The Hydrolysis of Ammonium Sulphide,
and the Dissociation of the
First and Second Hydrogen
of Hydrogen Sulphide.

Thesis submitted for the degree of
Master of Science by

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Previous Investigations.

From a review of the literature, it appears that no investigations have been made on the hydrolysis of ammonium salts. The following investigation was to ascertain the hydrolysis of ammonium sulphide from vapor pressure measurements of the ammonia and hydrogen sulphide gases, which exist above the solution, and from the concentration of the molecules and ions present in solution.

Assumptions.

Ammonium sulphide, dissolved in water, does not exist wholly as such, in dilute hyd- solution, but hydrolysis partially; that is, it is decomposed, by reacting

with water, to form ammonium
hydroxide, hydrogen sulphide and
ammonium hydrogen sulphide.

All these substances dissociate to
a certain extent into ions. So in
a dilute ammonium sulphide solution,
we have, besides the water molecules,
the following ten kinds of molecules
and ions present.

Molecules,

$$(NH_4)_2S, \quad NH_4SH, \quad NH_4OH, \quad NH_3, \quad H_2S.$$

Ions,

$$NH_4^+, \quad SH^-, \quad S^{--}, \quad H^+, \quad OH^-.$$
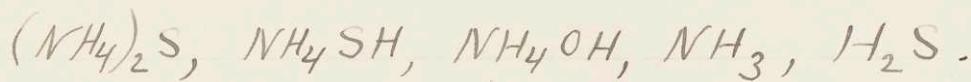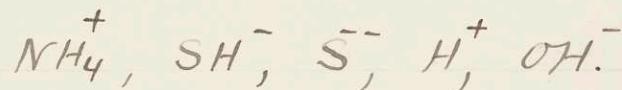
The NH_4OH and NH_3 concentrations cannot,
however, be determined separately;
hence their sum will always be
considered and represented by NH_4OH.
There are therefore nine quantities
to be determined. Of these, four
can be separately and directly derived,

namely, the NH_4OH, the H_2S, the $(NH_4)_2S$ and the OH.

Now we know that solutions give off vapors of their volatile constituents into the space above them; thus an ammonium sulphide solution gives off water vapor and vapors of ammonia and hydrogen sulphide. The concentration of these vapors depends upon their concentration in solution, and upon the temperature. But there always exists, in dilute solutions, according to a law derived by Henry, a constant relation between the concentration of a gas in solution too its concentration in the space above. Knowing this constant and the concentration of the vapor above the solution, one can readily calculate the concentration of this constituent in solution. In this

manner, the amounts of free NH_4OH and H_2S in the ammonium sulphide solution can be obtain, if the concentrations of these gases, respectively, ~~are determined~~ above the solution, are determined analytically.

The undissociated $(NH_4)_2S$ in solution will have to be determined from analogy with other ammonium salts, the dissociations of which are known.

The OH concentration may be determined by saponification. This is done by comparing the rate at which the ammonium sulphide solution will saponify an ester, with the rate at which this same ester is saponified by a sodium or ammonium hydroxide solution of known OH concentration.

Calculation.

From analysis of the solution the total ammonium and sulphur, respectively, can be obtained. The equations expressing the above concentrations, in mols per litre, may be written as follows;

Total ammonium:

$$(1) \quad 2(NH_4)_2S + NH_4SH + NH_4OH + NH_4 = a.$$

Total sulphur:

$$(2) \quad (NH_4)_2S + NH_4SH + H_2S + S + SH = b.$$
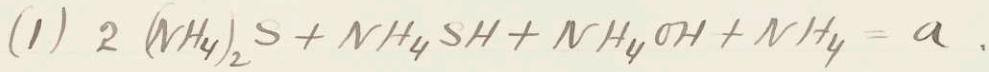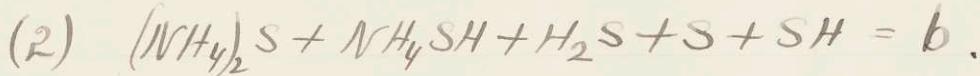
Free H_2S:

$$(3) \quad \frac{C_{H_2S}^{gas}}{C_{H_2S}^{sol}} = K_1. \qquad \therefore \quad C_{H_2S}^{sol} = H_2S = c.$$

Free NH_4OH

$$(4) \quad \frac{C_{NH_3}^{gas}}{C_{NH_3}^{sol} + C_{NH_4OH}^{sol}} = K_2. \quad \therefore \quad C_{NH_4OH}^{sol} = NH_4OH = d.$$

K_1^* and K_2^* can be calculated from data in the literature. A discussion of these values will be given later.

(5) $OH = e$ by saponification.

(6) $(NH_4)_2 S = f$ by analogy.

* For K_1, see Mc Lauchlan, Ztschr. Phys. Chem. 44, 600, (1903).

For K_2 see Gans. Ztschr. Anorg.Chem. 25, 236, (1900).

Goldschmidt, Ztschr. Anorg. Chem. 28, 97, (1901).

Abegg and Riesenfeld, Ztschr. Phys. Chem, 40, 84, (1902).

Perman, J. Chem. Soc. Trans. 79, 718, (1901).
81, 483, (1902).
83, 1168, (1903).

Locke and Forsall Amer. Chem. Jour. 31, 286, (1904).

In equation (4), strictly we should have written by Henry's law

$$\frac{C^{gas}_{NH_3}}{C^{sol}_{NH_3}} = K' \qquad [1]$$

but from the Law of Mass Action we know that there must be a constant ratio between the NH_3 in solution and the NH_4OH, so we may write,

$$\frac{C^{sol}_{NH_3}}{C^{sol}_{NH_4OH}} = K'' \qquad [2]$$

Multiplying these two equations together they become

$$\frac{C^{gas}_{NH_3}}{C^{sol}_{NH_4OH}} = K'K'' \qquad \text{or inverting}$$

$$\frac{C^{sol}_{NH_4OH}}{C^{gas}_{NH_3}} = \frac{1}{K'K''}$$

Inverting [1] and adding it to this

equation we derive

$$\frac{C^{sol}_{NH_4OH} + C^{sol}_{NH_3}}{C^{gas}_{NH_3}} = \frac{1}{K'K''} + \frac{1}{K'} = \frac{1}{K_2}$$

Inverting this it becomes

$$\frac{C^{gas}_{NH_3}}{C^{sol}_{NH_4OH} + C^{sol}_{NH_3}} = K_2$$

This equation is identical with equation (4) previously derived.

The NH_4OH and H_2S concentrations in solution, represented in equations (4) and (3), respectively, are the same as those in equations (1) and (2) respectively.

It is well to combine the equations obtained so far, to simplify their solution.

Subtracting (2) from (1) we obtain,

$$(NH_4)_2 S + NH_4 OH + NH_4 - H_2 S - S - SH = a - b$$
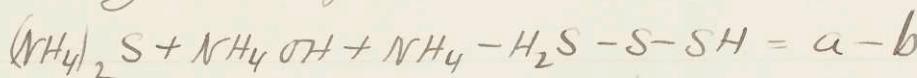
Substituting in this equation our known values it becomes

$$f + d + NH_4 - C - S - SH = a - b$$
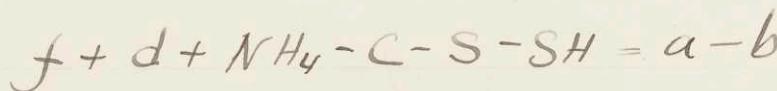
Transposing,

$$NH_4 - S - SH = a - b - f - d + c \qquad (7)$$

but in solution the ions, that are positively charged must be equivalent to those carrying negative charges, hence,

$$\overset{+}{H} + \overset{+}{NH_4} = \overset{-}{S}H + 2\overset{=}{S} + \overset{-}{OH} \qquad (8)$$

Subtracting this equation from (7) we have,

$$-H + S + OH = a - b - f - d + c \qquad (9)$$

The Mass Action Law states that in solution the product $H \times OH$ must always have a constant value, therefore

$$H \times OH = K_w \qquad (10)$$

but K_w is known and $OH = e$ from saponification, so $H = \dfrac{K_w}{e}$.

Substituting this value of H in (9) it simplyfies to

$$S + e - \frac{K_w}{e} = a - b - f - d + c$$

Transposing

$$S = a - b - f - d + c - e + \frac{K_w}{e} \qquad (11)$$

Further the Mass Action Law requires that

$$\frac{C_{NH_4} \times C_{OH}}{C_{NH_4OH}} = K_3 .$$

but NH_4OH has been determined, OH is known, and K_3 can be obtained from the literature,* therefore

$$NH_4 = \frac{K_3 \times d}{e} \tag{12}$$

Substituting this and the value of S in (7) we have

$$\frac{K_3 \times d}{e} - SH = 2a - 2b - 2f - 2d + 2c - e + \frac{K_w}{e}$$

Transposing

$$SH = -2(a - b + c - d - f) + e + \frac{K_3 d - K_w}{e}$$

* Gans, Ztschr. Anorg. Chem. <u>25</u>, 236, (1900)
  Bredig, Ztschr. Phys. Chem. <u>13</u>, 289, (1894)

Finally from the Mass Action Law we derive two more equations,

$$\frac{H \times HS}{H_2 S} = K_4 \qquad (14)$$

$$\frac{H \times S}{HS} = K_5 \qquad (15)$$

K_4 and K_5 are now the only unknowns as H, HS, H_2S, and S have all been calculated, hence the values of K_4 and K_5 can readily be deduced. They are the dissociation constants for the first and second hydrogens of hydrogen sulphide, respectively.

The calculation of K_4 and K_5 when the OH concentration is not determined, can be made as follows, provided the concentration of $NH_4 SH$ in solution is estimation by analogy as was done in the case of $(NH_4)_2 S$ in the above calculation.

Starting with the equations expressing the total ammonium and sulphur concentrations respectively, as in the previous calculation we have:

$$2(NH_4)_2 S + NH_4 SH + NH_4 OH + NH_4 = a \qquad (1)$$

$$(NH_4)_2 S + NH_4 SH + H_2 S + SH + S = b \qquad (2)$$
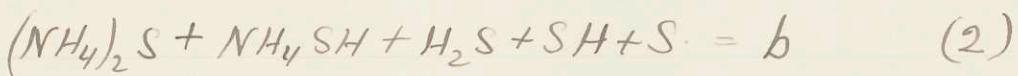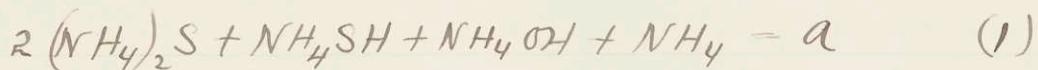
Substituting in (1) and (2) known values we obtain respectively,

$$2f + g + d + NH_4 = a \qquad (3)$$

$$f + g + c + SH + S = b \qquad (4)$$

where g is the value of the $NH_4 SH$ concentration, estimated by analogy, and a, b, c, d, f are the concentrations as previously shown.

Transposing (3) and (4) gives

$$NH_4 = a - d - g - 2f \qquad (5)$$

$$SH + S = b - c - g - f \qquad (6)$$

Now all the positive ions in solution must equal the negative, therefore,

$$\overset{+}{H} + \overset{+}{NH_4} = 2\overset{=}{S} + \overset{-}{SH} + \overset{-}{OH} \qquad (7)$$

Multiplying both sides of equation (6) by (2) we obtain

$$2SH + 2S = 2b - 2C - 2g - 2f \qquad (8)$$

Adding (7) to this gives

$$H + NH_4 + SH - OH = 2b - 2C - 2g - 2f. \qquad (9)$$

Substituting in the value of NH_4 from (5) and transposing, we have,

$$H + SH - OH = -a + 2b - 2C + d - g \qquad (10)$$

From the Mass Action Law, however,

$$\frac{NH_4 \times OH}{NH_4 OH} = K_3^* \qquad or$$

$$OH = \frac{K_3 \, d}{(a - d - g - 2f)} \qquad (11)$$

But also from the Law of Mass Action

$$H \times OH = K_w \qquad (12)$$

K_w is known.

Substituting the value of OH found in (11) in this equation gives:

* Gans, Ztschr. Anorg. Chem. <u>25</u>, 236, (1900)

Bredig, Ztschr. Phys. Chem. <u>13</u>, 289, (1894)

$$H = \frac{K_W(a-d-g-2f)}{K_3 d} \qquad (13)$$

Now from equation (10) if the H and OH values are substituted we obtain,

$$\frac{K_W(a-d-g-2f)}{K_3 d} + SH - \frac{K_3 d}{(a-d-g-2f)} = -a+2b-2c+d-g.$$

Transposing and simplifying gives,

$$SH = \frac{(K_3 d)^2 - K_W(a-d-g-2f)^2}{K_3 d(a-d-g-2f)} - (a-2b+2c-d+g) \quad (14)$$

All the factors on the right hand side are known. So substituting this value of SH in equation (6) we obtain,

$$S = (a-b+c-d-f) - \frac{(K_3 d)^2 - K_W(a-d-g-2f)^2}{K_3 d(a-d-g-2f)} \qquad (15)$$

as shown before from the Mass action law,

$$\frac{H \times SH}{H_2 S} = K_4 \qquad\qquad (16)$$

$$\frac{H \times S}{HS} = K_5 \qquad\qquad (17)$$

The only unknowns are K_4 and K_5 which are the dissociation constants of the first and second hydrogens of hydrogen sulphide, respectively.

I. Previous Vapor Pressure Measurements with Ammonia and Hydrogen Sulphide Solutions.

There are five principle investigations on the distribution of ammonia between the liquid and gaseous phase, the which are tabulated below.

Investigator	Temp.	NH_3 Conc.	Press in mm Hg.	$\dfrac{C^{gas}_{NH_3}}{C^{sol}_{NH_3}}$
*Gaus				
	25°	1.000	13.45	0.000724
	25°	0.702	9.35	0.000717
	25°	0.456	5.97	0.000705
*Abegg and Riesenfeld.				
	25°	1.000	13.45	0.000724
	25°	0.506	13.27 Mol	0.000715

*See References on page

Investigator	Temp.	NH_3 Conc	Press in mm Hg	$\dfrac{C^{gas}_{NH_3}}{C^{sol}_{NH_3}}$
*Goldschmidt				
	25°	0.553	7.09	0.000 690 .
	25°	0.820	10.81	0.000 710 .
	25°	1.106	14.73	0.000 717 .
*Perman				
	25°	1.503	19.5	0.000699
**Locke and Forsall				
	25°	0.096	1.29	0.000 724
	25°	0.242	3.23	0.000 719
	25°	0.406	5.41	0.000718
	25°	0.729	9.80	0.000 724
	25°	0.993	13.42	0.000 728

* See References on page

** Am. Chem. J.   (1904)

The table indicates that the constant increases slightly with the concentration of the solution, changing by about two percent between the concentrations 0.5 and 1.0 normal. Averaging the values obtained by the several investigators for concentrations of about 0.5 normal, we obtain 0.000707 as the constant expressing the ratio of the NH_3 concentration in the gaseous phase to the NH_3 in the liquid phase, when the two phases are in equilibrium.

The only work done on the ratio of the hydrogen sulphide concentration in the gaseous phase to its concentration in the liquid phase is that of Mc Lauchlan.[*]

[*]   Ztschr. Phys. Chem. 44, 600, (1903).

His values are tabulated below.

These experiments were carried out at 25°.

Press. in mm. Hg.	Conc. of H_2S in millimols per liter	$\dfrac{C^{gas}_{H_2S}}{C^{sol}_{H_2S}}$
88.7	11.94	0.400
99.8	13.5	0.398
74.7	10.0	0.402
105.5	14.4	0.395
101.4	14.00	0.390
mean		0.397

The constant expressing the ratio of the distribution of hydrogen sulphide between the liquid gaseous and liquid phase, when these two phases are in equilibrium, is 0.397.

II. Effect of Salts on the Vapor Pressure of Ammonia and Hydrogen Sulphide Solutions.

Several & investigators [*] have determined the effect, on the vapor pressure of ammonia solutions, by the addition of various types of salts and of varying concentrations. The general conclusions arrived at from reviewing their results may be stated as follows:

Some salts increase the vapor pressure, some decrease it, and others effect it very slightly.

The effect is approximately proportional to the concentration of the

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[*] Gaus, Ztsch. Anorg. Chem. 25, 236, (1900)

[*] Abegg and Riesenfeld Ztsch. Phys. Chem. 40, 84, (1902)

[*] Perman, J. Chem. Soc. Trans. 81, II 168, (1903)

added salt.

Salts having an anion of one atom have a less effect on the vapor pressure than salts having more atoms as anion.

It appears that those anions which have the greatest tendency to hydrate produce the greatest rise in the vapor pressure.

*Gans determined the change of vapor pressure of an ammonia solution of normal concentration, produced by the addition of the following salts, the concentrations of which were 0.4 Normal. in the solution.

Salt.	Percentage change of Vapor Pressure.	Salt	Percentage change of Vapor Pressure
NH_4Cl	$+0.67$	$(NH_4)_2SO_4$	$+7.21$
NH_4NO_3	$+0.15$	$(NH_4)_2C_2O_4$	$+6.10$
NH_4I	$+1.86$	$(NH_4)_2C_4H_4O_6$	$+2.83$
NH_4SCN	-2.00	N	

* Taken from Abegg an Riesenfeld,
  Ztschr. Phys. Chem. 40, 41, (1902).

Abegg and Riesenfeld found that a
normal ammonia solution increased
its vapor pressure by 0.26 percent
when a half a gram mol of sodium
sulphide was added to it.

Thus it is clear that the
change of vapor pressure of ammonia
solutions, caused by the ~~and~~ presence of
dissolved salts, cannot be predicted
with an accuracy of less than
seven percent. Nevertheless it is
quite certain that in more dilute
solutions, example 0.2 normal, this
effect would not exceed one to
two percent.

The effect of dissolved salts
on the vapor pressure of hydrogen sulphide
solutions is not appreciable.*

* McLauchlan, Ztschr. Phys. Chem. 44, 600, (1903)

III. The Value of the Dissociation Constant of Ammonia.

The specific conductivities of ammonia solutions passes through a maximum value as the concentration of the solution is increased, as shown by Goldschmidt.[*] The maximum value lies at about a concentration of 3 normal. The specific conductivities at low concentrations, obtained by Goldschmidt are as follows:

NH_4OH conc.	Spec. Cond. 10^6
0.0109	22.4
0.0219	22.2
0.0553	21.5
0.1107	21.4
0.3148	20.3

[*] Ztschr. Anorg. Chem. 28, 117, 1901.

Goldschmidt calculated his dissociation constant for ammonia in solution and found it to be 18.5×10^{-6}. Bredig[*] found the dissociation constant to be 23×10^{-6}, but he used a Λ_∞ value which since his work has been found incorrect. If, however we calculate Bredig's constant using the value of Λ_∞ which Goldschmidt used, the constant comes out 17.6×10^{-6}. Hantzsch and Davidson[**] calculated the dissociation constant of ammonia and found it to be 18×10^{-6}. So 18×10^{-6} is probably the best value.

[*] Ztschr. Phys. Chem. 13, 289, (1894)
[**] Ber. deutch. Chem. Ges. 31 (1898)

IV. General Outline of Procedure
for the Vapor Pressure Measurement
of Ammonia and Hydrogen Sulphide
above an Ammonium Sulphide Solution.

The method to be used,
in determining the vapor pressures
of ammonia and hydrogen sulphide
gases, respectively, above an ammonium
sulphide solution, is to pass a
known volume of hydrogen gas, in
very small bubbles, through the
solution thereby saturating the
hydrogen, at constant temperature
with ammonia and hydrogen sulphide
gases, in proportion to their vapor
pressures above the solution. The
ammonia and hydrogen sulphide
are then absorbed by passing the
gases through a ~~normal~~ hydrochloric

acid solution of arsenious oxide. The acid has a concentration of one part of 1.20 acid to three parts of water. The concentration of the arsenious oxide is about six grams per litre. The hydrogen sulphide precipitates arsenic trisulphide, while the ammonia is absorbed as ammonium chloride. Thus the concentrations of the above two gases can be determined analytically. Then as already shown, by aid of Henry's Law the amounts of these two gases in solution can be ascertained.

V. Description of the Apparatus.

The hydrogen gas used must
be absolutely free from oxygen, since
the latter readily decomposes ammonium
sulphide. In order, therefore to obtain
pure hydrogen, the apparatus shown
in the diagram was devised; and to
have a convenient means of supply,
the electrolytic method of generation
is used.

The generator consists of an
upright glass cylinder (A), 5.5 cm. in
diameter, and 30 cm. high. The lower
end is closed by a large rubber
stopper (m). The upper end is fitted
with a similar stopper through which
passes a glass tube (B), 35 cm long,
and 2.5 cm. in diameter, reaching
nearly to the lower stopper of tube (A).

Generator.
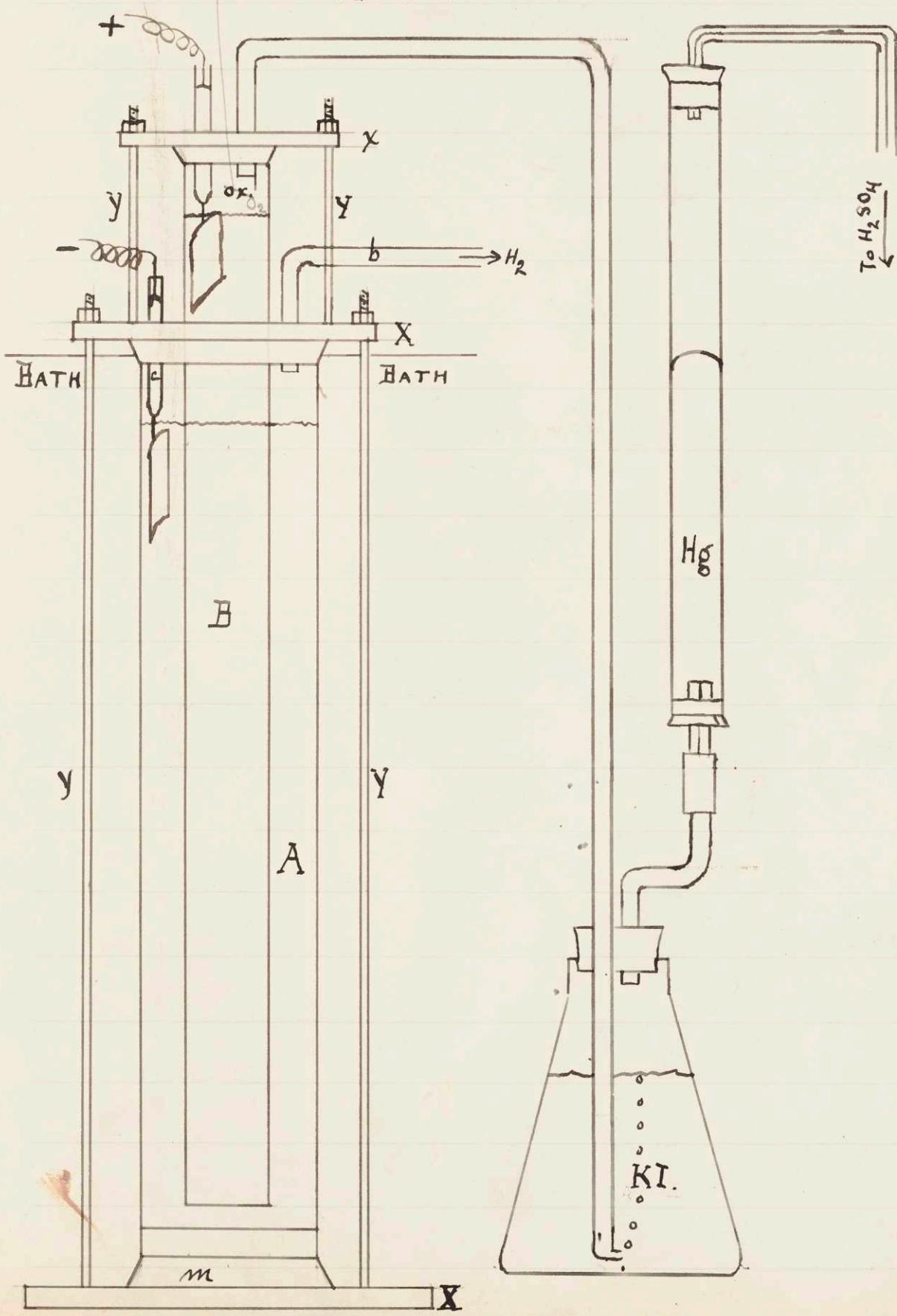
Also through this stopper, there extends
a delivery tube (b) 6 mm. in diameter,
to conduct away the hydrogen gas
generated. Another tube (c) of the same
size passes through the stopper and
has fused to its lower end a platinum
electrode 25 sq. cm. in area. Electrical
contact is made by filling the tube
with mercury. The upper end of
tube (B) is fitted with a rubber
stopper, through which pass two
tubes similar to those I just described
for tube (A). One of these tubes conducts
away the gas generated, and the other
has fused to it a platinum electrode
also 25 sq. cm. in area.

A considerable gas pressure
has to be produced in the apparatus,
tending to blow out the rubber stoppers,
so they are fastened down by the

brass plates (X), which are held
tightly together by the rods (Y),
fitted with removable nuts.

To minimize the heating of
the generator, during electrolysis, a
twenty five percent sulphuric
acid solution is used, and the
generator is placed in a bath of
running water which surrounds it
nearly to the top of tube (A).

In order to obtain a constant
pressure of hydrogen gas in the generator,
the rate at which the oxygen is conducted
away, from the electrode in tube (B),
must be regulated. It was found
that the ozone formed gave trouble by
destroying the rubber connections;
therefore the gas from (B) is conducted
immediately, through the delivery
tube, into a strong solution of

potassium iodide. From here it passes through a capillary tube and bubbles up into a column of mercury, some 10 cm. high. This column counterbalances most of the pressure. The remaining pressure is balanced by conducting the gas through a long capillary into a column of sulphuric acid, one meter high, the height of which can be rega varied. In this manner the gas pressure can is regulated so that it remains constant for a number of hours.

The hydrogen gas generated at the electrode in (A) is conducted from the delivery tube (b) through a thermometer capillary 6 cm. long. This is inserted by means of a rubber stopper in the end of a glass tube

1.1 cm in diameter and 1.5 meters long.
The tube is inclined at an angle
and contains a solution of potassium
pyrogallate. The hydrogen gas bubbles
through about 1.2 meters of this solution,
thereby removing any traces of oxygen
which may have been present owing
to diffusion from the anode.

The pyrogallate solution is made
by dissolving 5-grams of pyrogallic
acid in 100 ccm of a ten percent
solution of potassium hydroxide.

The pure gas is now led into
the saturating-apparatus, which contains
the solution of ammonium sulphide.
Two slightly different forms of this
apparatus were used.

The gas on leaving the
pyrogallate tube, passes through
6 cm of thermometer capillary tube,

Saturating Apparatus.
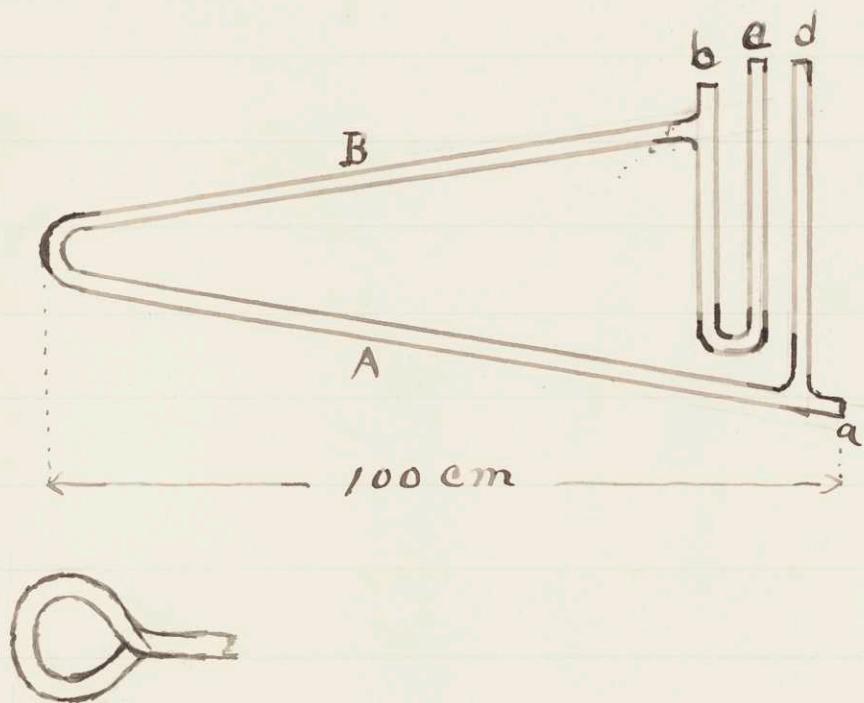


Fig. 1.
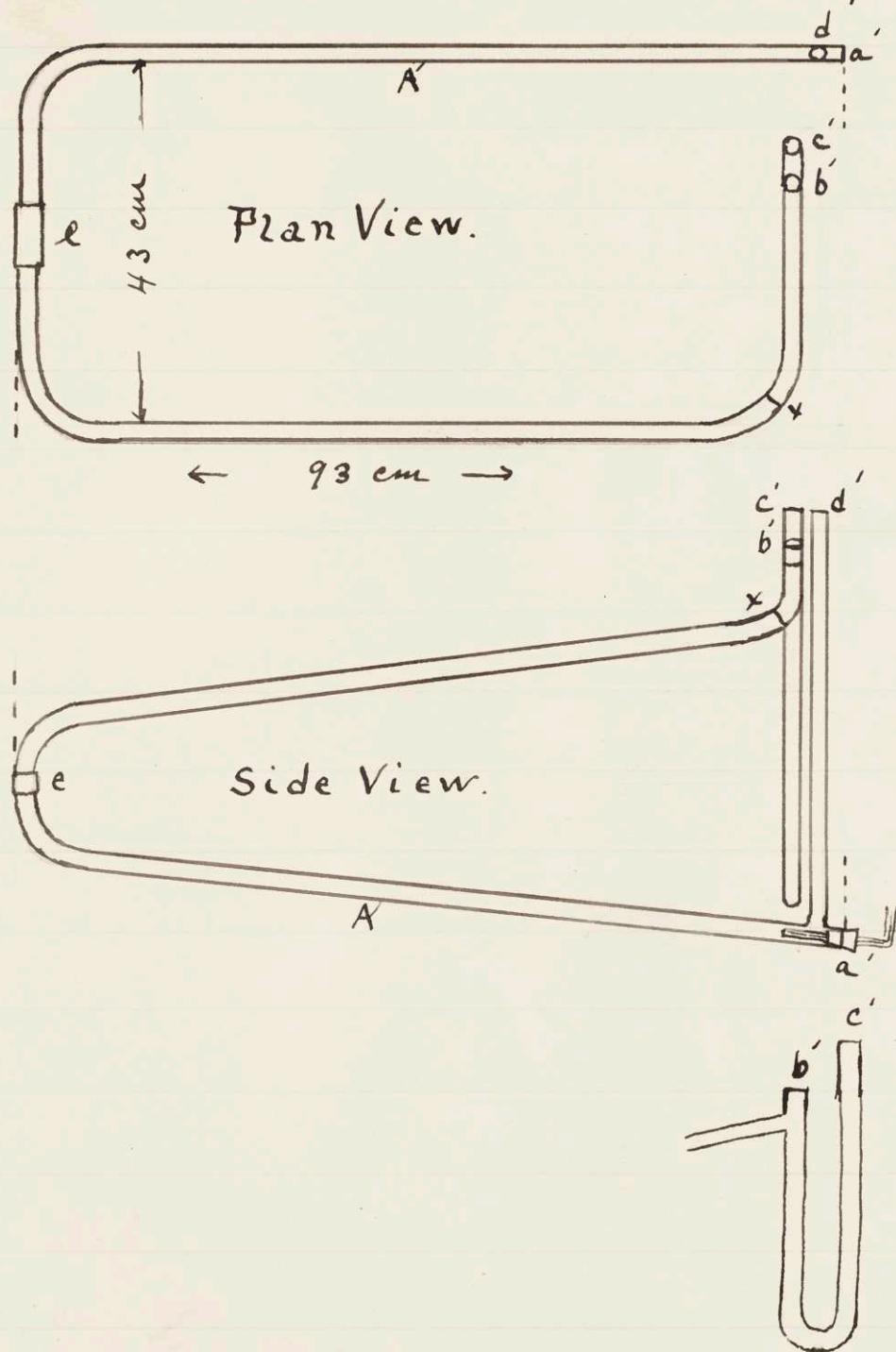
Saturating Apparatus.

Plan View.

43 cm

93 cm

Side View.

Fig. 2.

shown at (a), inserted, by a rubber
stopper, in the lower end of the
apparatus. Thermometer capillary
tubing has proven to be more
satisfactory than ordinary capillary
tubing. The latter had to be drawn
out to a very fine capillary to produce
small enough bubbles. This caused
a great deal of trouble through the
capillary becoming clogged readily
by particles of foreign matter
in the solution. The thermometer
capillary, being very much finer,
did not have to be drawn out,
and the tendency to become clogged
was reduced. Further these capillaries
serve the purpose of producing a
constant pressure of hydrogen gas.
This pressure is necessary to provide
a continuous flow of bubbles. With

the ordinary capillary tubing, it
required over three meters length
of tube, to establish this constant
pressure, which is now replaced
by 6 cm of thermometer capillary.

The saturating apparatus is
made of glass tubing 1 cm. in diameter.
The hydrogen gas issues from the
end of the capillary in very small
bubbles, 2 to 3 mm, in diameter, and
passes up the tube (A) which has a
very gradual grade. The tube is
bent, at the end, in a gradual curve
back to same vertical plane shown
at (B). The rise is about 10 cm to
the meter. The apparatus is filled
with solution to the mark (x). In
order that the solution may not
become reduced in concentration,
by the removal of hydrogen sulphide

and ammonia, fresh solution is flowed constantly from a large stock bottle, holding 8 to 9 litres. The solution enters the U tube CD, at C, and overflows at d, into an overflow bottle of 9 litres capacity.

From previous experiments it was found that complete saturation[*] was not obtain with this apparatus but only to the extent of about 90 to 95 percent, so a second tube, as shown in fig. 2., was connected to the apparatus just described. The hydrogen gas after passing through the first apparatus, saturating itself to within 5 or ten percent of completeness is conducted, from, into the second apparatus, through a thermometer capillary similar to that of the first. Small bubbles of gas pass up the

[*] It was thought that saturation could be obtained by filling the saturation tube with glass beads, thereby offering more surface to the gas but this was less effecent than the above process.

tute (A') which is made of two pieces
of glass tubing 1 cm in diameter.
and joined by a rubber connection
at (e). It was more easily made
in two pieces and further the grade
could be adjusted so that the bubbles
would pass up the tube more uniformly.
This second portion of the apparatus
was fed similarly to the first with
solution from the stock bottle. The
solution enters at c' and overflowed at
d' into the overflow bottle. The amount
of solution allowed to flow through
this second portion of apparatus was
about one fourth of that which flowed
f through the first — as the gas
becomes so nearly saturated in the
latter. The total length of solution
in which the gas becomes saturated
is about 4 meters.

The vapor pressure measurements
must be carried out at a constant
temperature, 25,° therefore the saturating
apparatus is immersed in a large
thermostat, the temperature of which
is kept within 0.02° by an electrical
heating circuit an efficient stirrer.

At the point (b'), in the second
tube is inserted a .T tube, one arm of
which connects with a mercury gauge,
which will be spoken of later, and
the other arm conducts the hydrogen
gas, through two Geissler bulls
which containing some of the stock solution.
No appreciable change in the concentration of the
solutions in these bulls, on analysis, indicates the
completeness of the saturation.

The gas, now saturated with
ammonia and hydrogen sulphide in
proportion to their vapor pressures, passes

to the absorber, first through 5 cm of
thermometer capillary tube, then through 10 cm
of ordinary capillary tubing which is
inserted into the end of the absorber by
a rubber stopper. The thermometer tube
is to establish back pressure to cause
a uniform flow of bubbles, while the
larger capillary is inserted into the
absorber to prevent the clogging of
the capillary with by the precipitate
of arsenic trisulphide produced in
the absorber it. The absorber is a
straight glass tube one meter long
and one cm in diameter, containing 60
ccm of the strong hydrochloric acid
solution of arsenious oxide already
spoken of. It is inclined at a slight
angle and the lower end is immersed
in the thermostat to prevent any
condensation of gases before they are absorbed.

To confirm the completeness of absorption,
a bulb containing some of the absorbing
solution is connected to the end of the
absorber.

Since ammonium sulphide solution
is easily oxidized by air, the solution
is made and kept under hydrogen
gas, generated from zinc and sulphuric
acid in a Kipp Generator. The latter
is connected to both the supply and
overflow bottle. The solution in the
overflow can be used again after
analysis.

In order to determine the
volume of hydrogen gas passed
through the solution a copper
voltameter is connected in series with
the generator. From the copper deposited
and the pressure of the gas, after
saturation, as determined by the

mercury gauge previously spoken of,
it is possible to calculate the
volume of the gas generated. To
check this volume, the gas is collected,
as it leaves the absorber, in a large
bottle, which is kept in the thermostat at
constant temperature, The volume of the
bottle has been determined.

VI Analytical Methods Used.

Total Ammonia and Sulphur in the
Ammonium Sulphide Solution.

The total ammonia in the
ammonium sulphide solution will be
determined by the ordinary process
of distillation.* After the addition
of a small amount of sodium hydroxide,
the ammonia is distilled from the
solution, into a standard solution of
hydrochloric acid, which may be
titrated back with standard sodium
hydroxide, using methyl orange as
an indicator. The accuracy of this
method was tested as follows. A
known weight of ammonium chloride
was taken. To it was added 10 ccm.

* Fresenius, Quantitative Analysis.

of approximately 30 percent sodium
hydroxide. The ammonia was then
distilled into 0.1587 normal hydrochloric
$^{25^{cc} of}$
acid solution. This was titrated back
with 0.1495 normal potassium hydroxide.
The ammonium chloride was obtained
pure by dissolving some of Merck's
C.P. in water, and precipitating it
by passing in hydrochloric acid gas.
This was filtered off and re-crystallized
twice from water solution. It was
then dried by heating over a flame
in a platinum dish until it commenced
to volatilize copiously. In two different
experiments using 0.1506 and 0.1502 grams
of ammonium chloride, there was found
0.1509 and 0.1501 grams respectively.
A blank determination using 10^{cc}
of the sodium hydroxide in water checked
as follows. The amount of standard

hydrochloric acid put in receiver was
24.89 ccm. The amount found by
titration with standard alkali was 24.85.

The total sulphur is determined
by adding a known volume of the
ammonium sulphide solution to
a slightly ammoniacal solution
of arsenious oxide dissolved in hydrochloric
acid, then the arsenic trisulphide
is immediately precipitated by
acidify the solution with hydrochloric
acid. The precipitate is filtered on
a Gooch, thoroughly washed, dried
at 100°, and weighed as arsenic
trisulphide. The constancy of the
weight of arsenic trisulphide,
when heated to 100°, was tested
with 0.0204 grams. The weight
did not change after several
hours heating.

VII. The Hydrogen Sulphide and Ammonia
from the Absorber.

The hydrogen sulphide and
ammonia removed from the ammonium
sulphide solution by the hydrogen
gas are, as stated above are absorbed
in a hydrochloric acid solution
of arsenious oxide, containing 6 grams
of the oxide per litre, and acid
of the strength of one part of
1.20 acid to three parts of water.
The ammonia is absorbed as ammonium
chloride and remains in solution,
and the hydrogen sulphide precipitates
arsenic trisulphide. This is filter
off on a Gooch, washed thoroughly,
dryed at 100° and weighed as such.
The filtrate containing the ammonia
as chloride is neutralized with an

excess of potassium hydroxide and
the ammonia distilled off into
standard acid.

VIII. Preliminary Experiments.

The vapor pressure of an ammonia solution was determined with the apparatus described.

The ammonia solution was made from absolutely pure ammonia, (free from hydrocarbons), and best distilled water.

Hydrogen gas, generated as has been described, passed through the ammonia solution contained in the saturating apparatus, thereby removing ammonia from the solution at a constant temperature of 25°. The ammonia in the gas was then absorbed in the absorber which contained hydrochloric acid of the strength of one part of 1.20 acid to three parts of water. The ammonia was then distilled from this solution

One run was made in this manner giving the results tabulated below.

Time hrs.	Press CM.	Copper Dep. grams	Vol. Gas litres	Temp.	NH₃ removed in mols	Conc. NH₄OH mols	Constant. $\frac{C_{gas}^{NH_3}}{C_{sol}^{NH_4OH}}=K$
7.5	81.9	16.88	6.02	25°	0.0004438	0.1069	0.000691

current = 1.8ᵃ

Equilibrium between vapor and solution was approached from the opposite direction, namely supersaturating the hydrogen gas with ammonia before it entered the saturating apparatus, and depending on its passage through the ammonia in this apparatus to regain equilibrium. This was accomplished by bubbling the gas through a stronger ammonia solution first, (a 0.20 solution was used), before it entered the solution under investigation.

Two runs were made in which this method of supersaturation was used giving the following results.

Time hrs	Press CM	Coffee Dep. Grams	Vol Gas litres	Temp.	NH_3 removed mols	Conc NH_4OH mols	Constant $\dfrac{C^{NH_3}_{gas}}{C^{NH_4OH}_{sol}}$ K
7.0	81.0	16.60	5.98	25°	0.0004356	0.1064	0.000685
6.0	81.1	16.64	5.99	25°	0.0004440	0.1064	0.000696

Averaging the three constants obtained, we derive, for the distribution coefficient of ammonia into the gaseous phase from its solution, the value 0.000691 for dilute solutions of approximately 0.100 normal.

In all three of the above runs the Geissler bulb, confirming the completeness of the saturation, did not change in concentration by 0.3 of a percent. This is within the experimental error. All tubes at the end of the

absorber confirmed the completeness of the absorption. The gas volumes check within the usual error of one percent.

This value 0.000691 for the distribution of ammonia between the liquid and gaseous phases agrees with the values obtained by previous investigators.

IX. Hydrolysis of Ammonium Sulphide.

Preparation of Solution.

Best distilled water was saturated with hydrogen sulphide. The hydrogen sulphide was generated from iron sulphide and sulphuric acid, and the gas washed with water. The gas was found to be free from carbon dioxide. After saturation, almost a sufficient amount of ammonia was added to make the normal sulphide, namely $(NH_4)_2S$. The solution was now analysed for ammonia and hydrogen sulphide. Then the sufficient amount of a standard solution of ammonia was added to form the normal salt.

Vapour pressure measurements were made with this solution, the

results being as follows :-

The ammonium sulphide solution contained 0.200 mols of ammonia to 0.095 mols of hydrogen sulphide per litre. The time of each run was about seven hours — and the temperature 25.°

Conc per litre of gas & mols of NH$_3$ and H$_2$S removed.		Free NH$_4$OH in sol. Const. 000691	Free H$_2$S in sol in mols 0.397
NH$_3$	H$_2$S.	mols	mols.
0.0000735	0.0001225	0.1064	0.0003094
0.0000739	0.0001156	0.1070	0.000291
0.0000735	0.0001145	0.1063	0.000288
0.0000737	0.0001005	0.1067	0.000253

In the last two runs equilibrium was reached by supersating the hydrogen gas before it entered the ammonium sulphide solution. This was accomplished by passing

the gas through a short tube filled
with the ammonium sulphide solution
but kept at 30°. It contained about 25ᶜᶜ of sol.

In the above four runs about
one and a half to two litres of
solution was flown in each case
to prevent the changeing of concentration
due to the removal of ammonia
and hydrogen sulphide. The Geissler
bulb which confirmed the saturation
changed less than one and a
half percent in concentration.
This is with-in the experimental error
of analysis.

From the above data it appears
as though the hydrolysis of an
ammonium sulphide solution of approximately
0.200 Normal concentration was about
53.3%.

X Hydrolysis of Ammonium Sulphydrate Solution.

This solution was made the same as the ammonium sulphide solution with the exception that there was only enough ammonia added to form the salt NH_4SH.

The solution contained. 0.0871 mols of ammonia per litre and 0.0864 mols hydrogen sulphide.

This solution was too concentrated for use with the apparatus devised, for after two hours running the absorber contained such a voluminous precipitate of arsenic trisulphide that the process stopped. The run was analysed with the following results:-

Mols NH_3 removed per litre of gas	Mols of H_2S rem per litre of gas	Free NH_4OH in mols in sol	Free H_2S in mols in sol.
0.0000.1246	0.001966	0.01803	0.00495

This indicates that the hydrolysis
of an NH_4SH solution, approximately
.08% molar, is from 30 to 40%.

A weaker solution could
not have been used as the
ammonia given off from the above
solution is even too small to
obtain an accuracy of less than
20 to 25%. The ammonia given off
only neutralized 0.9^{cc} of a 0.0195
normal hydrochloric acid solution.