutive distillations as described in the experimental section. This gave a beautifully clear sample of liquid sulphur, dioxide. Freezing point and vapor pressure determinations showed it to be extremely pure and it was considered ready for use.

The method of preparing the solutions has been described in the experimental section. In each case the temperature of the conductivity cell was held constant and the concentration was raised by consecutive injections of gas. This was considered to be a more accurate procedure than varying the temperature at one concentration. Time was also saved due to the fact that relatively high concentrations were reached and the greatest time lag

was involved in the injection of the gas.

Tables 1, 2; 3, and 4 and Figures 2 and 3 give the experimental data obtained for sulphur dioxide. It should be mentioned here that this is the second set of data for sulphur dioxide that has been obtained by the writer. A set of data was obtained in 1928-29 which was checked by a similar set in 1929-30. The two sets of results were quite gratifying in as much as they gave admirable checks. Only slight changes were noted in the 1929-30 conductivity measurements. These latter measurements, however, were taken as being the most nearly correct since a better conductivity outfit, the one described in the previous section, had been used. There was no noticeable difference in the vapor pressure data.

An inspection of the conductivity and vapor pressure curves shows that they are quite regular within themselves. This is a strong argument in their favor. It was possible to cross check them by taking a certain concentration at say $10^{\circ}C$. and raising the temperature to 18° and $25^{\circ}C$. and taking vapor pressure and conductivity readings. The greatest deviation found by this method of checking was 0.1%. In this way the regularity and accuracy of procedure was proven.

TABLE 1.

System Sulphur Dioxide-Water.
$0^{o}C.$

Reading.	%SO₂	Partial Pressure of SO₂ (cms Hg.)	Specific Conductivity.
1	0.1369	0.17	0.00339
2	0.3374	0.63	0.00650
3	0.8888	1.97	0.01253
4	2.284	6.05	0.02255
5	3.978	11.55	0.03135
6	5.597	17.30	0.03800
7	8.630	29.21	0.04804
8	11.52	41.63	0.05560
9	14.23	55.02	0.06158

Weight of water used = 116.010 gms.

TABLE 2.

System Sulphur Dioxide-Water.

10°C.

Reading.	% SO$_2$	Partial Pressure of SO$_2$ (cms Hg.)	Specific Conductivity.
1	0.1267	0.35	0.00366
2	0.3414	1.00	0.00748
3	0.6360	2.12	0.01136
4	1.261	4.71	0.01759
5	2.593	10.98	0.02727
6	4.256	19.52	0.03638
7	5.872	28.37	0.04355
8	8.937	46.62	0.05431
9	11.68	64.18	0.06189
10	13.03	73.58	0.06491

Weight of water used = 115.187 gms.

TABLE 3.

System Sulphur Dioxide-Water.

18°C.

Reading.	% SO$_2$	Partial Pressure of SO$_2$ (cms Hg.)	Specific Conductivity.
1	0.0816	0.32	0.00296
2	0.2605	1.10	0.00689
3	0.5563	2.68	0.01143
4	1.103	5.92	0.01757
5	2.458	14.83	0.02832
6	4.150	26.66	0.03800
7	5.773	39.01	0.04556
8	7.340	51.44	0.05169
9	8.831	63.69	0.05667
10	10.30	76.04	0.06108

Weight of water used = 116.518 gms.

TABLE 4.

System Sulphur Dioxide-Water.

25°C.

Reading.	% SO$_2$	Partial Pressure of SO$_2$ (cms Hg.)	Specific Conductivity.
1	0.1735	0.79	0.00545
2	0.5448	3.42	0.01174
3	1.056	7.37	0.01775
4	1.809	13.61	0.02443
5	3.116	25.28	0.03355
6	4.672	40.00	0.04201
7	6.184	55.00	0.04866
8	7.640	69.88	0.05416
9	8.756	81.17	0.05769

Weight of water used = 116.416 gms.

FIGURE 2.

System Sulphur Dioxide-Water.

Partial Vapor Pressures of Sulphur Dioxide.

SULPHUR DIOXIDE.
VAPOR PRESSURES.
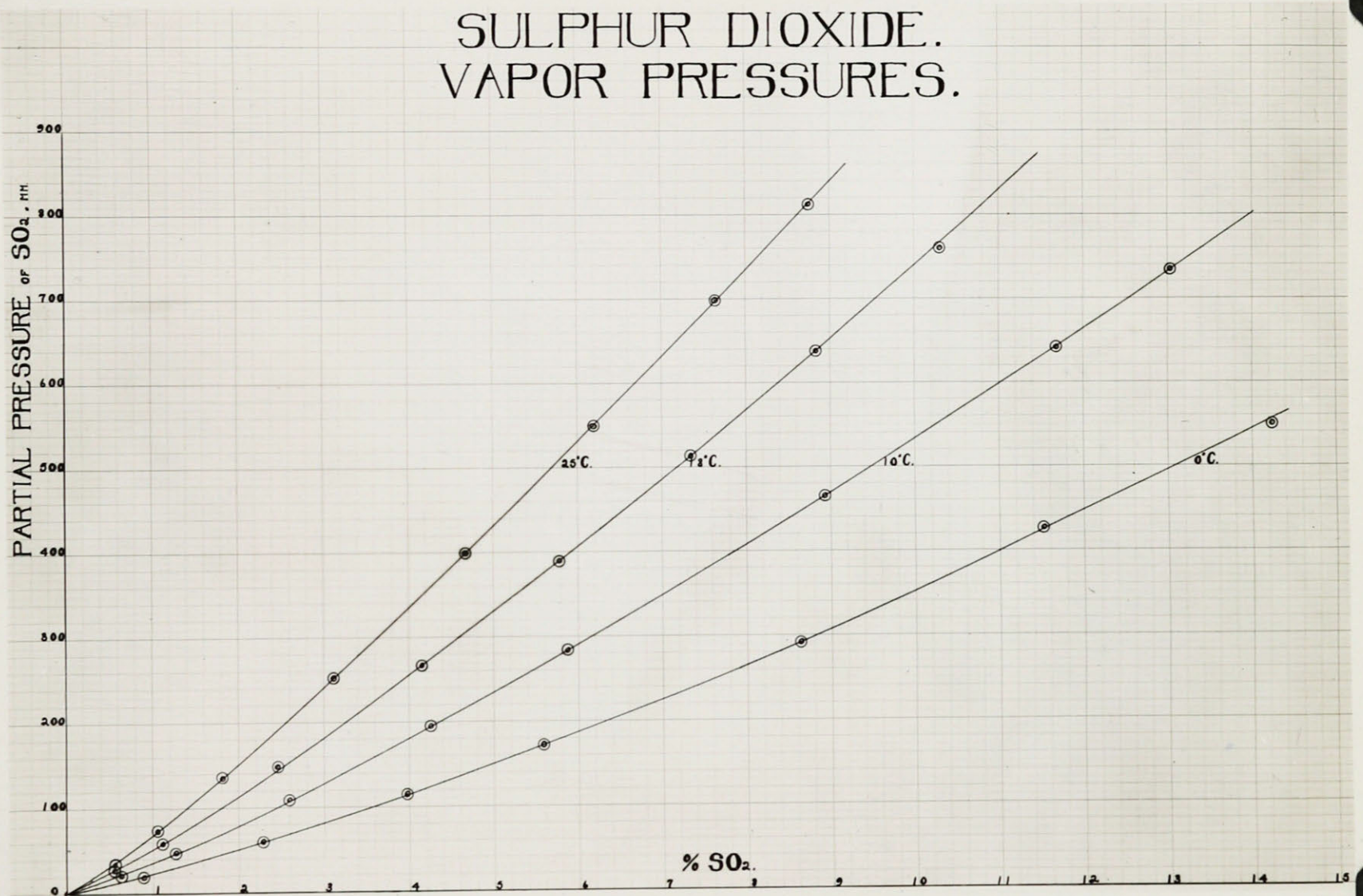
FIGURE 3.

System Sulphur Dioxide-Water.

Specific Conductivity of Sulphur Dioxide Solutions.

SULPHUR DIOXIDE.
SPECIFIC CONDUCTIVITY.
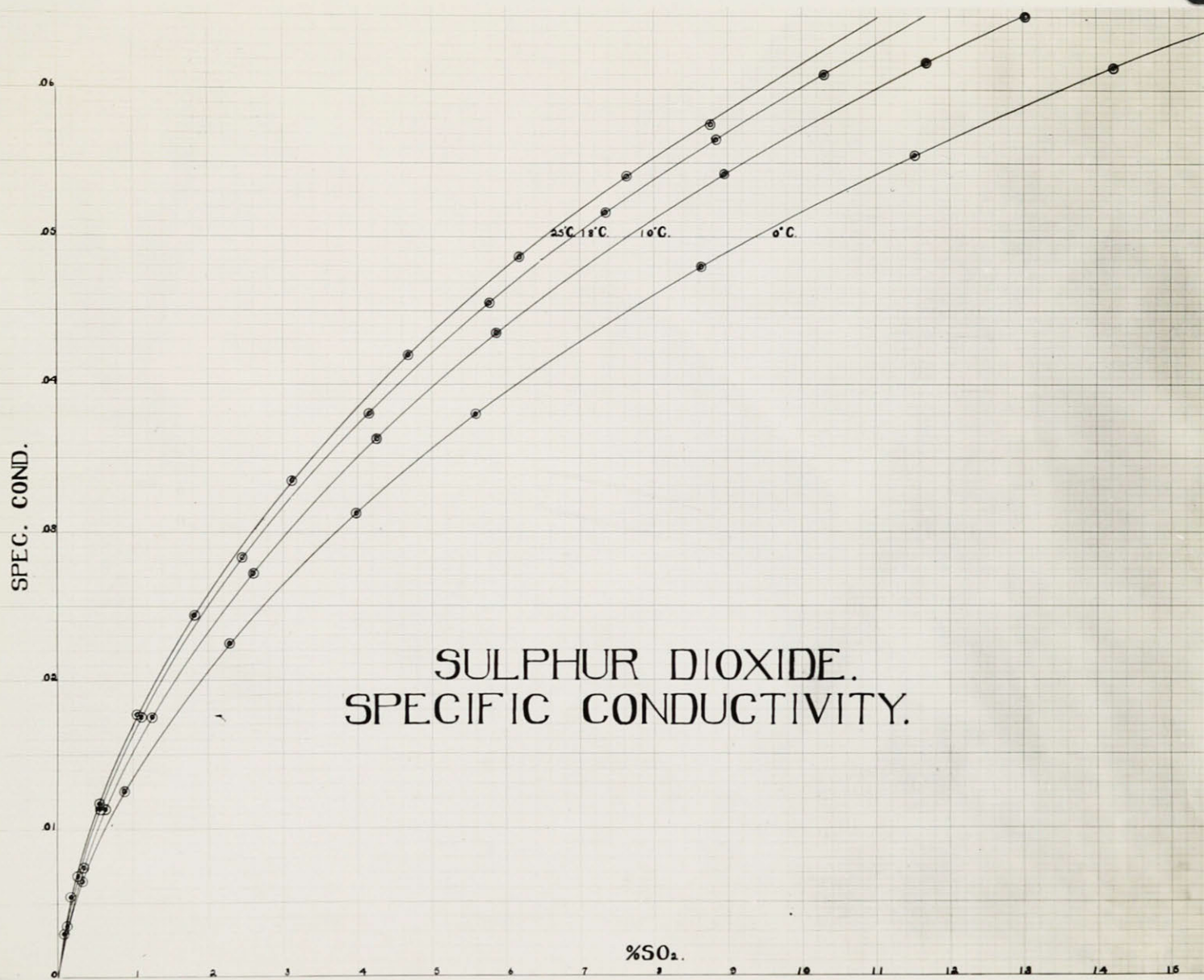
At $25^{\circ}C$. the vapor pressure values obtained by
C. Maass(16), and Campbell and Maass(17) are in
agreement with themselves but are 2% higher than
the values obtained in the present work. There is
also an irregularity in the lower pressures amount-
ing to about 1%. At $10^{\circ}C$. the results of C. Maass
(16) are even more seriously in error. The app-
aratus used by these experimenters, as mentioned
before, was designed to measure high pressures
and for this reason low pressures could not be
obtained with as great accuracy.

The conductivity data of C. Maass(16), and
Campbell and Maass(17) check to an approximation.
However their results are 0.66% higher than the
present values at the higher concentrations and
increase in error at the lower concentrations. The
deviation may be attributed to the use of a small
reaction chamber (20 to 25c.c.) thereby cutting
down the accuracy of the determination of the
concentration. Higher vapor pressures and cond-
uctivities would also point to the presence of
some volatile, soluble impurity. This latter is
not highly probable.

The theoretical treatment of sulphur dioxide
as developed to date has been discussed in the
introduction. It was quite apparent that over the

temperature and concentration range covered in this work that equation (13), as developed by C. Maass(16), was the most rigorous and should be the logical starting point for any further development.

The accompanying figure will show that the approximation due to Campbell and Maass(17) does not hold at the lower temperatures and with the more accurate data. When $C_{SO_2} - \left[HSO_3^-\right]$ is plotted against the partial pressure of sulphur dioxide above the solution a decided curvature is noted, which increases with decreasing temperature as is shown by the straight dotted lines. It is possible to predict this curvature from the equation

$$C_{SO_2} = Hp \left(1 + \frac{\left[H_2O\right]}{K_1} \right) + \left[HSO_3^-\right]$$

With increasing temperature K_1 increases rapidly and with increasing SO_2 concentration $\left[H_2O\right]$ decreases. The combined effect of these two factors tends to diminish the value of $1 + \frac{\left[H_2O\right]}{K_1}$ and at an infinitely high concentration and temperature this term would become unity and the equation would become that of a straight line. This proves that had the work of Campbell and Maass(17) been sufficiently accurate they would have obtained curved plots at their

FIGURE 4.

System Sulphur Dioxide-Water.

Plot of $C_{SO_2} - \left[HSO_3^-\right]$ against Partial Pressure of SO_2.
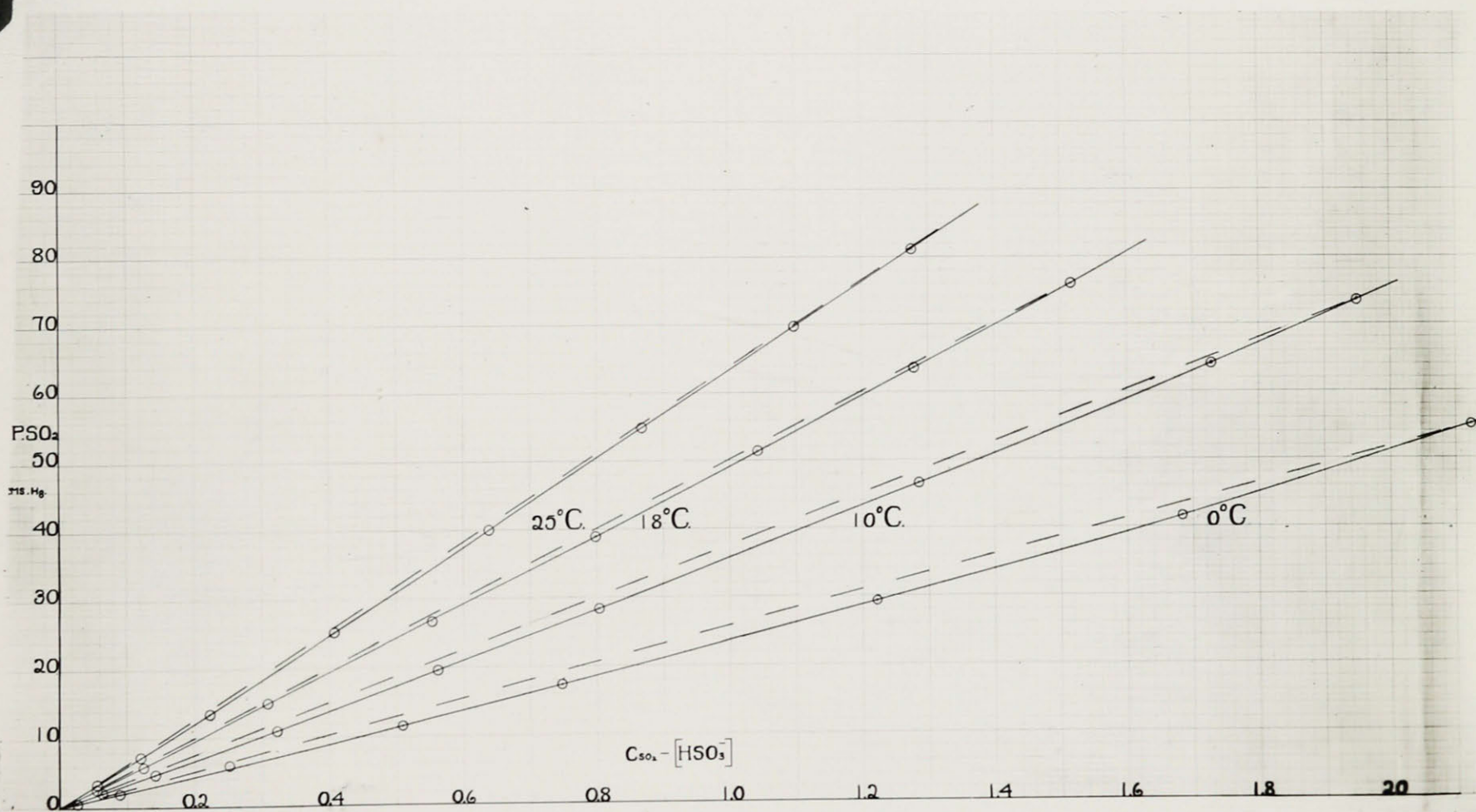
lower temperatures and approximations to straight lines at the higher temperatures. However, as has been stated before, their water concentration did not vary enough to warrant this.

In the evaluation of the constants H and K_1 in the present work equations (10) and (11) due to C. Maass(16) were taken as a starting point.

$$c_{H_2O} = \left[H_2O\right] + \left[H_2SO_3\right] + \left[HSO_3^-\right] \qquad (10)$$

$$c_{SO_2} = \left[SO_2\right] + \left[H_2SO_3\right] + \left[HSO_3^-\right] \qquad (11)$$

From (11)

$$c_{SO_2} = Hp \left(1 + \frac{\left[H_2O\right]}{K_1}\right) + \left[HSO_3^-\right] \quad (or\left[H^+\right])$$

$$c_{SO_2} - \left[H^+\right] = Hp \left(1 + \frac{\left[H_2O\right]}{K_1}\right)$$

$$= Hp \left(1 + \frac{c_{H_2O} - c_{SO_2} + Hp}{K_1}\right)$$

For convenience let $c_{SO_2} - \left[H^+\right] = a$

and $c_{H_2O} - c_{SO_2} = b$

Then

$$a = Hp \left(1 + \frac{b + Hp}{K_1}\right) \qquad (16)$$

H and K_1 are the only unknowns in equation (16). It was transformed into a quadratic and by inserting values for the other terms, a, b, and p, in two such equations values for H and K_1 were calculated.

From this calculation values of H were found to be very small and negative. It was quite obvious that H must be small and positive and that the negative value obtained could be attributed to small experimental errors which were just large enough to transform H from a small positive to a small negative quantity.

After a careful consideration of the situation the following procedure was adopted.

$$a = Hp \left(1 + \frac{b + Hp}{K_1} \right) \qquad (17)$$

$$A = HP \left(1 + \frac{B + HP}{K_1} \right) \qquad (18)$$

(17) and (18) are equations representing two points on a sulphur dioxide isothermal. From previous calculations it was concluded that the value of Hp was small compared with b. Hence, for the time being, Hp was disregarded in the term $(b + Hp)$ and the equations became

$$a = Hp \left(1 + \frac{b}{K_1} \right) \qquad (19)$$

$$A = HP \left(1 + \frac{B}{K_1} \right) \qquad (20)$$

Divide (19) by (20)

$$\frac{a}{A} = \frac{p \left(1 + \frac{b}{K_1} \right)}{P \left(1 + \frac{B}{K_1} \right)}$$

By letting $\frac{a}{p} = d$ and $\frac{A}{P} = D$ and rearranging it follows that

$$K_1 = \frac{b\left(\frac{B}{b} - \frac{D}{d}\right)}{\frac{D}{d} - 1} \qquad (21)$$

By substituting the value of K_1 obtained in (21) in equations (19) and (20) it was possible to calculate H.

There was considerable incoherent variation in K_1 and it appeared to be very sensitive to small errors in experimental data. This was overcome to a large extent by plotting % SO_2 against d for each temperature considered and by inspection picking out pairs of logical d points from which to calculate K_1. An average of the values for K_1 thus obtained at $25^\circ C.$ and $18^\circ C.$, when substituted in equation (16), permitted of a calculation of "a" (i.e. $c_{SO_2} - [H^+]$) within two or three percent. By trial and error, i.e. by varying the values of H and K_1 slightly, the correct values of "a" were obtained within 0.2%. In this way the validity of the constants H and K_1 at 25° and $18^\circ C.$ was established.

This work was lead farther afield than was originally expected. At $10^\circ C.$ the average approximate value of K_1, as calculated from (21),

was found to be -2.6, and at $0^{\circ}C.$ it was -12.1.
Equation (16) may be transformed to

$$K_1 = \frac{Hpb - H^2p^2}{a - Hp} \qquad (22)$$

In equation (22) H^2p^2 is small with respect to
Hpb. H is a constant and at any given concentrat-
ion and temperature p is a constant, hence an un-
usually small value of K_1 would be caused by an
excessive diminution of the value of b. Since
b is the value of the apparent concentration of the
water, a low value of b would indicate that water
was being removed by some means and would point
towards hydrate formation. This is in agreement
with the fact that below $12.1^{\circ}C.$ a stable hepta-
hydrate forms.

In order to determine the extent of the hydrate
formation a new equilibrium must be considered,
i. e. between the hydrate, the sulphur dioxide,
and the water:

$$SO_2 + nH_2O \rightleftarrows SO_2 \cdot nH_2O$$

$$[SO_2] \, [H_2O]^n = \propto [SO_2 \cdot nH_2O] \qquad (23)$$
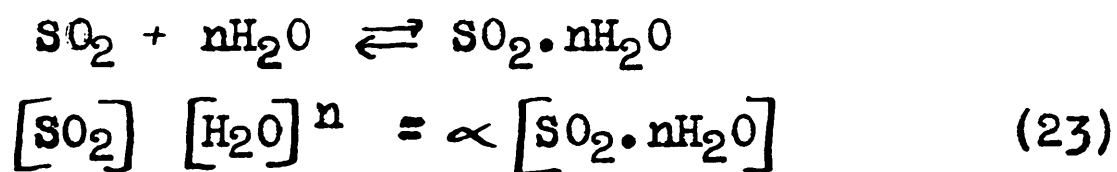
where n = the number of molecules of water in the
hydrate. The equilibrium

$$[SO_2] \, [H_2O] = K_1 [H_2SO_3]$$

must also be kept in mind.

As a starting point

$$c_{SO_2} = [SO_2] + [H_2SO_3] + [H^+] + [SO_2 \text{ aqu.}] \tag{24}$$

$$c_{H_2O} = [H_2O] + [H_2SO_3] + [H^+] + n[SO_2 \text{ aqu.}] \tag{25}$$

$$c_{H_2O} - c_{SO_2} = [H_2O] - [SO_2] + (n-1)[SO_2 \text{ aqu.}]$$

$$b = [H_2O] - [SO_2] + (n-1)\frac{[SO_2][H_2O]^n}{\alpha}$$

$$= [H_2O] - Hp + \frac{(n-1)Hp[H_2O]^n}{\alpha} \tag{26}$$

Also from equation (24)

$$c_{SO_2} = Hp + [H^+] + \frac{[H_2O]Hp}{K_1} + \frac{[H_2O]^n Hp}{\alpha}$$

and

$$c_{SO_2} - [H^+] = Hp\left(1 + \frac{[H_2O]}{K_1} + \frac{[H_2O]^n}{\alpha}\right)$$

For convenience let $[H_2O] = [x]$, then

$$a = Hp\left(1 + \frac{[x]}{K_1'} \frac{[x]^n}{\alpha}\right) \tag{27}$$

or

$$a - Hp - \frac{[x]Hp}{K_1} = \frac{Hp[x]^n}{\alpha} \tag{28}$$

From (26)

$$b + Hp - [x] = \frac{(n-1)Hp[x]^n}{\alpha} \tag{29}$$

and combining (28) and (29)

$$\frac{b + Hp - [x]}{n - 1} = a - Hp - \frac{[x]Hp}{K_1} \tag{30}$$

The value of $[x]$ may be calculated from equation
(30) provided that the values of H and K_1 are known
at $10\,^{\circ}C$. Furthermore the numerical value of 7 for
n may or may not be legitimate. What equation (30)
really represents is that water is removed from
active participation in the equilibrium in ways
other than the straightforward H_2SO_3 formation.
Whether water is used up in the hydration of the ions
is a moot question. Equation (30) in which n is
given the somewhat arbitrary value of 7 can therefore
only be looked upon as a crude approximation, valuable
however in showing that another factor has to be
taken into account.

What is said above has to be borne in mind in all
the calculations involving the above equation. All
that can be hoped for is that reasonable values of H,
K_1, and α will satisfy the experimental results.
At higher temperatures also hydrate formation prob-
ably has its influence, though the higher the temp-
erature the smaller will be its effect.

The values of H, and K_1 were known for $18\,^{\circ}$ and
$25\,^{\circ}C$. and it was a debatable question whether a
straight line extrapolation to $10\,^{\circ}$ and $0\,^{\circ}C$. would
be legitimate. On investigating constants similar
to H for inert gases, as given in the literature,
it was found that they did not vary with temperature
according to a straight line relationship. Reference

was made to the apparent H calculated for SO_2 from the relation $H = \frac{a}{p}$. This, of course, exhibited curvature when plotted against temperature. An arbitrary value of H at $10^{\circ}C$. was obtained by calculating a variation of the real H correspond- ing to the variation of the apparent H. To obtain the corresponding K_1 the ratios of $\frac{H}{K_1}$ were calc- ulated at 18° and $25^{\circ}C$. and were extrapolated to $10^{\circ}C$. Since H had already been determined it was possible to calculate K_1.

Using these values obtained for H and K_1 the corresponding values of $[x]$ at $10^{\circ}C$. were calculated. The values of α were then determined by inserting these approximations in equation (29) and an average value of α was obtained. These values were remark- ably constant. Then by supplying the necessary values in equation (27) it was possible to calculate values of "a" very accurately, there being only an average mean deviation of 0.1% from the experimental values.

The real dissociation constant

$$K_2 = \frac{[H^+]\,[HSO_3^-]}{[H_2SO_3]} \tag{6}$$

was calculated as follows:

$$K_1 = \frac{[H_2O]\,[SO_2]}{[H_2SO_3]} \tag{4}$$

On rearranging and substituting

$$[H_2SO_3] = \frac{[H_2O]\,[SO_2]}{K_1} = \frac{(b + Hp)(Hp)}{K_1}$$

Hence

$$K_2 = \frac{K_1\,[H^-]^2}{(b + Hp)(Hp)}$$

K_2 is only calculated at 18° and $25^\circ C$. since the $10^\circ C$. calculations, as pointed out above, are only the result of arbitrary approximations.

The theoretical data calculated in connection with this work is presented in Tables 5, 6, 7, and 8 for temperatures of 0°, 10°, 18°, and $25^\circ C$. respectively. C_{SO_2} is the total amount of sulphur dioxide in the solution expressed in gram mols per litre. C_{H_2O} is the concentration of the water in the solution also expressed in gram mols per litre. The density values are those obtained by Campbell and Maass(17). $[HSO_3^-]$ is the concentration of the HSO_3^- ion and is obtained by dividing the specific conductivity by the limiting value given in the following table for the conductivity of H_2SO_3 and multiplying by 1000 to bring it to gram mols per

TABLE 5.

System Sulphur Dioxide-Water. 0°C.

% SO_2	Density.	C_{SO_2}	C_{H_2O}	Specific Cond. x 10^3
0.1369	1.0004	0.0213	55.46	3.39
0.3374	1.0015	0.0523	55.40	6.50
0.8888	1.0048	0.1393	55.26	12.53
2.284	1.0127	0.3608	54.92	22.55
3.978	1.0223	0.6342	54.46	31.35
5.597	1.0317	0.9005	54.05	38.00
8.630	1.0488	1.412	53.18	48.04
11.52	1.0604	1.905	52.08	55.60
14.23	1.0663	2.367	50.76	61.58
......	......	.....	.....	.....

$[HSO_3^-]$	"a"	"b"	K_a x 10^3
0.0135	0.0078	55.44	23.47
0.0259	0.0263	55.35	25.59
0.0500	0.0893	55.12	28.00
0.0900	0.2708	54.56	29.91
0.1251	0.5091	53.83	30.74
0.1517	0.7488	53.15	30.72
0.1917	1.221	51.77	30.11
0.2219	1.683	50.18	29.26
0.2458	2.123	48.40	28.46

TABLE 6.

System Sulphur Dioxide-Water. 10°C.

% SO_2	Density	c_{SO_2}	c_{H_2O}	Specific Cond. x 10^3
0.1267	1.0001	0.0197	55.43	3.66
0.3414	1.0012	0.0558	55.39	7.48
0.6360	1.0028	0.0995	55.29	11.36
1.261	1.0061	0.1978	55.12	17.59
2.593	1.0131	0.4097	54.75	27.27
4.256	1.0219	0.6784	54.30	36.38
5.872	1.0305	0.9436	53.80	43.55
8.927	1.0465	1.459	52.85	54.31
11.68	1.0575	1.926	51.82	61.89
13.03	1.0613	2.156	51.22	64.91
.....	......	.....	.....	.....

$[HSO_3^-]$	"a"	"b"	K_a x 10^3	"a" (calc.)
0.0117	0.0080	55.41	17.26	-----
0.0240	0.0318	55.34	18.13	0.0298
0.0365	0.0629	55.19	21.13	0.0631
0.0564	0.1414	54.93	22.55	0.1393
0.0875	0.3222	54.34	23.78	0.3207
0.1168	0.5616	53.62	24.29	0.5616
0.1398	0.8038	52.86	24.32	0.8041
0.1744	1.285	51.39	23.65	1.286
0.1986	1.728	49.90	22.84	1.732
0.2084	1.948	49.07	22.28	1.954

TABLE 7.

System Sulphur Dioxide-Water. $18^{\circ}C.$

% SO_2	Density.	c_{SO_2}	c_{H_2O}	Specific Cond. x 10^3	$[HSO_3^-]$
0.0816	0.9988	0.0127	55.39	2.96	0.0083
0.2605	0.9997	0.0406	55.35	6.89	0.0192
0.5563	1.0012	0.0868	55.25	11.43	0.0319
1.103	1.0040	0.1727	55.11	17.57	0.0491
2.458	1.0108	0.3877	54.71	28.32	0.0791
4.150	1.0195	0.6594	54.19	38.00	0.1061
5.773	1.0278	0.9255	53.74	45.56	0.1273
7.340	1.0357	1.186	53.26	51.69	0.1444
8.831	1.0432	1.436	52.76	56.67	0.1582
10.30	1.0498	1.687	52.28	61.08	0.1706

"a"	"b"	K_a x 10^3	K_2 x 10^3	"a" (calc.)
0.0044	55.38	15.53	17.52	
0.0214	55.31	17.31	27.64	
0.0549	55.16	18.57	31.29	
0.1236	54.94	19.48	33.58	0.1232
0.3086	54.32	20.27	35.18	0.3069
0.5533	53.53	20.36	35.69	0.5476
0.7982	52.82	20.29	35.46	0.7958
1.042	52.08	20.01	35.02	1.042
1.278	51.32	19.60	34.43	1.281
1.516	50.59	19.20	33.91	1.520

TABLE 8.

System Sulphur Dioxide-Water. 25°C.

% SO_2	Density.	C_{SO_2}	C_{H_2O}	Specific Cond. x 10^3	$[HSO_3^-]$
0.1735	0.9978	0.0270	55.27	5.45	0.0137
0.5448	0.9996	0.0849	55.20	11.74	0.0295
1.056	1.0010	0.1649	54.96	17.75	0.0446
1.809	1.0059	0.2838	54.81	24.43	0.0613
3.116	1.0123	0.4918	54.42	33.55	0.0842
4.672	1.0200	0.7433	53.96	42.01	0.1045
6.184	1.0275	0.9906	53.47	48.66	0.1222
7.640	1.0346	1.233	53.04	54.16	0.1360
8.756	1.0403	1.420	52.66	57.69	0.1449
.....	......	.....	.....	.....	......

"a"	"b"	K_a x 10^3	K_2 x 10^3	"a" (calc.)
0.0133	55.24	14.08	27.48	
0.0554	55.12	15.70	29.49	
0.1203	54.80	16.52	31.52	
0.2225	54.53	16.91	32.40	0.2194
0.4076	53.93	17.41	33.18	0.4055
0.6379	53.22	17.45	33.33	0.6379
0.8684	52.48	17.19	32.83	0.8720
1.097	51.81	16.86	32.37	1.102
1.275	51.24	16.46	31.92	1.273

litre. The values for the limiting conductivity of the HSO_3^- ion were obtained from the formula of Kohlrausch(18)

$$u_t = 44.3 \left\{ 1 + 0.0242(t - 18) + 0.00011(t - 18)^2 \right\}$$

using Kerp and Baur's(11) value at 25°C. as revised by Lindner(15). The values for the H^+ ion of course have been well established.

TABLE 10.

Limiting Conductivities of H_2SO_3.

Temperature (°C.)	H^+	HSO_3^-	H_2SO_3
0	224.2	26.4	250.6
10	275.5	36.0	311.5
18	315.0	44.3	359.3
25	348.5	49.7	398.2

The values given for "a" are those of $c_{SO_2} - \left[HSO_3^- \right]$ and represents the undissociated H_2SO_3 providing that all the SO_2 is combined with water. $c_{H_2O} - c_{SO_2}$ is the "b" value given and represents the amount of uncombined water assuming that all the SO_2 is combined with water. These assumptions are not true but this mode of tabulation serves as a convenient means in the calculations. The calculation of K_a and K_2 has been previously discussed, also the method of calculating "a".

The equilibria constants have been obtained

more accurately than ever before and fit in with
the experimental data within the range of experiment-
al error. The results of previous experimenters
have failed to show up definitely various fine
points which are quite important. For instance,
Campbell and Maass(17), Lindner(15), and Kerp and
Baur(11) noted that the value of the apparent dissoc-
iation constant, K_a, varied with temperature but they
did not notice any regular variation with changing
concentration. Figure 5 shows that there is a
distinct variation of K_a at all temperatures con-
sidered, the rate of increase being greater at the
lower concentrations. With increasing temperature
there is decreasing variation. This is quite in
agreement with the theory evolved above provided
that another factor, only important at very low
concentrations, is taken into account. This new
factor is the secondary dissociation of the H_2SO_3,
the additional H^+ ion causing an increase in K_a.

The equilibrium

$$H_2O + SO_2 \rightleftharpoons H_2SO_3$$
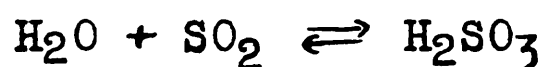
has the opposite effect causing a decrease in K_a
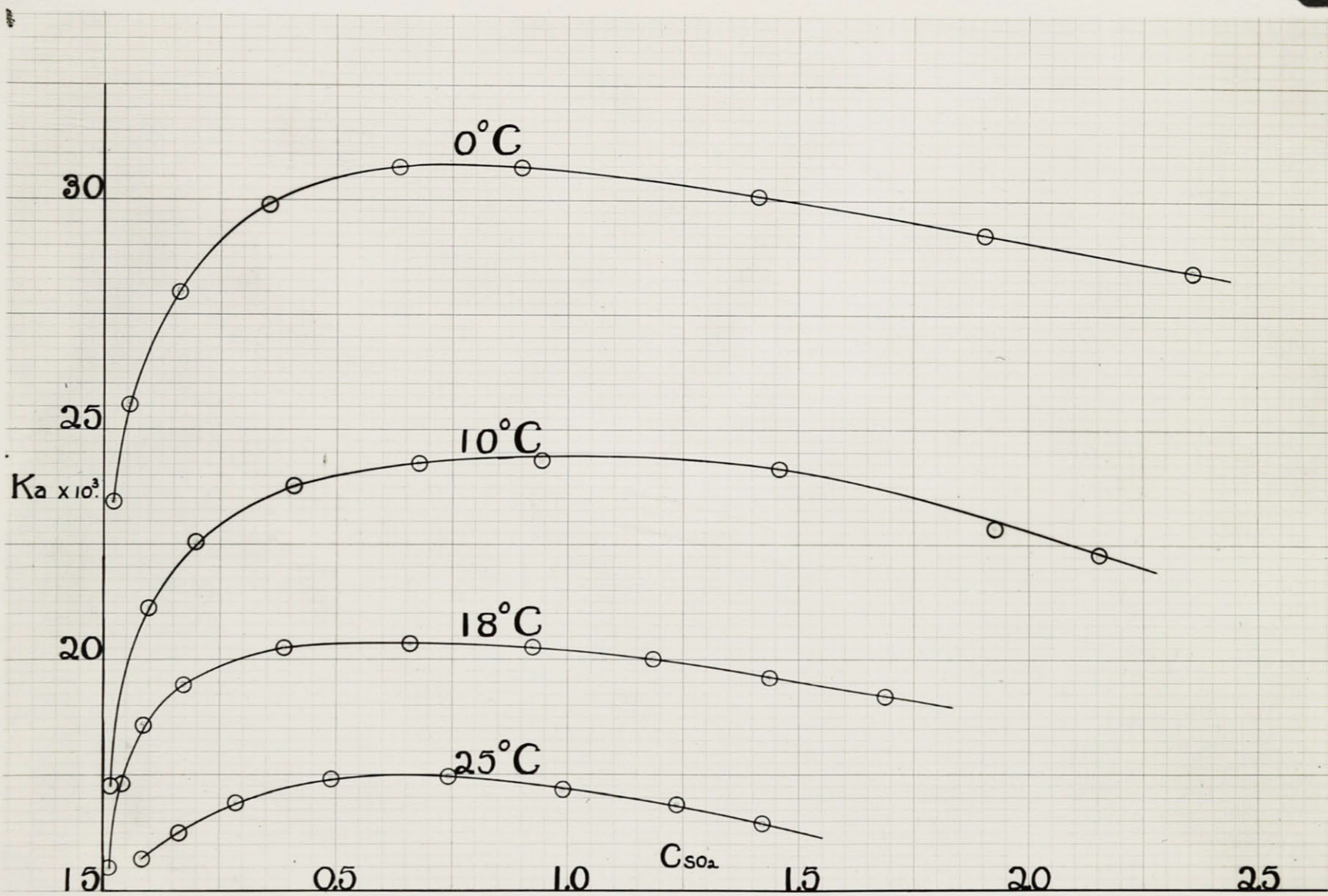with rise in concentration as given by the equation

$$K_a = \frac{K_2 [H_2O]}{K_1 + [H_2O]}$$

Since the secondary dissociation loses its effect

FIGURE 5.

System Sulphur Dioxide-Water.

K_a plotted against Concentration.

with increasing concentration a maximum value of
K_a must be reached. Since K_1 increases with rise
in temperature the rate of decrease in K_a beyond
the maximum concentration should be less at the
higher temperatures which was pointed out above.
Furthermore it can be predicted that the maximum
value of K_a is shifted to a higher concentration
with rise in temperature. This variation in K_a is
therefore, one of the best proofs of the existence
of uncombined SO_2, and also that the amount of free
SO_2 increases with rise in temperature.

In the comparison of the observed values with
those calculated on the basis of equation(16) it
is apparent that the poorest agreement is found
at the very low concentrations. This is due to
the secondary dissociation which has not been taken
into account.

The value of K_a reaches a maximum and remains
practically constant over a short range of concent-
ration but it then begins to fall off again. For
this reason it is illegitimate to strike an average
value. The maximum values agree very well with
the average values of previous experimenters.
Comparison is only possible at 0° and $25^\circ C$.

TABLE 11.

Comparison of Apparent Dissociation Constants.

Temperature	0°C.	25°C.
Kerp and Baur	----	17.4
Lindner	31.1	17.4
Campbell and Maass	31.3	17.3
This Work	30.7	17.4

Dissociation constants do not ordinarily vary to any great extent with temperature. The large variation in K_a proves that it is only an apparent dissociation constant. The values of K_2 at $18°$ and $25°C.$, which vary only slightly, prove that it is a true dissociation constant. K_2 varies with the concentration to about the same extent that K_a does. This follows from what has gone before. It is evident that K_2 will always be larger than K_a but will approach it in value when K_1 is small.

The following table contains the values for H and K_1 at the three temperatures investigated.

TABLE 12.

Temperature (°C.)	H	K_1
10	0.01080	36.80
18	0.00870	39.50
25	0.00758	48.51

It will be noted that the value of H decreases and that of K_1 increases with rising temperature. This is what would be expected from the respective equilibria

$$[SO_2] = Hp \qquad (2)$$

and

$$K_1 = \frac{[H_2O][SO_2]}{[H_2SO_3]} \qquad (4)$$

From equation(2) the percent of uncombined SO_2 can be readily calculated. The values given in the table below show their order of magnitude.

TABLE 13.

c_{SO_2} (percent)	SO_2 (percent)	
	18°C.	25°C.
2	0.626	0.732
4	1.407	1.608
6	2.221	2.573
8	3.071	3.457
10	3.962	-----

The constants H, K_1, and K_2 have not been evaluated for the 0°C. data. It was deemed sufficient proof for the theory to have consistent data at three temperatures. The calculations at 10°C. were very lengthy and it was foreseen that it would take even longer to handle the 0°C. data since it would necessitate finding values for H

and K_1 by trial. The extrapolation of the values of H and K_1 from 10^0 to 0^0C. could not be expected to follow the same ratio as from 18^0 to 10^0C. An immense amount of data covering carbon dioxide and ammonia still remained to be dealt with and it was considered more advisable to proceed with that rather than to continue with the sulphur dioxide.

After a discussion of the carbon dioxide and ammonia systems the conclusions to be drawn from the sulphur dioxide system will be summed up once more.

CARBON DIOXIDE

An investigation of the equilibria existing in aqueous
solutions of carbon dioxide presents essentially diff-
erent problems to those encountered in sulphur dioxide
systems. Sulphur dioxide has a solubility in water
sixty times greater than that of carbon dioxide.
Sulphurous acid behaves as a strong acid while carbonic
acid is very weak and has an extremely small dissociat-
ion constant. For these reasons the equilibria must
be investigated from a different standpoint as will be
seen in this section.

The carbon dioxide was generated in a Kipp loaded
with very pure marble and dilute hydrochloric acid.
The gas was passed through a water wash bottle to
remove any acid spray and then through two more wash
bottles, one containing alkaline potassium permanganate
and the other a solution of sodium carbonate. It was
then passed slowly through a large phosphorus pentoxide
tube to dry it and was condensed with liquid air. This
was followed by a triple distillation similar to the
one discussed in the experimental section.

The only possible impurity in the gas was a trace
of hydrogen chloride. A test was made for this by
bubbling a sample of the gas through a solution of
silver nitrate. After half an hour no precipitation
of silver chloride was noted which was considered

sufficient evidence that no hydrogen chloride was present.

Due to the fact that carbon dioxide possessed such a small solubility in water every precaution had to be taken in the measurement of the amount of gas injected. The rate of solution was very slow and a long time was necessary to reach equilibrium, usually about 90 minutes. After completing a run at 0°C. it was decided that much time would be saved if solutions were prepared at 10°C. and after making measurements raise the temperature to 18° and 25°C. since equilibrium was reached more rapidly when the gas was coming out of the solution than when it was going into solution. This procedure was found to be much more satisfactory.

Tables 13, 14, 15, and 16 contain the experimental data and the theoreticaldata derived from it. The units are the same as those used for sulphur dioxide. Figure 6 presents the vapor pressure relationships and Figure 7 the specific conductivity.

It should be stated at this point that the vapor pressure data at 0°C. is inaccurate. The plot in Figure 6 would indicate that the evacuated arm of the manometer had sprung a leak at some time after a concentration of 0.25% CO_2 had been reached since the vapor pressure as measured is too low. Hence the 10°, 18°, and 25°C. data only will be considered in the discussion.

TABLE 14.

System Carbon Dioxide-Water. $0^{\circ}C$.

% CO_2	c_{CO_2}	Specific Cond. $x\ 10^6$	Partial Pressure of CO_2 (cms Hg)
0.0202	0.00458	7.19	5.70
0.0661	0.01503	14.02	16.00
0.1412	0.03208	20.89	35.27
0.2143	0.04870	25.90	53.02
0.2929	0.06656	30.57	68.13
0.3676	0.08354	34.42	85.30
......	....	......	......

$[H^+]$	"a"	$K_a\ x\ 10^8$	$H\ x\ 10^5$
0.000028	0.00456	17.44	80.00
0.000055	0.01497	20.18	93.58
0.000082	0.03200	20.93	90.72
0.000101	0.04860	21.23	92.06
0.000119	0.06640	21.65	97.47
0.000135	0.08341	21.85	97.81
			......
			Av.=91.94

TABLE 15.

System Carbon Dioxide-Water. $10^\circ C$.

% CO_2	c_{CO_2}	Specific Cond. x 10^6	Partial Pressure of CO_2 (cms Hg)
0.0240	0.00545	12.30	8.17
0.0611	0.01389	20.18	20.61
0.1297	0.02947	29.89	42.41
0.1975	0.04488	37.00	64.48
0.2475	0.05624	41.34	83.56
....	....	....	....

$[H^+]$	"a"	K_a x 10^8	H x 10^5
0.000038	0.00541	26.87	66.22
0.000062	0.01383	28.30	67.11
0.000092	0.02938	29.22	69.28
0.000115	0.04477	29.39	69.45
0.000128	0.05611	29.27	67.16
			....

Av. $=67.84$

TABLE 16.

System Carbon Dioxide-Water. $18^{\circ}C$.

% CO_2	c_{CO_2}	Specific Cond. x 10^6	Partial Pressure of CO_2(cms Hg)
0.0216	0.00491	14.92	9.23
0.0580	0.01318	24.80	22.98
0.1140	0.02590	35.25	49.14
0.1740	0.03954	43.69	74.45
....	....	....	....

$[H^+]$	"a"	K_a x 10^8	H x 10^5
0.000039	0.00487	32.48	52.82
0.000066	0.01312	33.35	57.10
0.000094	0.02581	34.23	52.52
0.000116	0.03942	34.44	52.94
			....

Av. = 53.84

TABLE 17.

System Carbon Dioxide-Water. 25°C.

% CO_2	c_{CO_2}	Specific Cond. x 10^6	Partial Pressure of CO_2(cms Hg)
0.0200	0.00454	16.71	9.89
0.0502	0.01141	27.00	25.32
0.1025	0.02329	39.33	54.00
0.1559	0.03542	48.64	82.22
....	....	....	....

$[H^+]$	"a"	K_a x 10^8	H x 10^5
0.000040	0.00450	35.22	45.50
0.000064	0.01135	36.46	44.83
0.000093	0.02320	37.84	42.96
0.000116	0.03530	38.04	42.93
			....

Av. = 44.05

FIGURE 6.

System Carbon Dioxide-Water.

Partial Vapor Pressures of Carbon Dioxide.

CARBON DIOXIDE.
VAPOR PRESSURES.
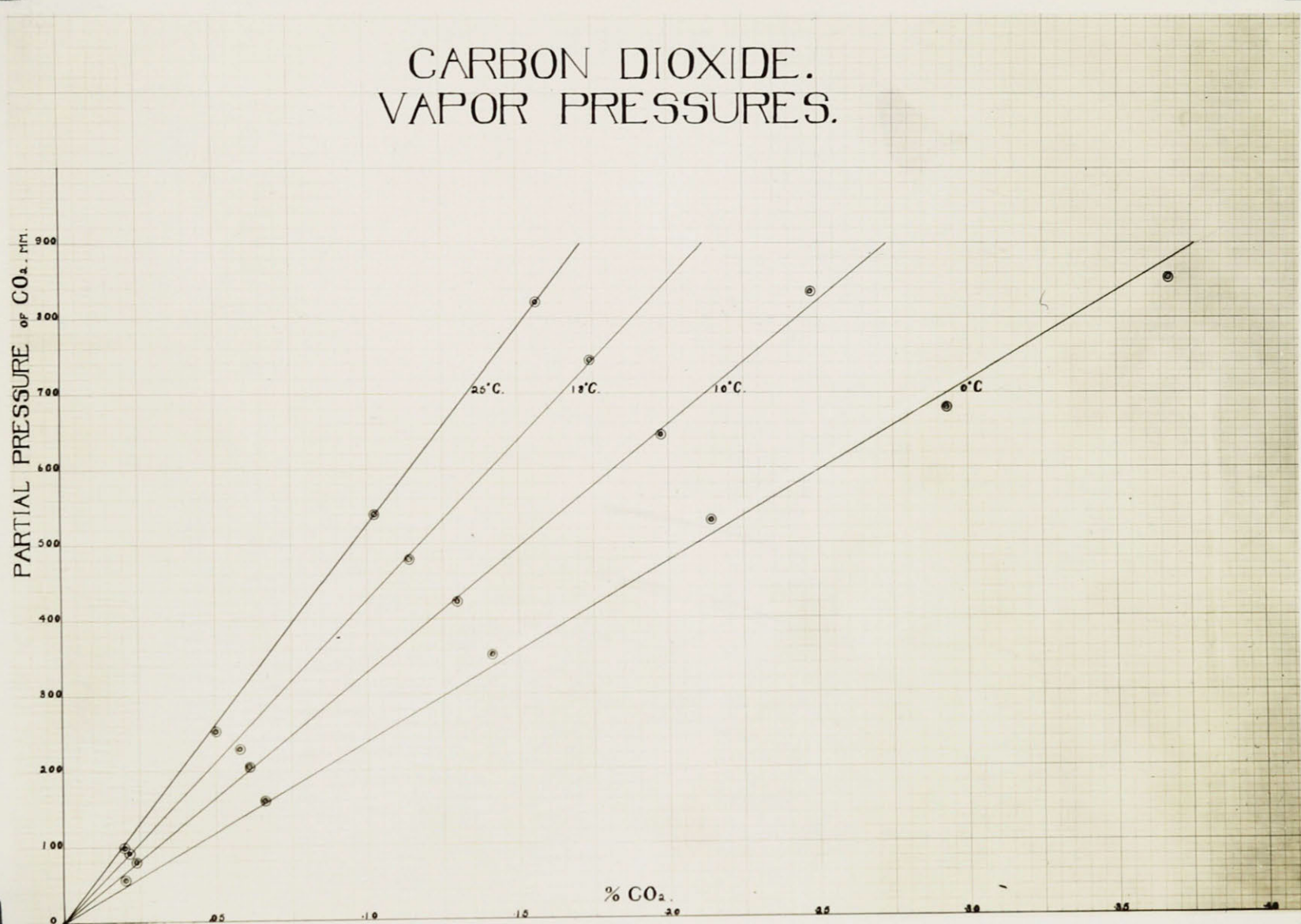
FIGURE 7.

System Carbon Dioxide-Water.

Specific Conductivity.

CARBON DIOXIDE.
SPECIFIC CONDUCTIVITY.
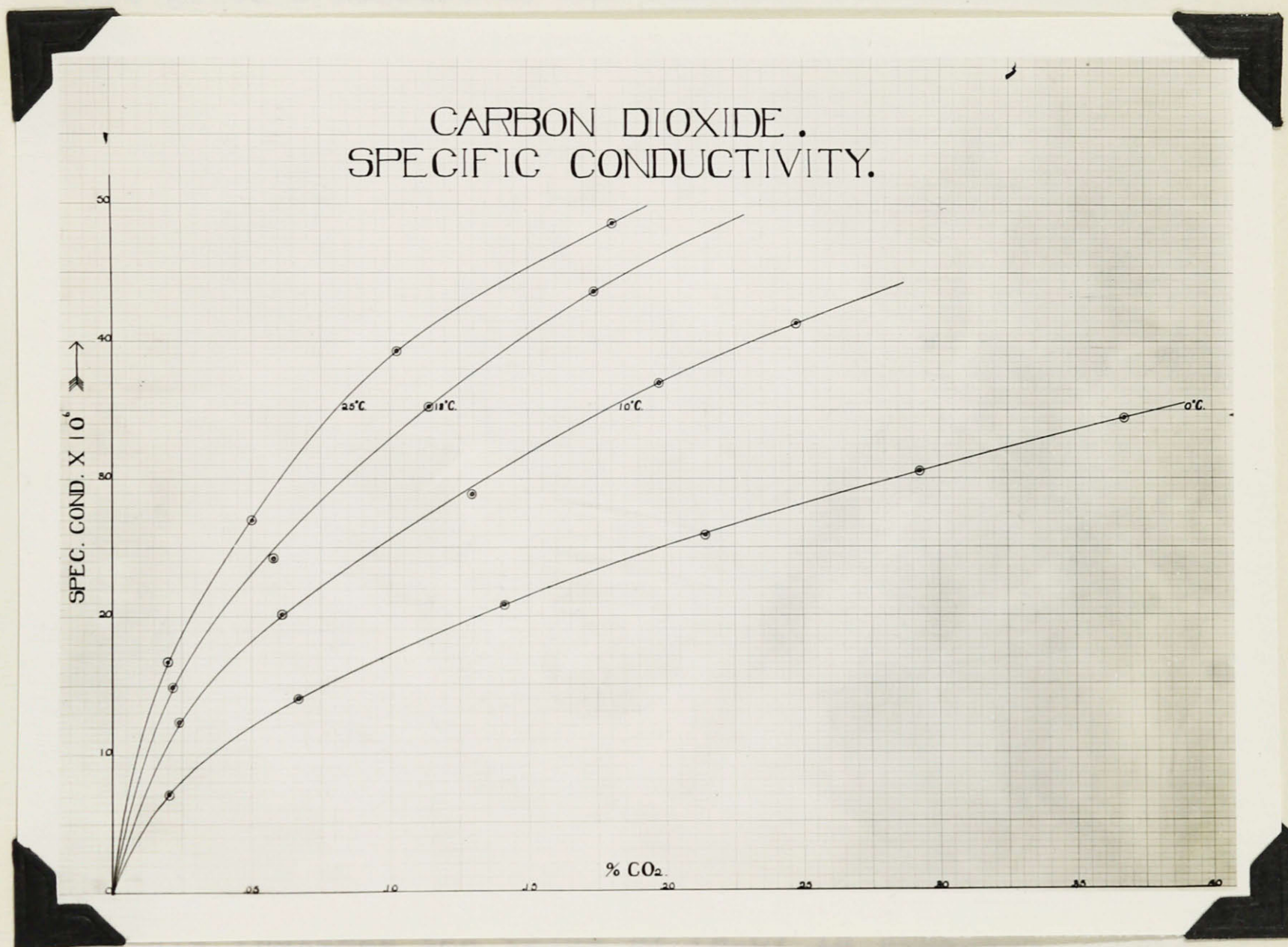
The vapor pressure and conductivity data at 10°, 18° and 25°C. are consistent within themselves and the curves show the regularity that is to be desired. It will be noticed that the maximum concentration reached at 0°C. was 0.36% as compared with a maximum concentration of 14.2% for sulphur dioxide. In this region of concentration the vapor pressure of both gases is approximately atmospheric. This gives a measure of the relative solubilities.

Since carbon dioxide solutions having vapor pressures of one atmosphere or less are of very low concentration, in every case less than 0.5%, there is only a very slight change in the water concentration, in fact it may be considered as being constant. Hence it has not been possible to treat the equilibria in the same manner as that of sulphur dioxide.

Consider an equation of the form of (13a) in connection with carbon dioxide

$$C_{CO_2} = Hp\left(1 + \frac{[H_2O]}{K_1}\right) + [H^+] \tag{31}$$

In this instance the value of $[H_2O]$ is constant, hence the term $\left(1 + \frac{[H_2O]}{K_1}\right)$ is a constant. Equation (31) is, therefore, that of a straight line. When $C_{CO_2} - [H^+]$ was plotted against the partial pressure of CO_2 a straight line relationship was obtained as predicted.

This is illustrated in Figure 8. If concentrations of CO_2 as high as 5 to 10% were obtained there would be sufficient change in the water concentration to make the above approximation illegitimate and a plot, similar to that given in Figure 8. would show curvature such as is exhibited in Figure 4. for sulphur dioxide. Such a procedure would necessitate the measurement of vapor pressures up to approximately 100 atmospheres. Vapor pressures of this order of magnitude have been measured by Sander (43) but with insufficient accuracy and no conductivity data at these pressures is available.

In Table 18. P_S is the vapor pressures in atmospheres as obtained by Sander (43) experimentally. The column P_H contains the pressures corresponding to the concentrations in the first column calculated using the Henry's Law constant (1.105×10^6) obtained in the present work.

TABLE 18

C_{CO_2} (g.mols/l.)	P_S	P_H
0.7278	25	18.8
0.8974	35	23.1
1.067	45	27.4
1.199	53	30.1

It would be expected that the values of P_S were plotted against concentration that they would exhibit

curvature. On the other hand they give a straight line relationship, curvature if any being not perceivable. This straight line when extrapolated does not pass through the origin as it theoretically should but meets the pressure axis at a point corresponding to -18 atmospheres. The improbability of Henry's Law holding at these high pressures combined with the strange results obtained from extrapolation indicates that Sander's (43) data is inaccurate and shows additional reason for continuing this work at higher pressures.

The apparent dissociation constant has been calculated from the relationship

$$K_a = \frac{[H^+]\left[\frac{1}{2}CO_3\right]}{c_{CO_2} - [H^+]}$$

The limiting value of the conductivity of the $\frac{1}{2}CO_3^-$ ion was obtained at the various temperatures from the value given by Kohlrausch (18) at $18^\circ C$. by applying the equation

$$\Lambda_T = 60\left[1 + 0.0270\ (T - 18)\right]$$

The values are given in Table 19.

TABLE 19

Temp. $^\circ$C.	H^+	$\frac{1}{2}CO_3^-$	H_2CO_3
0	224.2	30.8	255.0
10	275.5	47.0	322.5
18	315.0	60.0	375.0
25	348.5	71.3	419.8

FIGURE 8.

System Carbon Dioxide-Water.

Plot of $C_{CO_2} - [H^+]$ against Partial Pressure of CO_2
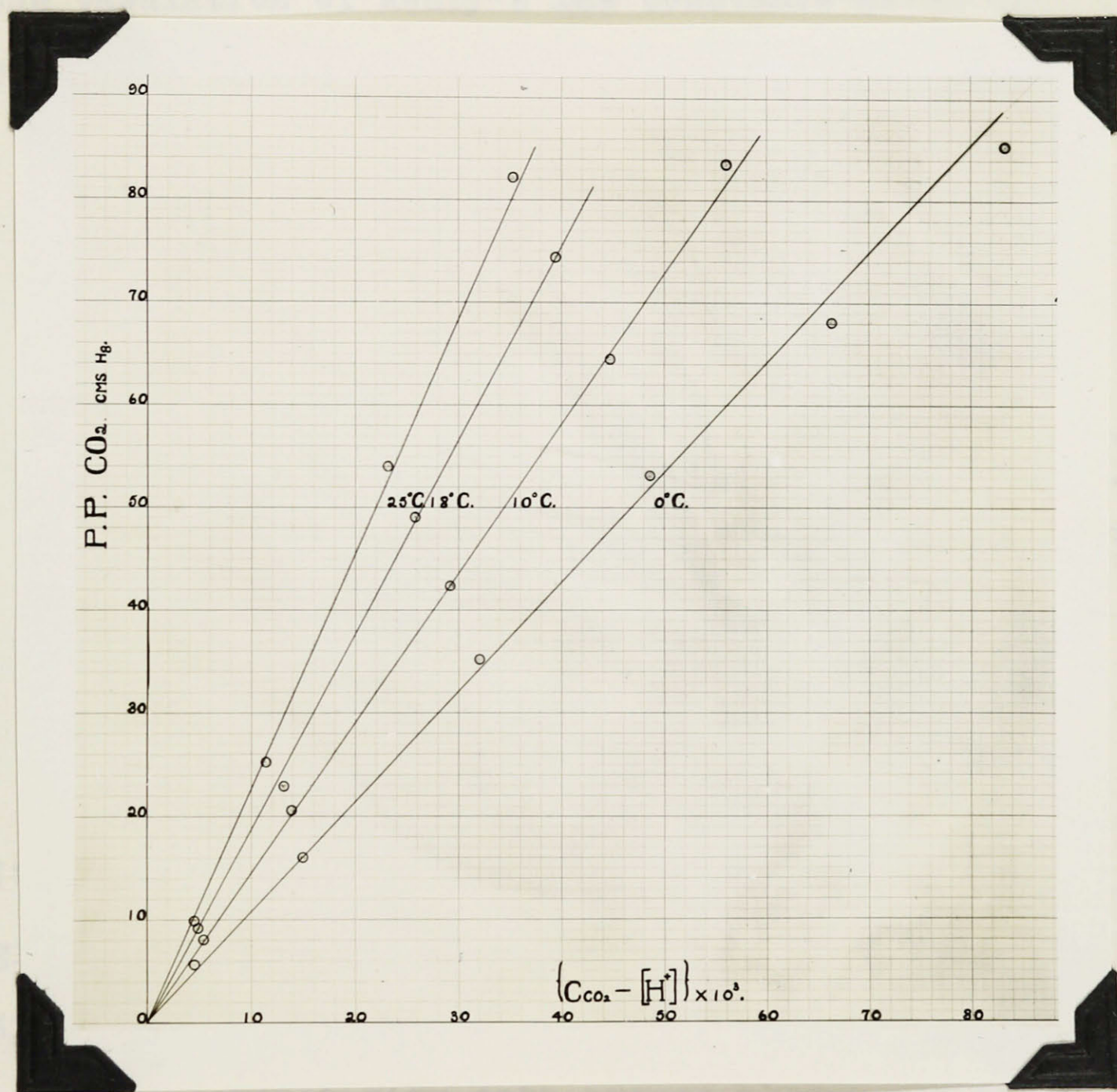
The concentration of the H^+ ion was calculated by the same method as HSO_3^- in the previous section.

The constant H calculated from the values of $\frac{a}{p}$ is the reciprocal of the Henry's Law constant given in the International Critical Tables, the value of "a" in this case being in gram mols per litre rather than in mol. fraction as in the tables.

The vapor pressure data agrees very well with that of Bohr (26). This agreement is indicated in the tabulation of Henry's Law constants given in Table 20. In this case

$$H_1 = \frac{\text{partial pressure of } CO_2 \text{ in mms. of Hg}}{\text{Mol. fraction of } CO_2}$$

TABLE 20.

Temp. $^{\circ}C.$	Henry's Law Constants $\times 10^{-6}$	
	Bohr	Present Work
10	0.791	0.797
18	1.018	1.039
25	1.243	1.255

It will be noted that in each case the present work gives a slightly higher value for the constant, the difference being fairly regular.

The conductivity data agrees almost perfectly with that of Knox (34) and fairly well with that of Pfeiffer (35), but is constantly higher than that due

to Kendall (33). This is brought out in Table 21 which compares the present work with that of Knox (34) and Kendall (33) at $18^{\circ}C$.

TABLE 21.

Specific Conductivity of H_2CO_3 at $18^{\circ}C$.

c_{CO_2} gm. mols/l.	Specific Conductivity x 10^6		
	Kendall	Knox	Present Work
0.0080	17.30	19.56	19.00
0.0188	27.20	29.70	29.69
0.0400		43.77	43.80

Data at other temperatures where comparison is possible is not tabulated since the same percentage deviation is noted in each case.

A good part of this deviation may be accounted for in Kendall's determination of the CO_2 concentration. Due to the fact that it is only possible to prepare solutions of very low concentrations at the pressures here considered, a small error in the determination of this concentration would cause a large percentage error. Kendall, using a modification of Pettenkofer's method (45), ran the solution directly from the cell into a bottle containing air free from CO_2, excess of baryta solution of known concentration was added and the CO_2 was determined as barium carbonate. For larger concentrations of

CO_2 this would be considered by the writer as a
sound procedure but in this case it verges on the
brink of microanalysis. An average concentration
of CO_2 as determined by Kendall (33) was 0.02 gram
mols per litre. Working with 30 c.c. of such a
solution, as he did, meant the absolute determination
of approximately 0.003 grams of $BaCO_3$ by titrating
the excess of $Ba(OH)_2$ with HCL. Kendall stated that
his determinations checked within 0.2% but this would
not mean that his determination was correct within
that amount. A rough calculation shows that his
possible error is in the region of 5%.

In the present work the amount of gas added to
the solution is measured by taking pressure and
temperature readings of the gas in a calibrated
volume before injecting it into the reaction chamber.
This combined with vapor pressure readings good to
0.02 cms permits of the calculation of the concentrat-
ion with an accuracy of 0.1%.

Kendall (33), in his conductivity measurements,
used a rotating commutator as a source of alternat-
ing current. The frequency of the current used is
not stated. It has been shown by Wilke (37) that
carbonic acid is a very sensitive compound and is
decomposed by slight influences such as the current
used for measurements of conductivity. A relation-
ship between frequency and the amount of decomposition

is not given but doubtless some such relationship does exist. Where the error due to this might show up cannot be predicted until such time as data is provided.

A comparison of the conductivity data due to Kendall(33) and that of the present work may also be obtained from Table 22. which contains the dissociation constants, maximum values being given in each case.

TABLE 22.

Dissociation Constants x 10^8

Temp. ^{o}C.	Kendall	Present Work.
18	31.4	34.4
25	34.9	38.0

Another point which is not brought out in Kendall's work is the regular variation of K_a with concentration as is shown in Figure 9. The values of Knox(34), on the other hand, shows this variation. This would indicate more precise measurements in the present work. Kendall also claims that his K_a is a true dissociation constant but previous discussions in this paper have proven that it is only an approximate constant.

As has been previously stated, such a small range of concentration only permits of an approximate

FIGURE 9.

System Carbon Dioxide-Water.

Plot of K_a against Concentration.
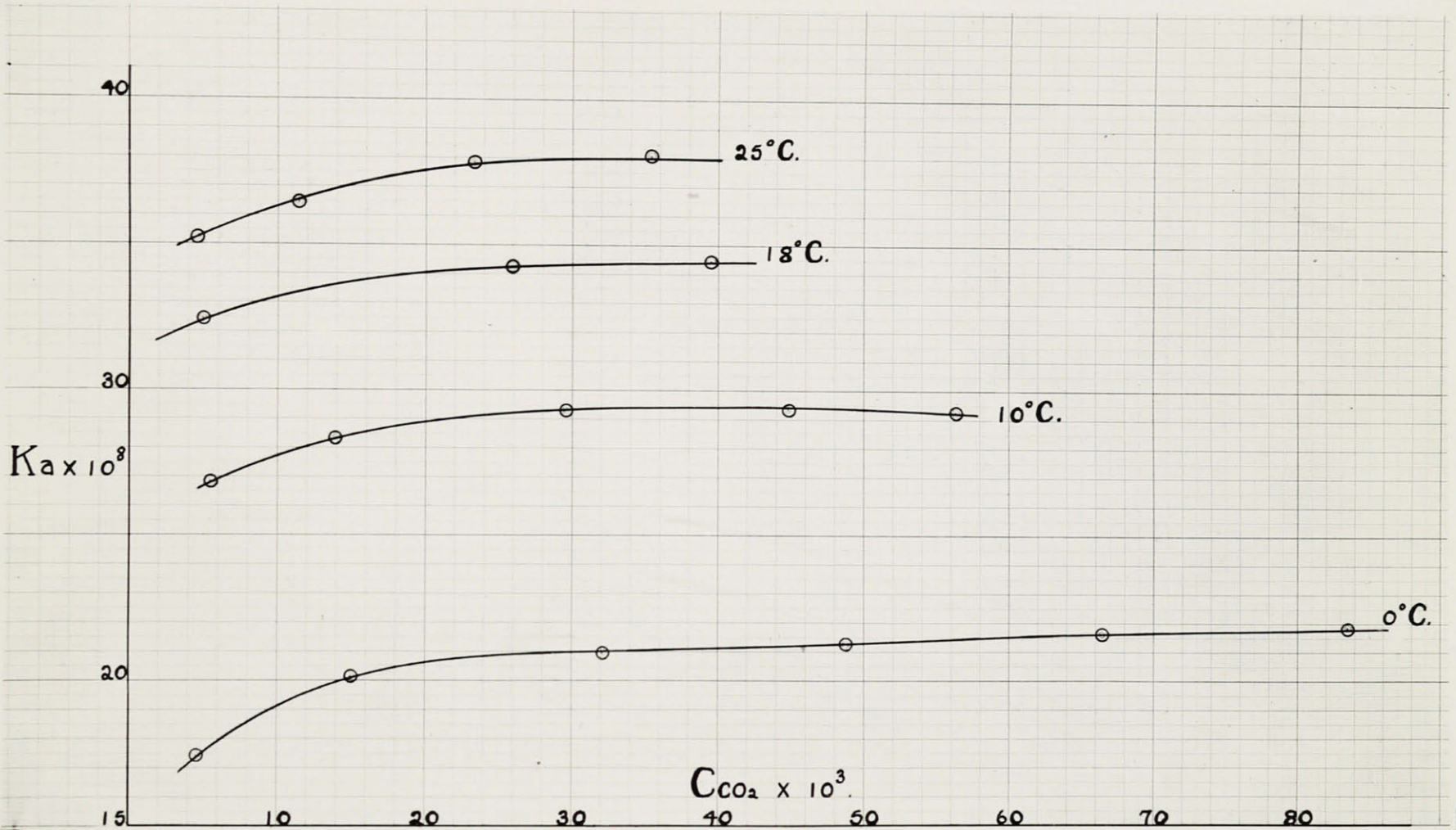
determination of the equilibrium existing in solutions of carbon dioxide. This work has been merely preliminary and it is hoped that it may be continued by future workers who are interested in this type of research. The value of such data as would be obtained has been previously been discussed.

AMMONIA.

The system ammonia-water differs from the two
previous systems studied in several ways. For
vapor pressures of corresponding magnitudes ammonia
is two hundred times more soluble in water than
is sulphur dioxide. The specific conductivity of
ammonia solutions rises sharply to a maximum at low
concentrations and then decreases rapidly becoming
asymtotic to zero at very high concentrations. At
the concentrations covered for sulphur dioxide and
carbon dioxide the conductivity rose steadily and
there was not much indication of a maximum being
reached.

-      A cylinder of liquid ammonia was obtained
from the Matheson Company, North Burgen, N.J.
Freezing point and vapor pressure determinations
showed it to be very pure, there being only a trace
of water present. Purification was effected by
passing the ammonia, in the gaseous state, through
long tubes of lime and condensing it again with
a dry ice-ether mixture. The drying process was
followed by two fractional distillations, rejecting
heads and tails, and retaining the middle 75%
fraction. The solutions were prepared as previously
discussed in the experimental section. The cond-
uctivity cell allowing for 100% expansion of the

solution was used.

The experimental data is given in Tables 23, 24, 25, and 26 for temperatures of 0°, 10°, 18°, and 25°C. respectively. Figures 10 and 11 present the vapor pressure and specific conductivity data relationships at the four temperatures. The lower vapor pressures, where the change in pressure with increasing concentration is very small, were measured with a cathetometer. In the calculation of the concentrations the molecular weights of ammonia as found by Carpenter(46) were used. The densities given in the above tables are those due to Nichols and Wheeler(19). The column C_{NH_3} represents the concentration of ammonia in gram mols per litre.

As in previous sections the regularity of the data, as exhibited by the plots, is a favorable point. Both the vapor pressure and specific conductivity curves lie in legitimate regions with respect to the different temperatures at which they were obtained.

The best vapor pressure data available with which to compare the present work is that due to Perman(22). Table 27 contains the comparison of the data. At the higher concentrations Perman's data is slightly higher than that obtained in this work. A higher vapor pressure would indicate either the presence of some volatile impurity in

TABLE 23.

System Ammonia-Water.

0°C.

% NH$_3$	Density	C$_{NH_3}$	Specific Cond. x 10^4	Partial Pressure of NH$_3$ (cms Hg)
0.419	0.9984	0.246	2.721	0.15
1.072	0.9958	0.628	4.167	0.29
3.882	0.9847	2.249	5.992	0.70
6.241	0.9759	3.583	6.421	1.43
8.474	0.9682	4.827	6.152	2.00
10.56	0.9610	5.970	5.584	2.72
14.51	0.9482	8.095	4.327	4.46
19.76	0.9324	10.84	2.791	7.75
24.42	0.9191	13.20	1.754	12.05
28.58	0.9078	15.26	1.138	17.71
32.28	0.8983	17.06	0.741	24.38
35.60	0.8900	18.64	0.488	32.18

Weight of water used = 21.124 gms.

TABLE 24.

System Ammonia-Water.

10°C.

% NH_3	Density	C_{NH_3}	Specific Cond. x 10^4	Partial Pressure of NH_3 (cms Hg)
0.213	0.9990	0.125	2.732	0.10
0.448	0.9979	0.263	3.943	0.21
1.221	0.9946	0.714	6.198	0.48
3.162	0.9866	1.835	8.313	1.24
5.475	0.9766	3.149	8.837	2.27
7.626	0.9694	4.349	8.520	3.38
9.705	0.9616	5.491	7.795	4.60
11.68	0.9546	6.560	7.105	5.92
15.35	0.9424	8.511	5.373	8.82
18.72	0.9316	10.26	4.106	12.40
21.95	0.9217	11.91	3.135	16.73
25.00	0.9127	13.42	2.329	22.15
27.78	0.9047	14.79	1.764	28.03
30.38	0.8974	16.03	1.343	34.73
33.92	0.8880	17.72	0.914	46.27
36.12	0.8821	18.74	0.727	54.27

Weight of water used = 21.525 gms.

TABLE 25.

System Ammonia-Water.

18°C.

% NH$_3$	Density	c_{NH_3}	Specific Cond. x 10^4	Partial Pressure of NH$_3$ (cms Hg)
0.397	0.9984	0.233	4.500	0.21
1.168	0.9937	0.683	7.382	0.70
3.109	0.9851	1.801	10.18	1.81
5.421	0.9759	3.113	10.90	3.35
7.632	0.9675	4.343	10.51	4.96
9.729	0.9594	5.492	9.641	6.72
13.61	0.9450	7.565	7.643	10.82
17.24	0.9328	9.461	5.837	15.61
20.55	0.9222	11.15	4.407	21.40
23.54	0.9126	12.64	3.376	27.93
27.69	0.9000	14.66	2.261	39.51
31.42	0.8890	16.44	1.529	53.17
34.73	0.8794	17.97	1.069	68.73

Weight of water used = 21.110 gms.

TABLE 26.

System Ammonia-Water.
25°C.

% NH_3	Density	c_{NH_3}	Specific Cond. x 10^4	Partial Pressure of NH_3 (cms Hg)
0.404	0.9971	0.237	5.290	0.31
1.042	0.9931	0.608	8.207	0.84
3.732	0.9810	2.154	11.76	2.38
5.259	0.9749	3.016	12.75	4.43
7.456	0.9660	4.238	12.36	6.66
9.517	0.9581	5.364	11.42	9.09
11.51	0.9504	6.436	10.35	11.74
15.22	0.9370	8.389	8.100	17.60
18.61	0.9250	10.13	6.254	24.56
23.20	0.9100	12.42	4.193	36.76
27.30	0.8974	14.42	2.857	51.63
30.97	0.8864	16.15	1.965	68.67

Weight of Water used = 21.016 gms.

FIGURE 10.

System Ammonia-Water.

Partial Vapor Pressures.

AMMONIA.
VAPOR PRESSURES.

FIGURE 11.

System Ammonia-Water.

Specific Conductivity.
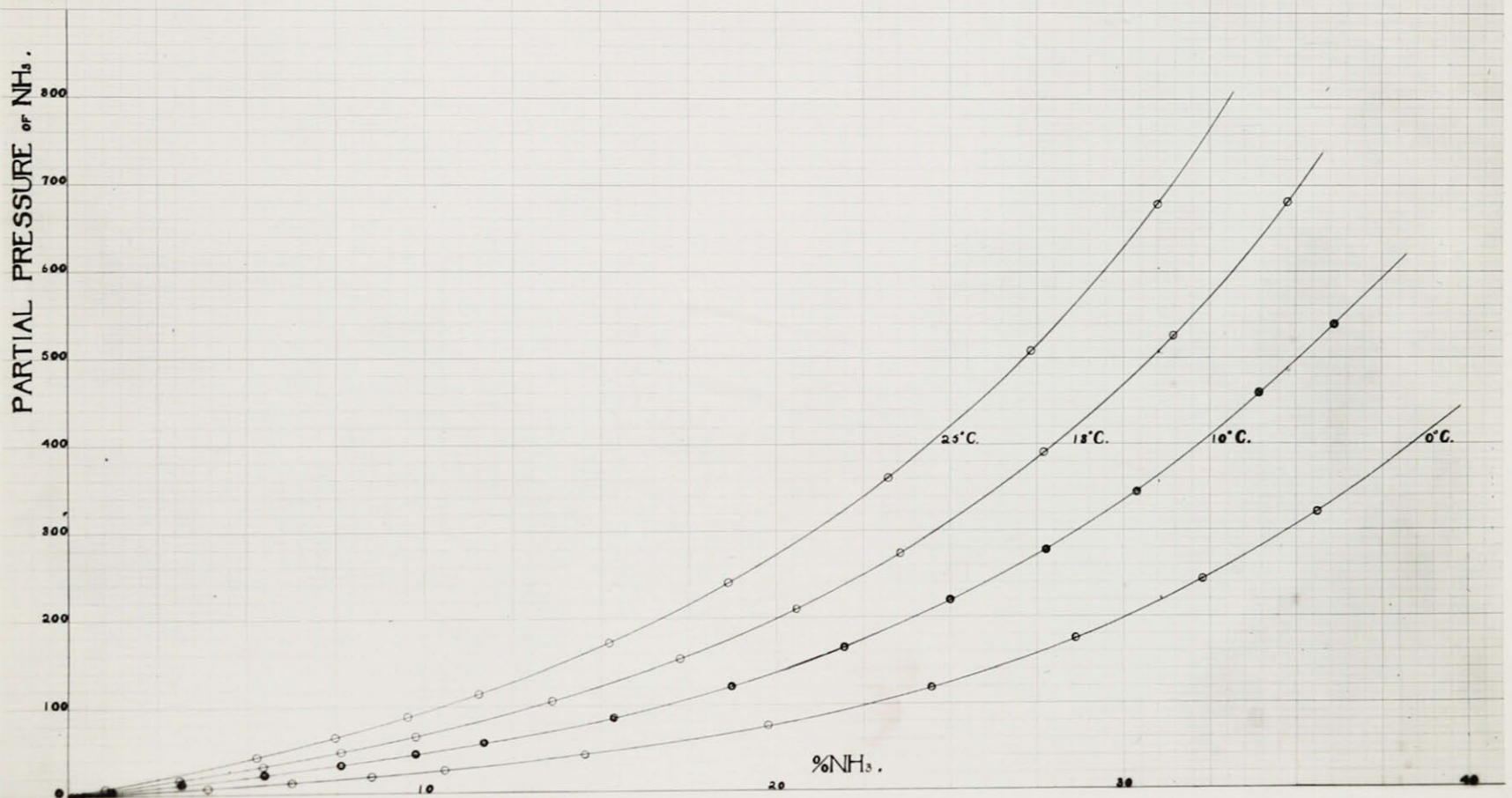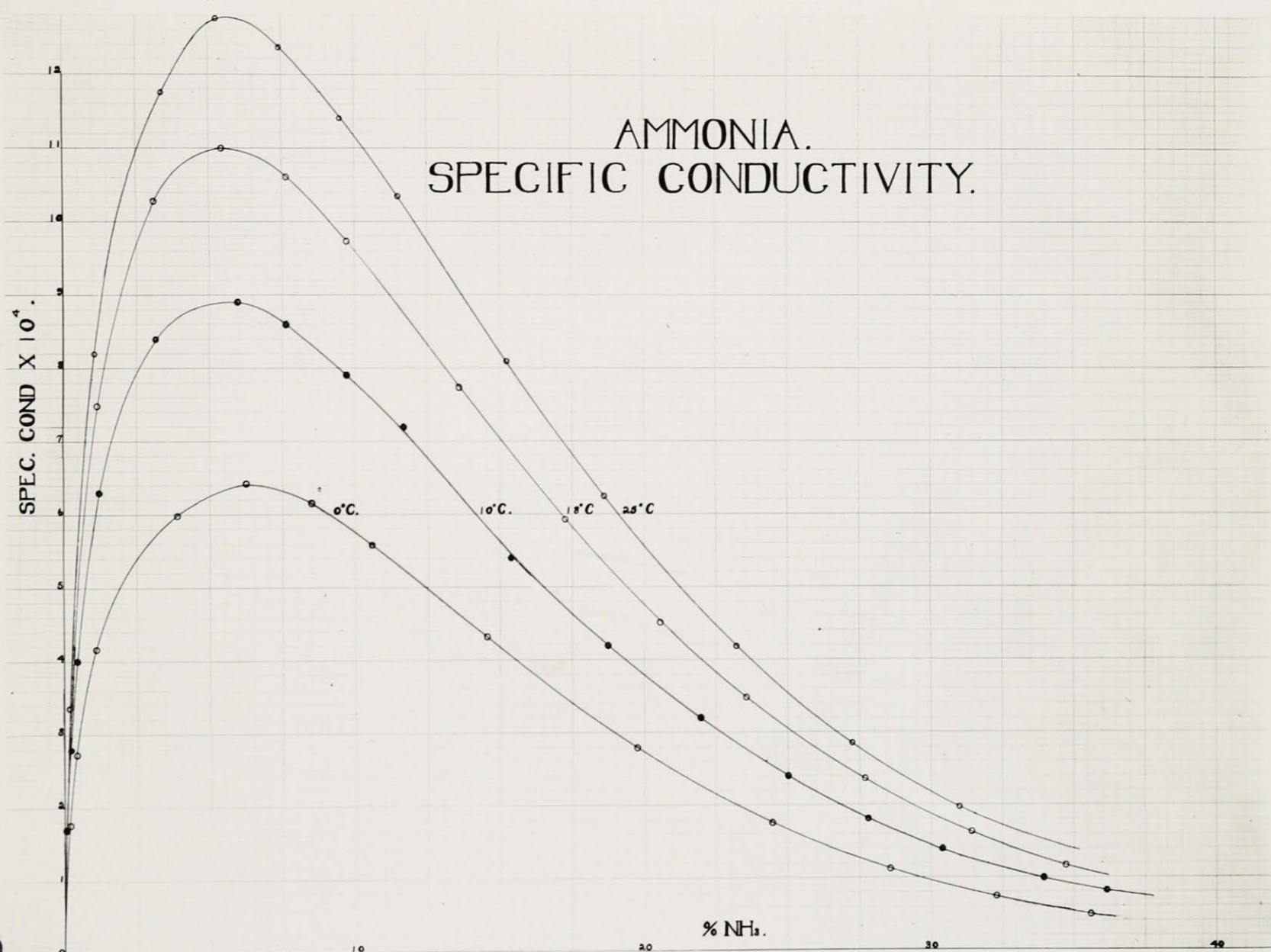

AMMONIA.
SPECIFIC CONDUCTIVITY.

the ammonia, a slight difference in temperature,

or incomplete equilibrium. A temperature difference

of $0.2^{\circ}C$. would account for this.

TABLE 27.

Partial Pressures of Ammonia Solutions at $10^{\circ}C$.

% NH_3	P. P. NH_3 (Perman)	P. P. NH_3 (Work (Present))
4.16	1.65	1.65
8.26	3.72	3.72
12.32	6.42	6.30
15.88	9.51	9.20
20.54	14.92	14.50
21.83	16.98	16.40

On account of the great solubility of ammonia in

water the vapor pressures are much lower than those

of the two systems dealt with previously. Another

reason for such low vapor pressures will be dis-

cussed later.

Conductivity data for ammonia is plentiful

for dilute solutions but rather scarce for solutions

of concentrations greater than 0.1N. Considerable

deviation is found in the low concentration data.

The chief investigators have been Noyes and Kato(40)

and Lunden(39). It has only been possible to

overlap their range of concentration at two points

in the present work and the agreement there is not

good. However great accuracy is not claimed at the extremely low concentrations in this work since a slight amount of the ammonia injected into the cell at the beginning of a run might be absorbed by the stopcock grease and adsorbed on the glass walls of the system. This amount, though slight, would have a relatively large effect on the first value. The values obtained by Kohlrausch(21) up to concentrations of 30.5% check very well with the present data. Comparisons of the above mentioned data are given in the following tables.

TABLE 28.

Specific Conductivity of Ammonia Solutions x 10^4

(Low Concentrations.)

Temp. ^{o}C.	c_{NH_3}	Lunden	Noyes & Kato	Present Work.
18	0.083	----	2.81	2.66
	0.10	3.18	3.10	----
25	0.10	3.70	3.62	3.41

It will be noted from the last column of Table 29, which will follow, that the Kohlrausch conductivity curve intersects that of the present work in two places but the difference is never very large. The average mean deviation over the whole range is 0.03 mhos.

TABLE 29.

Specific Conductivity of Ammonia Solutions   x 10^4

(High Concentrations)

% NH_3	Kohlrausch	Present Work	Difference.
0.1	2.51	2.51	----
0.4	4.92	4.92	----
0.8	6.57	6.57	----
1.6	8.67	8.52	0.15
4.01	10.95	10.76	0.19
8.03	10.38	10.48	- 0.10
16.15	6.32	6.46	- 0.14
30.50	1.93	1.79	0.14

The conditions existing in aqueous solutions of ammonia may be expressed in two equations similar to (10) and (11) for sulphur dioxide

$$c_{H_2O} = [H_2O] + [NH_4OH] + [OH^-] \tag{32}$$

$$c_{NH_3} = [NH_3] + [NH_4OH] + [OH^-] \tag{33}$$

By following a procedure similar to that used in the previous section an equation of the form of (16) is obtained.

$$a = Hp \left(1 + \frac{b + Hp}{K_1} \right) \tag{34}$$

In this case $a = C_{NH_3} - \left[OH^-\right]$

and $b = C_{H_2O} - C_{NH_3}$

On solving (34) for H and K_1, H was found to be extremely small and in some cases negative. In every case it was extremely small compared with the corresponding value of H for sulphur dioxide. This showed that the amount of uncombined ammonia in the liquid phase was negligible. It was borne out by the fact that the vapor pressures were relatively low as compared with those of solutions of SO_2 where there is a considerable amount of uncombined reactant present.

Assuming that the amount of uncombined ammonia was negligible it was necessary to rearrange equation (34) to fit the case, if possible, and to prove that the above assumption was correct. Since H is small, Hp in the term (b + Hp) is negligible compared with b. K_1 is also very small and the value of $\dfrac{b}{K_1}$ is very large compared with 1. Hence equation (34) becomes

$$a = \frac{Hpb}{K_1}$$

or $\qquad\qquad \dfrac{a}{b} = \dfrac{Hp}{K_1} = kp \qquad\qquad (35)$

which is the same as

$$\frac{c_{NH_3} - \left[OH^-\right]}{c_{H_2O} - c_{NH_3}} = kp \qquad (36)$$

Since the value of $\left[OH^-\right]$ is very small (36) may be written

$$\frac{c_{NH_3}}{c_{H_2O} - c_{NH_3}} = kp \qquad (37)$$

without affecting the accuracy appreciably.

When $\frac{a}{b}$ was plotted against the partial vapor pressure of the ammonia at each temperature investigated straight lines were obtained as predicted by equation (35). From equation (37) the conclusion may then be drawn that the ratio of the concentration of the ammonia to that of the uncombined water is a constant function of the vapor pressure. It is of course impossible to differentiate between H and K_1 since the constant k gives the ratio of the two. But since a straight line relationship holds it follows that the value for K_1 must be very small which means that by far the greatest part of the ammonia is combined. Since there is so little free ammonia in the solution the partial vapor pressure will be small in contrast to the two previous systems.

The conclusion drawn above is at variance with the results of Moore(48). Moore, using the partition coefficient of ammonia between water and chloroform, heats of neutralization, and heats of solution calculated ionization constants for ammonia solutions and from the data thus obtained arrived at the conclusion that at $20^{\circ}C$. the ratio $\dfrac{NH_3}{NH_4 OH}$ was approximately 2. The assumptions made by Moore are not justified and it was pointed out that they were at variance with the partial vapor pressures as registered by ammonia solutions.

Tables 30, 31, 32, and 33 contain the theoretical data calculated from the experimental data contained in Tables 26, 27, 28, and 29 respectively. C_{H_2O} represents the water concentration in gram mols per litre. $\left[OH^-\right]$ is the concentration of the OH^- (or NH_4^+) ion, also in gram mols per litre. The values of "a", "b", and $\dfrac{a}{b}$ have been explained already. K_a is the true dissociation constant calculated in a similar manner to that used for the apparent dissociation constant for sulphur dioxide and carbon dioxide. In this case it is the true dissociation constant on account of the complete combination of the ammonia with water, the conductivity thus giving a true measure of the fraction of NH_4OH which is ionized.

TABLE 30.

<u>System Ammonia-Water.</u>

$0^{\circ}C.$

c_{H_2O}	$[OH^-] \times 10^4$	a	b	$\frac{a}{b} \times 10^2$	$K_a \times 10^7$
55.17	11.29	0.244	54.92	0.445	124.6
54.67	26.71	0.625	54.04	1.157	114.1
52.53	38.41	2.245	50.28	4.465	65.70
50.78	41.16	3.579	47.20	7.580	47.34
49.18	39.44	4.823	44.35	10.87	32.25
47.69	35.80	5.967	41.72	14.30	21.47
45.00	27.74	8.092	36.91	21.93	9.51
41.53	17.89	10.84	30.69	35.33	2.95
38.55	11.24	13.20	25.35	52.07	0.95
35.98	7.29	15.26	20.72	73.64	0.35
33.76	4.75	17.06	16.70	102.1	0.13
31.81	3.13	18.64	13.17	141.6	0.05

TABLE 31.

System Ammonia-Water.

$10^{\circ}C.$

c_{H_2O}	$[OH^-] \times 10^4$	a	b	$\frac{a}{b} \times 10^2$	$K_a \times 10^7$
55.33	13.55	0.124	55.21	0.22	148.2
55.13	19.56	0.261	54.87	0.47	146.4
54.54	30.75	0.711	53.83	1.32	132.9
53.04	41.25	1.831	51.21	3.57	92.92
51.29	43.84	3.144	48.14	6.53	61.13
49.69	42.27	4.344	45.34	9.58	41.12
48.19	38.68	5.487	42.70	12.85	27.26
46.79	35.26	6.566	40.23	16.29	18.95
44.29	26.66	8.508	35.78	23.78	8.35
42.04	20.37	10.26	31.78	32.27	4.04
39.93	15.55	11.91	28.02	42.50	2.03
37.99	11.55	13.42	24.57	54.62	0.99
36.25	8.75	14.79	21.46	68.93	0.51
34.67	6.66	16.03	18.64	86.00	0.28
32.56	4.53	17.72	14.84	119.00	0.12
31.27	3.61	18.74	12.53	149.60	0.07

TABLE 32.

System Ammonia-Water.
$18^{\circ}C.$

c_{H_2O}	$[OH^-] \times 10^4$	a	b	$\frac{a}{b} \times 10^2$	$K_a \times 10^7$
55.20	18.91	0.231	54.97	0.42	154.6
54.50	31.01	0.679	53.82	1.26	141.5
52.97	42.76	1.796	51.17	3.51	101.7
51.23	45.80	3.108	48.12	6.46	67.47
49.60	44.16	4.339	45.26	9.59	44.93
48.06	40.51	5.488	42.57	12.89	29.89
45.31	32.11	7.562	37.75	20.03	13.64
42.85	24.52	9.459	33.39	28.32	6.36
40.66	18.52	11.14	29.51	37.79	3.07
38.73	14.19	12.64	26.09	48.45	1.59
36.12	9.49	14.66	21.46	68.32	0.61
33.84	6.42	16.44	17.40	94.50	0.25
31.86	4.49	17.97	13.89	129.30	0.11

TABLE 33.

System Ammonia-Water.
25°C.

c_{H_2O}	$[OH^-] \times 10^4$	a	b	$\frac{a}{b} \times 10^2$	$K_a \times 10^7$
55.11	19.61	0.235	54.87	0.428	163.4
54.53	30.42	0.605	53.92	1.123	152.8
52.42	43.59	2.149	50.27	4.275	88.43
51.26	47.25	3.011	48.24	6.241	74.15
49.62	45.81	4.233	45.38	9.326	49.57
48.11	42.33	5.360	42.75	12.54	33.42
46.68	38.35	6.432	40.24	15.99	22.88
44.09	30.02	8.386	35.70	23.48	10.75
41.78	23.18	10.13	31.65	32.00	5.30
38.79	15.53	12.42	26.37	47.10	1.94
36.21	10.59	14.42	21.79	66.18	0.77
33.95	7.28	16.15	17.80	90.72	0.33

FIGURE 12.

System Ammonia-Water.

Partial Vapor Pressure plotted against values of $\frac{a}{b}$.
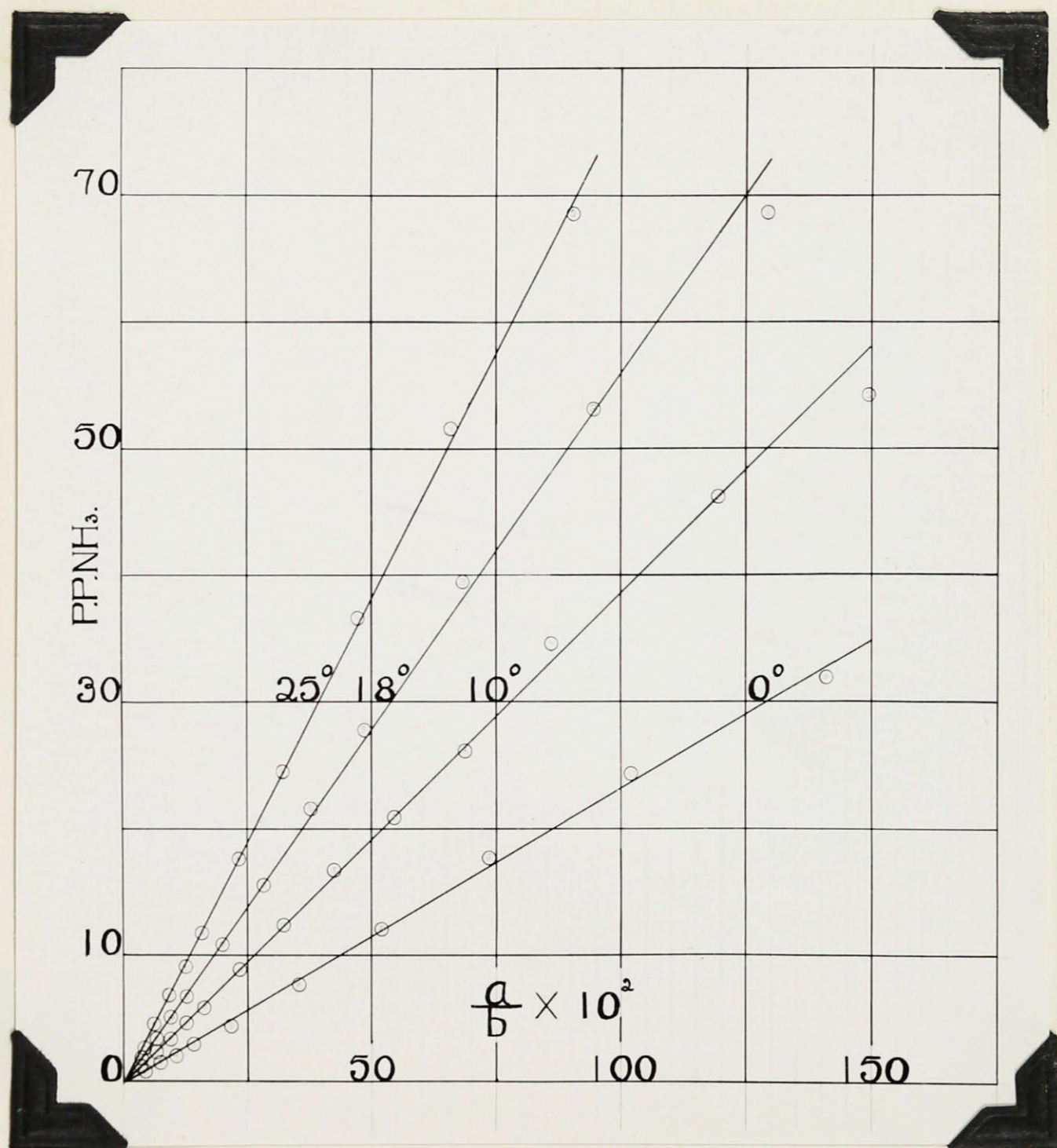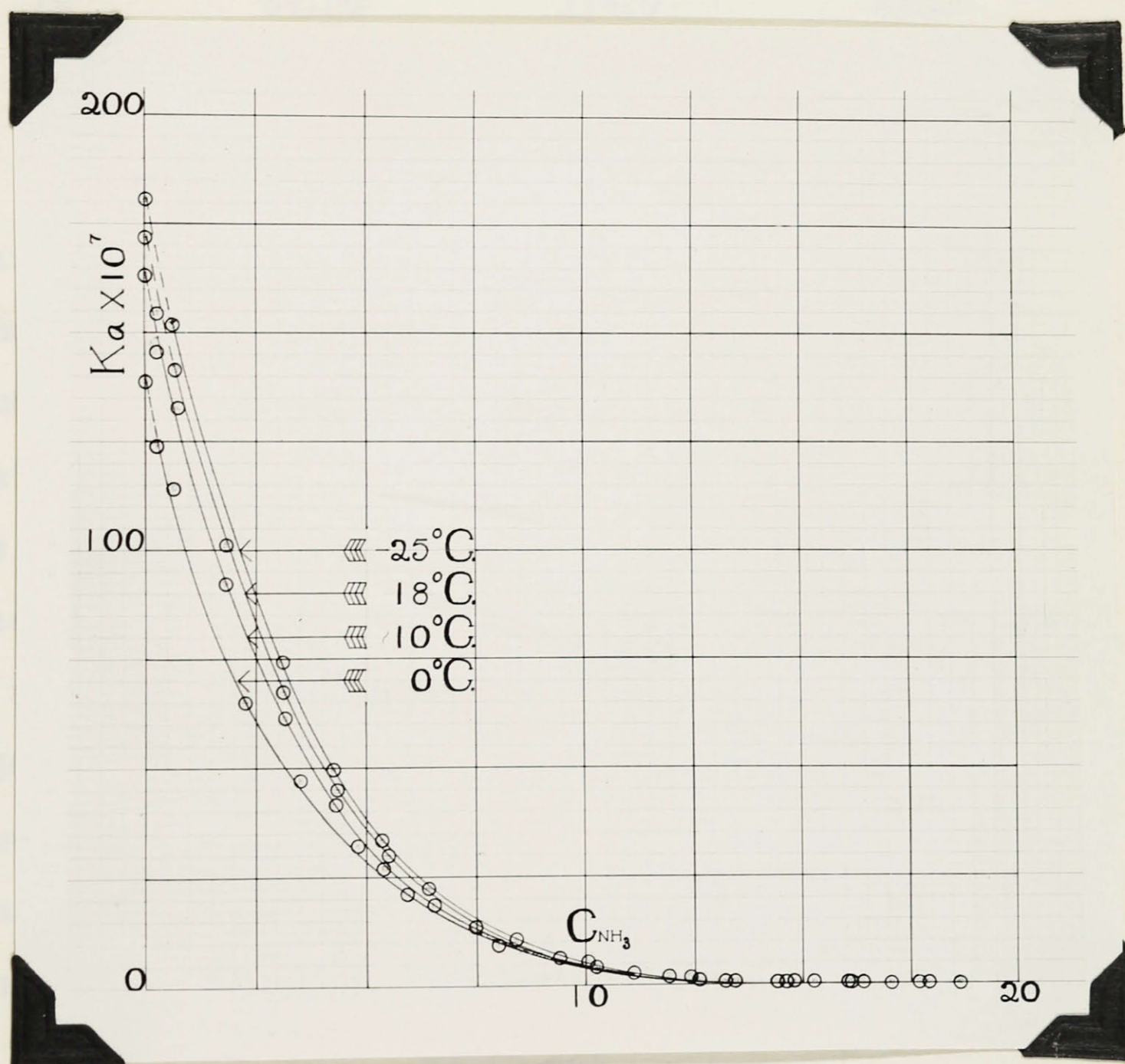
FIGURE 13.

System Ammonia-Water.

K_a plotted against C_{NH_3}.

FIGURE 13.

The ionic mobilities were calculated from the data of Kohlrausch(18) and are given in the following table.

TABLE 34.

Temp. $^{\circ}$C.	NH_4	OH^-	NH_4OH
0	38.43	117.6	156.0
10	52.64	148.9	201.5
18	64.00	174.0	238.0
25	73.92	195.9	269.8

Figure 12 shows the straight line relationships obtained by plotting partial pressure of ammonia against the values of $\frac{a}{b}$. Figure 13 indicates the variation of K_a with rising concentration. In Figure 12 it will be noted that there is a slight wave in the points before and after the value of the concentration where $[OH^-]$ reaches a maximum. This would be expected from equation (36) but the deviation from a straight line is so small that the assumption of almost complete combination of ammonia with water is not invalidated. The values of the constant k are given below.

TABLE 35.

Temp. $^{\circ}$C.	k
0	0.0431
10	0.0258
18	0.0178
25	0.0130

The decrease of k with rise in temperature is to be expected since $k = \frac{H}{K_1}$ since H is bound to decrease and K_1 to increase with rise in temperature. An investigation at high temperatures would therefore be of interest since in that region $\frac{b}{K_1}$ will no longer be extremely large compared to 1.

In Figure 13 the dotted portions of the curves are the extrapolations to the values given in the literature for very dilute solutions. It will be noted that these extrapolations continue quite regularly from the maximum values of K_a obtained in the present work. A further discussion of K_a will be included in the following section.

GENERAL DISCUSSION.

It is evident that in the three systems investigated in this work there is a distinct variation of properties. Carbon dioxide is relatively insoluble, weakly acidic, and is ionized only to a slight extent. Sulphur dioxide is more soluble, more highly ionized, and strongly acidic while ammonia is extremely soluble, slightly ionized, and basic. Due to the wide variation of the properties of these systems, marked differences in the types of equilibria existing would be expected. This has been found to be the case.

Vapor pressure data shows that ammonia has the greatest affinity for water, sulphur dioxide is next, and carbon dioxide is the smallest of the three. For this reason it was impossible to reach sufficiently high concentrations of CO_2, with the means at hand, to arrive at a true measure of the equilibrium. Some advance has been made but it will be necessary to proceed to higher concentrations in order to subject it to the type of theoretical treatment used in the case of sulphur dioxide and ammonia where the change in the water concentration plays an important part.

The relative magnitudes of the affinity of

of each of these gases for water may be deduced.
By multiplying the mol fraction of the gas present
in the solutions investigated by the vapor pressure
of the pure gas in the liquid state at the same
temperature it is possible to calculate the vapor
pressure if an ideal solution results. The following
table shows the vapor pressures obtained from this
calculation compared with the experimental pressures.
C_{gas} is the concentration in gram mols per litre
and the pressures are given in centimeters of Hg.

TABLE 36.

Gas	C_{gas}	$P_{calc.}$	$P_{meas.}$	$\dfrac{P_{meas.}}{P_{calc.}}$
CO_2	0.0835	3.93	85.30	21.70
SO_2	0.1393	0.29	1.97	6.79
NH_3	0.2460	1.44	0.15	0.104

It will be noted that $P_{meas.}$ is much greater than
$P_{calc.}$ for CO_2 and SO_2 and much less for NH_3.
This is in good agreement with the data since CO_2
was found to be least combined of the three, a
smaller amount of uncombined gas was present in
the SO_2 solutions, while ammonia, to an approxim-
ation, was totally combined. Hence the vapor
pressures of the two former gases would be greater,
and of the latter smaller than that of a perfect
solution.

It should be stated here that the partial vapor pressure above solutions of ammonia is due to NH_3 and not to NH_4OH as might be expected. It has been shown by Carpenter(46) that the amount of combination between ammonia and water in the vapor phase is much below 1%.

On reviewing previous tables one will see that the values of K_a, the apparent dissociation constant, decrease with rising temperature in the case of SO_2 and increase in the cases of CO_2 and NH_3. It will be remembered from a previous section that the constants K_a, K_1, and K_2 are connected by the relation

$$K_a = \frac{K_2 [H_2O]}{K_1 + [H_2O]}$$

$$= K_2 \frac{1}{1 + \dfrac{K_1}{[H_2O]}} \qquad (38)$$

and that

$$K_1 = \frac{[H_2O][SO_2]}{[H_2SO_3]}$$

taking sulphur dioxide as an example. The more uncombined gas that there is in the liquid phase the greater will be the value of K_1. Remembering also that K_1 was of the same order of magnitude as $[H_2O]$ in the case of sulphur dioxide it is possible to predict from the vapor pressures of CO_2 solutions that K_1 would have a much larger

value than that of $\left[H_2O\right]$. Conversely for ammonia solutions K_1 would be much smaller than $\left[H_2O\right]$. From the above facts for CO_2 in equation (38) the term

$$\frac{K_1}{\left[H_2O\right]} > 1$$

For SO_2

$$\frac{K_1}{\left[H_2O\right]} \quad \text{has the same magnitude as 1}$$

and for NH_3

$$\frac{K_1}{\left[H_2O\right]} < 1$$

It is quite plain from equation (38) that if K_1 increases with rising temperature the value of K_a will decrease and vice versa. This is so in the case of sulphur dioxide. However in the case of CO_2 and NH_3 K_a increases with rising temperature and K_1 decreases. It was impossible to calculate K_1 for the CO_2-water systems but it was found to decrease in the ammonia-water systems. Also, for ammonia systems, K_a was found to be equal to K_2. This follows from equation (38) also. When K_1 is extremely small the term $\frac{K_1}{\left[H_2O\right]}$ becomes very small compared to 1 and may be disregarded. Hence $K_a = K_2$.

A means of checking the temperature coefficient of the ionization constants is given by the thermo-dynamic relationship

$$\ln \frac{K_{t_1}}{K_{t_1'}} = \frac{Q}{R} \left(\frac{1}{t_1} - \frac{1}{t_2} \right) \qquad (39)$$

where K_{t_1} is the real dissociation constant at a temperature t_1.

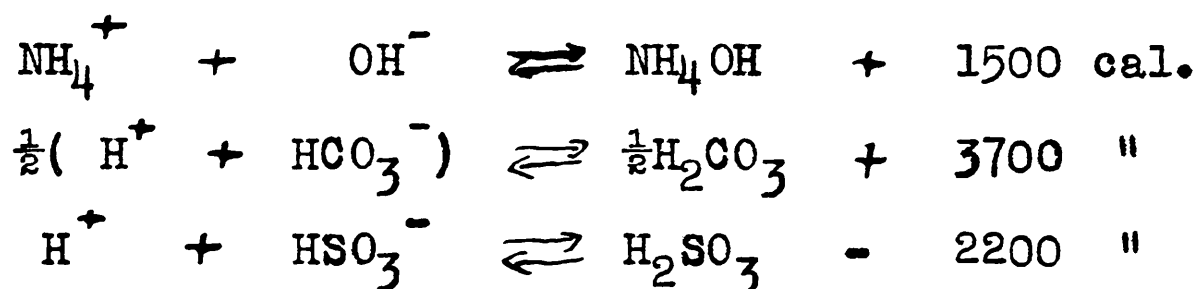K_{t_2} is the real dissociation constant at a temperature t_2.

Q is the heat of ionization

R is 2 calories.

In the present discussion constants at 18° and 25°C. will be considered. From heat of neutralization data in the literature(49) together with the heat of formation of water from its ions the following values of Q were derived at this temperature:-

NH_4OH	1500 calories.
$\frac{1}{2}H_2CO_3$	3700 "
H_2SO_3	-2200 "

When these are expressed as follows

$$NH_4^+ + OH^- \rightleftharpoons NH_4OH + 1500 \text{ cal.}$$
$$\frac{1}{2}(H^+ + HCO_3^-) \rightleftharpoons \frac{1}{2}H_2CO_3 + 3700 \text{ "}$$
$$H^+ + HSO_3^- \rightleftharpoons H_2SO_3 - 2200 \text{ "}$$

it may be seen that a rise in temperature for the first two will shift the equilibrium to the left, and for the latter it will be shifted to the right. A shift to the left means an increase in the ion concentration and consequently an increase in K_2, the true ionization constant, likewise an increase

in K_a, the apparent ionization constant. The opp-
osite is true if the equilibrium is shifted to
the right. This coincides with the experimental
results obtained in this work, K_a increasing with
rising temperature in the case of ammonia and
carbon dioxide, and decreasing in the case of
sulphur dioxide.

To check the present data even farther the
ratio of $K_a(18^\circ)/K_a(25^\circ C)$ was calculated using
equation (39). These ratios afe compared with
those obtained by solving the ratio of the values
of K_a obtained experimentally in the following
table.

TABLE 37.

$$K_a(18^\circ)/K_a(25^\circ C.)$$

Gas.	Calc. from equation (39)	Calc. from data.
SO_2	-9%	-16%
CO_2	+16%	+10%
NH_3	+6%	+5%

The ratios are expressed in percent increase (+)
or decrease (-) over the seven degree interval
between 18° and $25^\circ C.$

For sulphur dioxide the deviation of K_a calc-
ulated from equation (39) is less than that calcul-
ated from the data. For carbon dioxide and ammonia
the opposite is true. When the fact that the

dielectric constant of water decreases with rising temperature is taken into consideration, and also that the ionization constant decreases with decreasing dielectric constant, which is a well known experimental fact, a good part of this deviation in the two ratios may be accounted for as follows. Take the case of sulphur dioxide. A 9% decrease in K_a is calculated from equation (39) in passing from 18° to $25^\circ C$., while the actual constants give a 16% decrease. Over this range of temperature one would be safe enough in assuming a 2% decrease in the ionization due to the decrease in the dielectric constant of water. There still remains a 5% decrease but this can be accounted for since K_2 decreases with rise in temperature and K_a decreases accordingly (from (38)) because $\dfrac{K_1}{[H_2O]}$ is of the same magnitude as 1.

Consider carbon dioxide. K_a increases by 16% when calculated from equation (39), and only 10% when calculated from the data. By taking into account the change in the ionization due to the change in the dielectric constant of water a 14% increase would be obtained which leaves 4% to be accounted for. In this case K_1 increases with rise in temperature causing K_a to decrease. Hence this 4% deviation is qualitatively accounted for.

For ammonia a 6% increase in K_a is calculated

and a 5% increase is found. Correcting for the
effect of the dielectric constant, as in previous
cases, a 4% increase would be the result. However
since K_1 for ammonia is very small and the term
$\frac{K_1}{[H_2O]}$ becomes negligible in equation (38), and since
K_a increases with temperature, K_2 will increase
accordingly and a 5% increase, as calculated from
the ratio of the actual constants, will be of the
right order of magnitude.

It is admitted that the above treatment is
merely qualitative but it proves that the variations
of the constants are in the right directions. If
heats of neutralization were obtainable over a
wide range of temperature and concentration it
would be possible to check the temperature coeff-
icient of the dissociation constant at all temp-
eratures investigated. Unfortunately the available
data has all been obtained at approximately room
temperature.

As has been stated previously the dissociation
constant decreases as the dielectric constant of
water decreases with rising temperature. Hence it
is to be expected that in the case of systems in
which K_2 increases with rise in temperature that
a maximum value will be reached.

SUMMARY.

The work covered in this research may be summed up in the following manner.

Vapor pressure data, accurate to 0.2% has been obtained for solutions of sulphur dioxide, carbon dioxide, and ammonia, up to and in some cases slightly above atmospheric pressure. Coincident with the vapor pressure measurements conductivity measurements were made on the above solutions. These were accurate to 0.1%. In the case of sulphur dioxide the maximum concentration attained was 14.2%, for carbon dioxide 0.36%, and for ammonia 35.6%.

The technique involved in this type of work has been improved in several ways. Pressures were measured to ± 0.1m.m., and volumes were calibrated to 0.1 c.c. Calibrated glass mirror scales were used on the pressure guages. Large reaction chambers were used which facilitated more accurate preparation of dilute solutions. More attention was paid to the obtaining of a true equilibrium by means of vigorous stirring over an extended period of time.

The equilibria equation

$$C_{gas} - [ion] = Hp\left(1 + \frac{C_{H_2O} - C_{gas} + Hp}{K_1} \right) \quad (a)$$

has been developed and tested out. The values
obtained for the constants H and K_1 for sulphur
dioxide have shown that in solutions of SO_2 at
$18^{\circ}C$. approximately 37% of the gas in the solution
is not combined with the water. At $25^{\circ}C$. there is
41% uncombined. The above equation also showed
up hydrate formation when applied at $10^{\circ}$and $0^{\circ}C$.
and had to be changed into the form

$$C_{H_2O} - C_{SO_2} \quad = \quad Hp(\ 1 + \frac{[H_2O]}{K_1} + \frac{[H_2O]^n}{\alpha}\ ) \qquad (b)$$

in order to conform with the experimental facts.

In the case of carbon dioxide where very low
concentrations were all that were attainable and
there was very little change in the water conc-
entration it was impossible to differentiate
between H and K_1. However when equation (a) was
changed into the form

$$C_{CO_2} \quad = \quad Hp(\ 1 + \frac{[H_2O]}{K_1}\ ) + [H^+] \qquad (c)$$

the term $1 + \dfrac{[H_2O]}{K_1}$ is a constant and the equation
is that of a straight line. This was borne out by
the data.

For ammonia the values obtained for H and K_1
indicated complete combination of the ammonia with
water. H and K_1 were very small and it was im-
possible to differentiate between them. In the

case of complete combination it follows that the equation would take the form

$$c_{NH_3} - \left[NH_4^+\right] = Hp \left(\frac{c_{H_2O} - c_{NH_3}}{K_1} \right) \qquad (d)$$

or

$$\frac{c_{NH_3} - \left[NH_4^+\right]}{c_{H_2O} - c_{NH_3}} = kp \qquad (e)$$

which is that of a straight line. This has been shown to be the case.

The variation of the dissociation constants with temperature has been shown to be in the right direction in all cases, and has been checked by calculations from heat of neutralization data.

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