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Determination of Minute Amounts of Ammonia in Gas Mixtures by a Potentiometric Method.

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Part I

Özet : Bu çalışmada, gaz karışımlarında bulunan çok az miktardaki amonyağın potansiyometrik olarak tayini incelenmiştir. Kauka'nun havadaki karbondioksit tayinine tatbik ettiği potansiyometrik metod, % 0,001 civarında amonyak ihtiva eden gaz karışımlarının analizine hassasiyetle tatbik edilebilir. Bunun için asidik gazların bazik ortamda adsorpsiyonundan sonra gaz karışımı 1,0ʋ-M- NH_4Cl çözeltisi içine gönderilir, dengeye geldikten sonra pH ölçülür ve tekabül eden basınç termodinamik olarak hesaplanır. 25,0° C da denge müddeti uzundur, 40,0° C da 30 dakikada dengeye erişilebilmektedir. Metodun hassasiyeti denge sabitlerine bağlı olduğundan, çok hassas çalışmalar için sabitlerden gelen hatayı gidermek üzere yine Kauka tarafından CO_2 tayinine tatbik edilen fark metodu ile çalışılmalıdır.

$k_2 = \overline{NH_4} \cdot \overline{OH'} / {}^P NH_3$ denge sabitinin termodinamik olarak hesaplanan her değerinin, tecrübî olarak hesaplanan k_2 ye uymadığı görülmüştür.

Bu metod idrardaki, topraktaki ve dolayısıyla çözeltilerdeki amonyak tayinine tatbik edilebileceği gibi, gaz karışımlarında bulunan SO_2 ve H_2S tayinine de tatbik edilebilir.

The possibility of potentiometric determination of minute amounts of ammonia in gas mixtures was first put forward by Airola and later by Pekkarinen. However, the matter has not so far been settled. The lack of any satisfactory method of such an estimation has led us to undertake the present investigation.

Methods of Determination of Ammonia :

Titration :

The gas mixture containing ammonia is absorbed in a definite volume of standardized acid solution; such as sulfuric,

hydrochloric or boric acid, then the excess acid is titrated with standardized sodium hydroxide solution. This method cannot be applied accurately when the amount of ammonia is too small [1].

Colorimetric and Nephelometric Methods:

Ammonia can be determined *colorimetrically* with the aid of a) Nessler's reagent [2], b) phenolsodium hypochloride; c) silver nitrate and tannin; and *nephelometrically* with mercuric chloride potassium-ammonium complex [3].

Oxydation Method:

Calcium hypochlorite [4], sodium hypobromite [5] and potassium biiodate [6] are used to oxidize ammonia.

In order to determine NH_3 colorimetrically, nephelometrically or by the oxidation method a quantitative absorption is essential. Therefore these methods fail to give accurate results in the case of mixtures containing minute amount of ammonia.

Conductimetric Method:

Hendricks [7] and coworkers have absorbed ammonia in boric acid and measured the conductivity. In order to obtain the amount of ammonia; known amounts of ammonia were added to a boric acid solution, diluted and to the same volume as of the unknown and the conductivities of each solution were determined. The results were plotted to give an empirical calibration curve. It is indicated that, in the estimation of ammonia of the order of 10 micrograms, contained in 25 ccs. of solution, a difference of 10 % is observed. It is suggested to change the shape of the absorber and the conductivity cell and to dilute to 5-10 ccs before the measurements, while working with small amounts of ammonia. It is clear, that to absorb ammonia quantitatively in a still smaller volume is impossible.

Aeration Method:

In this method the ammonia is carried with a strong air current and absorbed by an acid. This method which is proposed by Folin [8], has been applied to the determination of ammonia in urine and soil [9]. The rate of air flow has been changed from 250 1 it./h [10] to 1080 1 it./h [11] and the absorption time from one hour to 19 hours. Tall wash towers are used to arrest the traces of ammonia carried by this rapid air current.

Since the alkali used to decompose the sample is also spattered; the acids are transferred to a distilling flask and redistilled after addition of excess alkali. We believe that for the absorption of the traces of ammonia, larger towers convenient for technical purposes, should be used. Naturally this will not be practical and will result in greater error.

The experimental method used in the present work is, in principle, the same as that used by Kauko in the determination of carbon dioxide in air. Here, we would like to describe the Kauko method briefly.

Part II

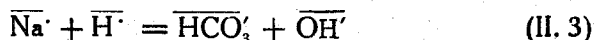### Determination of Carbon Dioxyde by the Kauko-Method[12]

Kauko and his co-workers [13] determined carbon dioxide potentiometrically. Writing the equilibrium of carbonic acid :

$$CO_{2\,(g)} + H_2O \overset{\rightarrow}{\leftarrow} H^{\cdot} + HCO_3' \qquad (II.\,1)$$
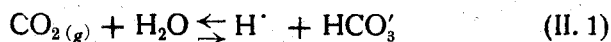
we have

$$k_1 = \frac{\overline{\overline{H^{\cdot}}} \cdot \overline{\overline{HCO_3'}}}{p_{CO_2}} \qquad (II.\,2)$$

Where k_1 is the equilibrium constant.

It follows from the condition of electroneutrality that :

$$\overline{Na^{\cdot}} + \overline{H^{\cdot}} = \overline{HCO_3'} + \overline{OH'} \qquad (II.\,3)$$

when $\overline{HCO_3'}$ of (II. 3) is substituted in (II. 2) and the logarithm taken, we obtain

$$\log p_{CO_2} = -pH + \log (s + \overline{H^{\cdot}} - \overline{OH'}) - \log \frac{k_1}{f_1} \quad (II.\,4)$$

(Here single bars and double bars represent the concentration, and activities, respectively, f_1 is the activity coefficient of bicarbonate ion and s is the concentration of $NaHCO_3$). The activity coefficient can be calculated according to the Debye-Hückel theory. It can be argued that $\overline{H^{\cdot}}$ and $\overline{OH'}$ are negligible compared to s. Thus the equation (II. 4) is simplified to :
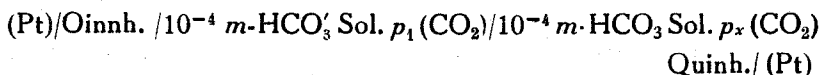
$$\log p_{CO_2} = -pH + \log s - \log \frac{k_1}{f_1} \qquad (II.\,5)$$

Where s, k_1, f_1 are all known; the pH is measured and p_{CO_2}, i. e. the partial pressure of CO_2 which is in equilibrium with the solution of this pH is calculated.

The Differential Method : [14]

To avoid the errors resulting from the junction potential and the constants, k_1 and f_1, a differential method was developed by Kauko. If the equation (II. 5) is written for a known partial pressure p_1 and for the unknown partial pressure p_x and subtracted from one another, the last two terms in equ. (II. 5) are eliminated; thus we have

$$\log p_1 - \log p_x = -pH_1 + pH_x \qquad (II.\,6)$$

Now consider the following concentration cell

$$(Pt)/Oinnh. /10^{-4}\, m\text{-}HCO_3'\, Sol.\, p_1\, (CO_2)/10^{-4}\, m\cdot HCO_3\, Sol.\, p_x\, (CO_2)$$
$$Quinh./ (Pt)$$

The e. m. f. of this cell is given by

$$\log \overline{\overline{H_1^{\cdot}}} - \log \overline{\overline{H_x^{\cdot}}} = \frac{F}{2.303\ RT}\ E \qquad (II.\,7)$$

From equs. (II. 6) and (II. 7) we get :

$$\log \frac{p_1}{p_x} = \frac{F}{2.303\ RT}\ E \qquad (II.\,8)$$

Thus, when the e. m. f. of the above mentioned cell is measured, since the other data are known, p_x can be calculated. The e. m. f. of the cell had been measured with an accuracy of $\pm\ 0.5$ mV. by means of a potentiometer [15]

Colorimetric Method : [16]

This method also depends upon the same principle as the potentiometric method, however, the pH is determined colorimetrically.

Determination of Minute Amounts of Ammonia in gas Mixtures by pH Measurements :

In 1941 Airola [17] has put forward that ammonia can also be determined by pH measurements and gave the following relationship :

$$\frac{k}{k_w} \cdot p = \frac{c}{\overline{\overline{H^{\cdot}}}} - 1$$

Where k_w is the dissociation constant of water; c is the concentration of NH_4Cl in the solution; p is the partial pressure of ammonia and k is the equilibrium constant defined by:

$$k = \frac{\overline{NH_4^{\cdot}} \cdot \overline{OH'}}{p}$$

The same subject has been reinvestigated by Pekkarinen [18] in 1949 and the following relationship was given:

$$\log p = \log \frac{c}{\overline{H^{\cdot}}} + \log \left(\frac{k_w}{f_{OH'} \ \overline{H^{\cdot 2}}} - \frac{1}{f_{H^{\cdot}}} \right) f_{HN_4^{\cdot}} - \log k$$

In this investigation it is recommended to work at pH 7-9 using 0.1 m $NH_4 Cl$ solutions. Having observed a very slow equilibration the workers were directed to finding more suitable solvents.

Part III

Determination of Minute Amounts of Ammonia in Gas Mixtures by Potentiometric Method:

Theory: When gaseous ammonia is passed through an NH_4Cl solution, the following equilibria are to be considered:

a) Equilibrium between gaseous ammonia and water:

$$NH_3 (g) + H_2O \rightleftharpoons NH_4^{\cdot} + OH' \qquad \text{(III. 1)}$$
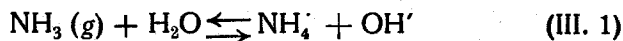
$$k_2 = \frac{\overline{NH_4^{\cdot}} \cdot \overline{OH'}}{p_{NH3}} \qquad \text{(III. 2)}$$

b) Equilibrium in the aqueous solution:

$$NH_3 (sol.) + H_2O \rightleftharpoons NH_4^{\cdot} + OH' \qquad \text{(III. 3)}$$

$$k_1 = \frac{\overline{NH_4^{\cdot}} \cdot \overline{OH'}}{\overline{NH_3} (sol.)} \qquad \text{(III. 4)}$$

The condition of electroneutrality for NH_4Cl solution is:

$$\overline{NH_4^{\cdot}} + \overline{H^{\cdot}} = \overline{OH'} + \overline{Cl'} \qquad \text{(III. 5)}$$

Where p_{NH3} is the partial pressure of ammonia in equilibrium with NH_4Cl solution, f is the mean activity coefficient of NH_4Cl in the solution and $\overline{NH_{3(t)}}$ is the sum of $\overline{NH_3}$ and $\overline{NH_4^{\cdot}}$ viz.

$$\overline{NH_{3(t)}} = \overline{NH_3} + \overline{NH_4^+} \qquad (III. 6)$$

using (III. 4), (III. 5) and (III. 6) the following relationship is obtained:

$$\overline{NH_{3(t)}} = (\overline{\overline{OH'}} + \overline{\overline{Cl'}} - \overline{\overline{H^.}})\left(\frac{\overline{\overline{OH'}}}{k_1} + \frac{1}{f}\right) \qquad (III. 7)$$

When working with 1.00 m. NH_4Cl solution $\overline{H^.}$ and $\overline{OH'}$ can be neglected compared to Cl' since $p_{NH_3} = 10^{-3} - 10^{-5}$ and pH — 5.5 — 8. When the dissociation constant of water is introduced, equ. (III. 7) becomes

$$\overline{NH_{3(t)}} = \overline{\overline{Cl'}}\left(\frac{k_w}{\overline{\overline{H^.}} \cdot k_1} + \frac{1}{f}\right) \qquad (III. 8)$$

In this equation if the activity of chloride ions is kept constant and the $\overline{NH_{3(t)}}$ calculated for various $\overline{\overline{H^.}}$ values, and plotted vs. pH, different curves are obtained for various NH_4Cl solutions. These curves are shown for 1.00 m, 0.1 m, 0.3 m, 0.7 m—NH_4Cl solutions in Fig. 1. The corresponding activity coefficients of NH_4Cl in these solutions at 25°C. are: 0.5797, 0.763, 0.658 and 0.600 [24, 25] respectively.

A relationship between the partial pressure of ammonia and $\overline{NH_{3(t)}}$ can be derived using (III. 2) and (III. 6) and introducing the dissociation constant of water, viz.

$$\overline{NH_{3(t)}} = \frac{k_2 \cdot p_{NH_3}}{k_1} + \frac{k_2 \cdot p_{NH_3} \cdot \overline{\overline{H^.}}}{k_w \cdot f} \qquad (III. 11)$$

If at constant p_{NH_3} the $\overline{NH_{3(t)}}$ is calculated for various $\overline{\overline{H^.}}$ values and then plotted vs. pH another set of curves are obtained which intersect the ones obtained for constant chloride activities perpendicularly. These curves are also shown in Fig. 1.

From a study of these curves it is seen that when a very small amount of ammonia is dissolved in NH_4Cl solution, the pH changes considerably. For instance, for a 1.00 m NH_4Cl solution the pH changes from 6.24 to 8.20 when p_{NH_3} changes from 10^{-5} to 10^{-3} atm., which corresponds to a change in the 0.058 mol/lit.$^{-1}$ amount of ammonia dissolved. Therefore, for the present investigation the NH_4Cl concentration should be so chosen that a great variation of pH can be affected by the dissolution of small amounts of ammonia, and at the same time
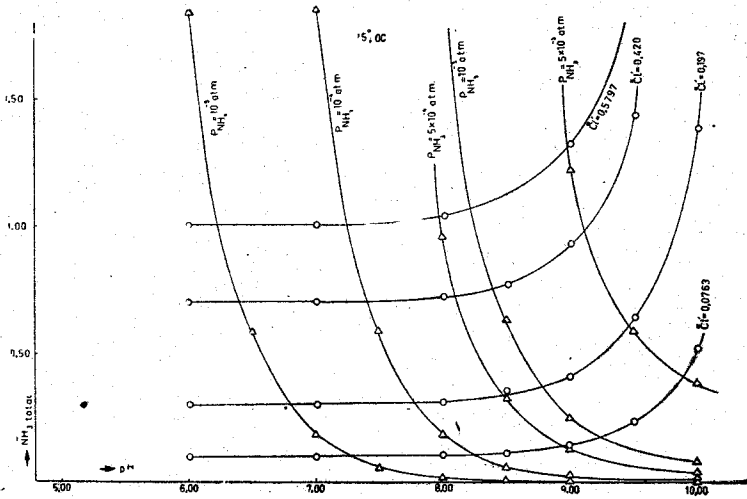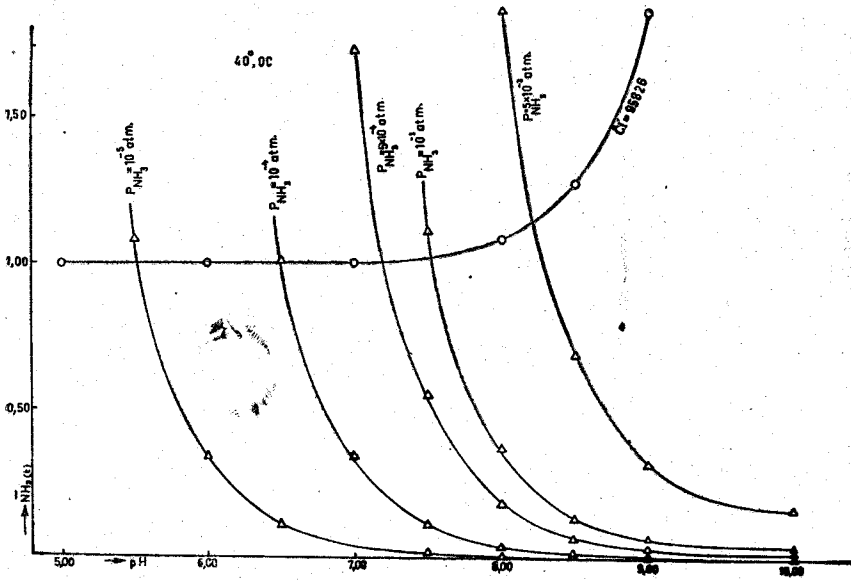
Fig. 1.

Fig 1'.

the pH of this sensitive zone should not be above 8. Although
the effect of CO_2 will be noticeable only when pH 10, we have
chosen a pH range lower than 8, because at higher pH a con-
siderable amount of ammonia is dissolved resulting in an incre-

ase in the equilibrium time. As can be seen from Fig. 1, the most convenient concentration for the present study is 1.00 m. For the sensitive zone is shifted to the alkaline region at lower NH_4Cl concentrations. If the partial pressure of ammonia in the mixture is greater than 10^{-3} atm. then the sensitivity may be increased by using more concentrated NH_4Cl solutions. From (III. 8) and (III. 11), we obtain :

$$p_{NH3} = \frac{k_w \cdot \overline{\overline{Cl'}}}{\overline{\overline{H'}} \cdot k_2} \qquad \text{(III. 12)}$$

or :

$$\log p_{NH3} = \log \frac{k_w}{k_2} + \log \overline{\overline{Cl'}} + pH \qquad \text{(III. 13)}$$

which is a lineer relationship between $\log p_{NH3}$ and pH. This relationship can be made use of as follows :

a) If an NH_4Cl solution of known concentration is taken and a gas mixture of known percentage is let through and the pH determined ; the ratio $\frac{k_w}{k_2}$ is obtained. Now, with an unknown mixture, since $\frac{k_w}{k_2}$ is known, the partial pressure of ammonia in equilibrium with the solution is easily calculated from the pH measurement. If the atmospheric pressure is known the percentage of ammonia can be calculated.

b) If two gas mixtures of known composition are available, the pH of these are measured and $\log p_{NH3}$ vs. pH is plotted. A straight line is drawn through these points. Now the pH of an unknown mixture is measured and the partial pressure of NH_3 in equilibrium with the solution can be found from this graph.

c) If k_w and k_2 are known, measuring the pH of the solution, partial pressure of ammonia in equilibrium with the solution can be evaluated either from a graph as mentioned in (b) or from (III. 13). Naturally the activity coefficients of NH_4Cl solution should be known in order to be able to use these methods. For the present study the third method has been used. The equilibrium constant k_2 which is not available in literature, was calculated thermodynamically as well as experimentally.

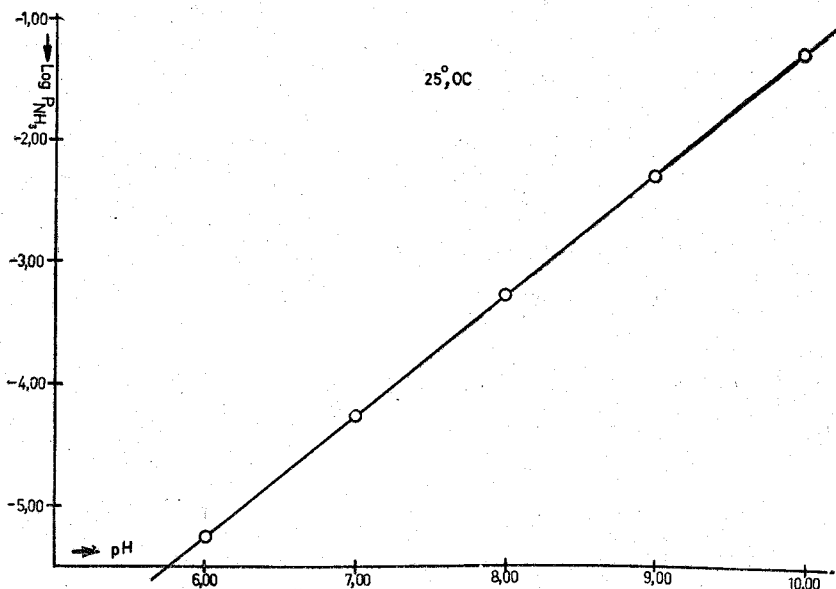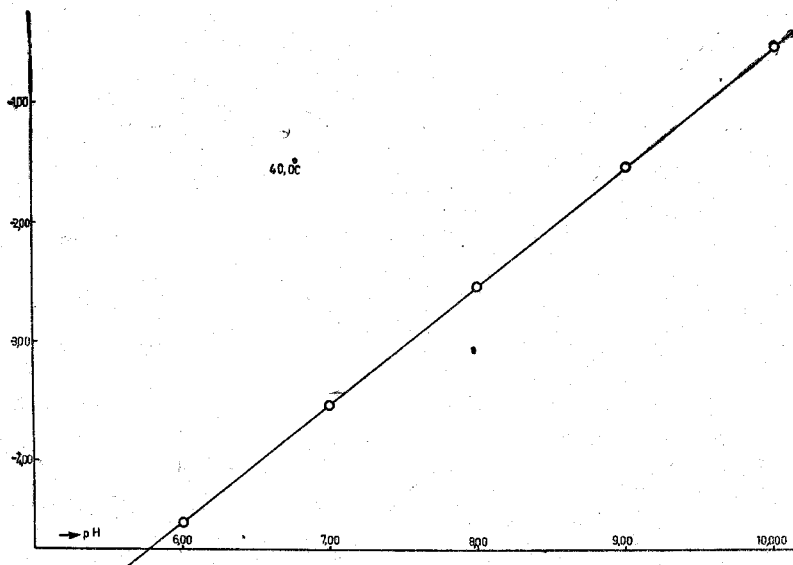Fig. 2.

Fig. 2'.

The Determination of Equilibrium Constants:

Principally the Kauko method used to determine CO_2 can also be applied to the determination of ammonia. But the time

of equilibration is rather long owing to the greater solubility of ammonia. This period can be shortened by taking smaller amounts of solution but still it is considerable. We have observed that this period is much shorter at higher temperatures because of the decrease in the solubility of ammonia. In order to carry out these experiments at higher temperatures, the equilibrium constants and activity coefficient at higher temperatures were calculated thermodynamically once these were determined at 25°C. The equilibrium constant k_2 was calculated at 25°C. and 1 atm. from the standard free energies [32] on one hand and from entropies and heat contents on the other. Thus we found k_2 (free energy) $= 1.01 \cdot 10^{-3}$, k_2 (entr. & heatc.) $= 4.62 \cdot 10^{-4}$

Fig. 8.
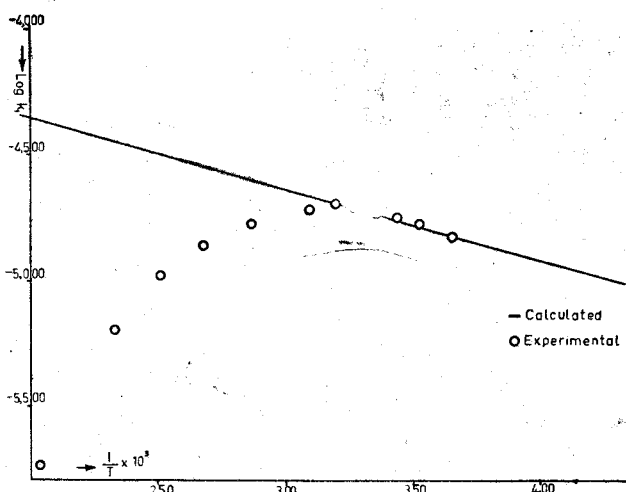
$mol^2 \cdot lit^{-2} \cdot atm^{-1}$. We also calculated k_2 from the experimental values of k_1 [29] and $k_0 = NH_3$ diss.$/p_{HN3}$ [19, 20, 21, 22, 23] given in the literature by $k_2 = k_0 \cdot k_1$ We checked these values of k_1 and k_0 by calculating them from the free energy data available in the literature. Their numerical values obtained in this manner are as follows :

$k_1 = 1.79 \cdot 10^{-5}$ mol. lit^{-1}. and $k_0 = 56.5$ mol. lit^{-1}. atm^{-1}

The fixed equilibrium constants and for higher temperatures calculated equilibrium constants are given together in (Table I).
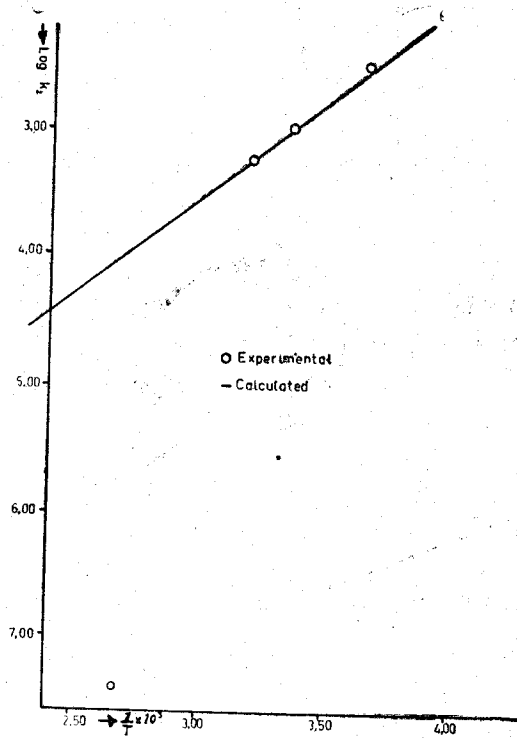
Fig. 4.
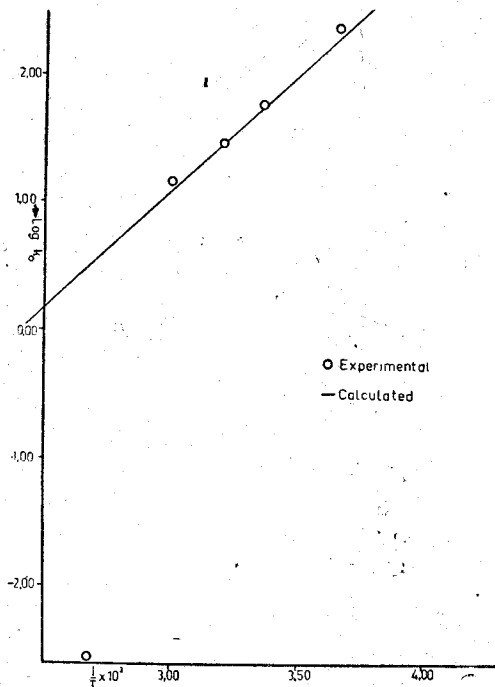
Fig. 5.

The variations of the constants k_1, k_2 and k_0 with tempera-

ture was calculated by $\dfrac{\partial Ln\, k}{\partial \dfrac{1}{T}} = -\dfrac{\overline{H}}{R}$ and were compared with

the experimental data as shown in figures 3,4 and 5. It is seen that the experimental points given for 100°C. do not coincide with the thermodynamical data in all three cases. The activity
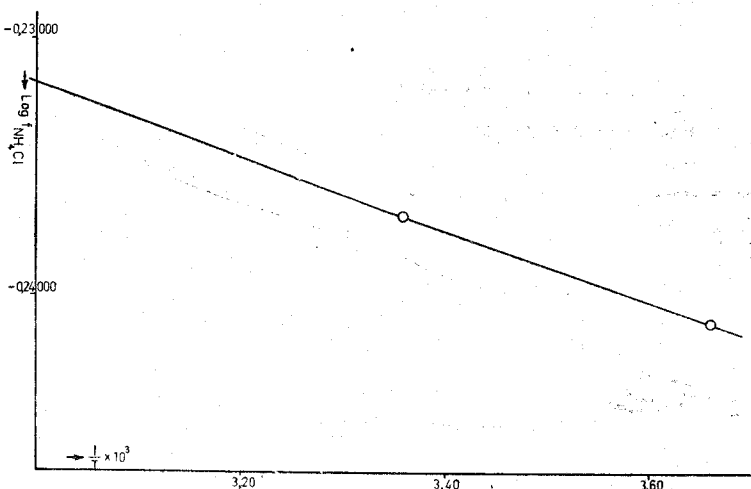
Fig. 6.

coefficient of NH_4Cl at 40.0°C was obtained by graphical extra-polation of those given for 0.0°C and 25.0° as shown Fig. 6.

Table 1.

t°C	0.0°	25.0°	40.0°	100.0°
k_0 mol. lit.$^{-1}$ atm.$^{-1}$ (expml.)	234.7	59.1	29.4	$2.72.10^{-3}$
k_0 mol. lit.$^{-1}$ atm.$^{-1}$ (Calc.)	199.6	56.5	28.8	$3.23.10^{-3}$
$k_1.\,10^5$ mol. lit.$^{-1}$ (expml.)	1.40	1.81	1.98	1.35
$k_1.\,10^5$ mol. lit.$^{-1}$ (Calc.)	1.47	1.79	2.00	2.84
$k_2.\,10^3$ mol.^{2} lit.$^{-2}$ atm.$^{-1}$ (expml.)	3.29	1.07	0.582	$3.67.10^{-5}$
$k_2.\,10^3$ mol.^{2} lit.$^{-2}$ atm.$^{-1}$ (Calc.)	2.95	1.01	0.575	$9.12.10^{-2}$

Part IV

Experiments and Results

Materials used: Ammonium chloride: Merck, pro analyse
Reagents used: Ammonia: E. & A. Tested purity reagent
Hydrochloric acid: Merck, pro analyse
Potassium hydroxyde: Merck
Only bidestilled water was used throughout the investigation.

The experiments were carried out in paraffine oil thermostat. During the pH measurements in order to avoid the magnetic interferences the relay and stirrer were switched off.

Equipments:

The pH meter used was a Beckman G model glass electrode pH meter, having a sensitivity of $\pm$ 0.01 pH

The capillary electrode wessels used were those of Kauko [18] type made of pyrex glass. The capillary tubing was 100 cms. long with 0,3 mm. bore.

Ammonia-air Mixture:

In order to prepare this mixture, a gas cylinder could have been evacuated and a small amount of ammonia admitted, then compressed air could have been let in. The hypersensitivity of the investigator towards mercury which she was going to use during this procedure in manometry, has forced her to use the following method: absorption bulb, containing glass rings to increase the surface were used, filled with ammonia solution of known concentration (Fig. 7) and air was passed through with a rate of 20.35 ccs./min. But it was observed that one absorption bulb was not enough at this rate of flow, so three bulbs were used in series The pH measurements using two and three bulbs gave identical results. We, therefore, concluded that two bulbs were sufficient. Nevertheless, the third bulb was used for the sake of safety. The concentrations of ammonia in the solution in the second and third bulbs were checked at the commencement and at the end of the equilibrium periods by titration and the relative concentration change found at 25°C was —0.24 percent and at 40°C was —0.65 per cent. These figures also give the relative change in the partial pressure of ammonia

in the gas. Since accuracy in our pH measurements is $\pm$ 0.01, this change cannot be detected in pH. At the end of the experiment ammonia in the first bulb was also titrated, and a decrease of approximately five times as much was observed.
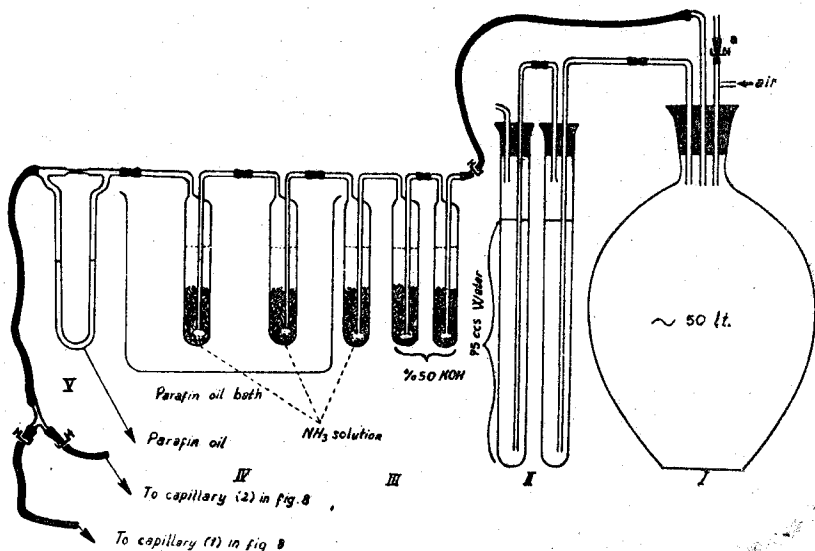
Fig. 7.

Experiment:

In the present investigation the air was let into the flask (I) by means of a comppressor in order to obtain a steady stream, (see Fig. 7). The screw (a) was so adjusted that the air could bubble through the tubes (II) in small bubbles, the greater portion being let out through (a). A pressure head of 150 cm water was enough to overcome the resistance in the wash bottles and the capillary. The absorption bulb (III) contained 50 percent KOH solution to absorb the acid gases in the mixture. The next three absorption bulbs contain ammonia solution. The gas inlet tubes of the absorption bulbs ended with a perforated bottom. Passing through a flow meter (V), the gas is let through capillaries 1 and 2 (see Fig. 8) Thus an efficient contact between the NH₄Cl solution and the gas to be analysed is secured. The screw (b) is so regulated that the greater portion of the gas passing through the capillary 1 is let out to develope just

enough pressure to passe the gas through the capillary 2. The
NH_4Cl solution which reaches a partial equilibrium with the gas
in the capillary 1, comes in contact with the fresh gas in the
capillary 2, accumulates in the electrode vessel where the pH
is measured by means of a glass electrode. When the equilib-
rium is reached pH becomes constant. This pH value is recor-
ded. Fine adjustments were made to the liquid flow rate by
means of a glass lever 10 cms. long fused to the liquid tap key.
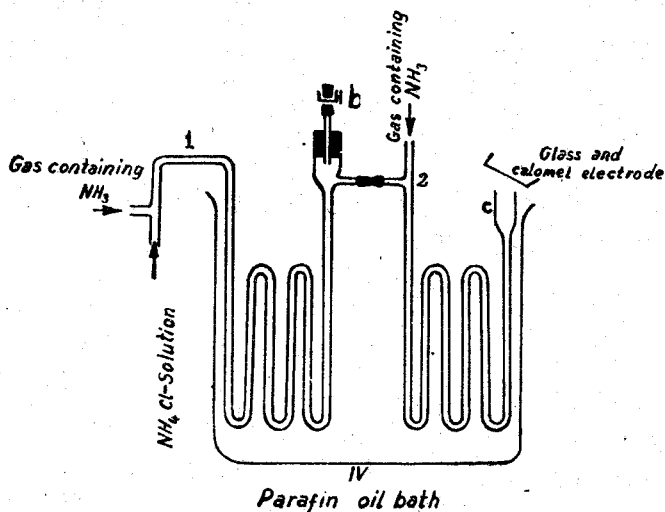
Fig. 8.

At the beginning the velocities of gas and liquid were 1.5
lit. per hour and 2 ccs. per hour respectively. Under these
circumstances the equilibrium was attained in 6 hours. During
the first two hours of this period the gas and liquid passed
simultaneously. Another 4 hours were necessary to let the gas
alone, turning the liquid off. The liquid which was collected in
the electrode vessel was about 4 ccs. Decreasing the amount
and the flow rate of the liquid it was possible to reach the
equilibrium in 90 minutes at 25°C. and in 30 minutes at 40°C.
As it will be seen in Tables II and III that the time required
for the equilibrium (columns 8 & 9) depends on the rate of flow
(column 10) and the amount of the liquid (column 7). The
flow rate of the gas was nearly the same as that of the first
experiments but the liquid rate was decreased in the actual

experiment. When liquid and gas are let simultaneously through the capillary the first equilibrium pH varies with the liquid rate. These first equilibrium pH values are shown in column 6.I while the corresponding equilibration times are tabulated incolumn 9. It is interesting to note, however, that if the liquid flow is stopped and the gas alone is passed through the solution, a constant pH value is obtained which is independent of the rate of flow the pH values obtained in this manner are given in column 6.II, and the corresponding equilibration times are tabulated in column 8. Assuming an equilibrium between the gas and liquid in the electrode vessel, it can be shown theoretically that the partial pressure of ammania in this vessel is, in general, differs from that of the original gas and that this pressure is a function of the rates of flow and initial NH_3 concentrations of both phases. Therefore, in principle, it is possible to caiculate the partial pressure of ammonia in the original gas from the pH measured in this general case, which we call the "first equilibrium pH,, and the rates of flow. In the limiting case where the rate of flow of liquid is negligible compared to that of gas, however, such theoretical consideratians show that, the partial pressure of ammania in the electrode vessel is the same as that of the original gas is independant of the rate of flow of gas. These considerations explain the obserwed behaviour mentioned above. The limiting case first mentioned was secured experimentally by stopping the liquid flow. It will be seen that the simultaneous passing of liquid and gas does not suffice to reach the equilibrium, it is necessary to pass the gas longer. The experimental results which are given in table II a were obtained using single, and those given in table II b were obtained using double capillaries as shown in Fig. 8. Although in the latter case a longer passage is ensured for the liquid and gas to reach the equilibrium times are nearly the same. This is because the gas and the liquid cannot reach the equilibrium in the capillary. Under these circumstances, in order to reach the equilibrium sonner, either the passage should be longer for the gas and liquid to pass simultaneously, or the experiment must be carried out at a higher temperature. Since it is more difficult to pass the gas through a longer capillary, we preferred to adopt the latter procedure. Therefore, the experiment was repeated at 40.0°C. (see table III. a and b) Nevert-

TABLE II 25,0°C

a) With one capillary

Expt. No.	Conc. of NH₃ Mol. lit.⁻¹ I.	Mean II.	$p_{NH_3}\cdot10^3$ calc. atm.	$p'_{NH_3}\cdot10^3$ Exptl. atm.	Initial pH	Equilibrium pH I.	II.	Vol. of solution ccs.	Total equilibration time Mins.	1st stage equilibration time, Mins.	Flow rate of liquid, ccs/h	Flow rate of gas ccs/h	$\frac{p_{NH_3}-p'_{NH_3}}{p_{NH_3}}$	$-\log c$
5	0.0605	0.061	1.03	0.741	8.63	8.45	8.13	0.9	150	25	2.0	25	27.4	11.12
6	0.0595				8.63	8.17		0.2	60	35	0.4	23		
		0.060	1.02	0.692			8.11						31.5	11.10
7	0.0592				8.63	8.21		0,4	90	60	0.4	23		
9	0.0613				5.33	8.06		0.2	90	50	0.2	25		
		0.061	1.03	0.676			8.10						34.0	11.09
10	0.0610				5.33	8.09		0.3	90	84	0.2	25		

b) With two capillary

Expt. No.	Conc. of NH₃ Mol. lit.⁻¹ I.	Mean II.	$p_{NH_3}\cdot10^3$ calc. atm.	$p'_{NH_3}\cdot10^3$ Exptl. atm.	Initial pH	Equilibrium pH I.	II.	Vol. of solution ccs.	Total equilibration time Mins.	1st stage equilibration time, Mins.	Flow rate of liquid, ccs/h	Flow rate of gas ccs/h	$\frac{p_{NH_3}-p'_{NH_3}}{p_{NH_3}}$	$-\log c$
1	0.0605	0.061	1.03	0.661	6.20	8.04	8.09		140	140		30	35.2	11.08
2	0.0563				8.63	8.37		0.5	130	20	1.4	33		
		0.057	0.964	0.741			8.13						23.1	11.15
4	0.0577				8.63	8.21		0.3	90	40	0 5	33		

heless, we also found even at 40.0°C. that at higher rate of
liquid the equilibrium could not be reached in the capillary. It
was therefore necessary to pass the gas for some time switching
off the liquid. Also at 40.0°C. the experiments carried out with
one and two capillaries, show no difference between the equilib-
ration times. Thus it can be concluded that the second capillary
is not necessary. It will be seen from this table that, although
the pressure of ammonia (column 3) and the amount of solution
(column 7) in the twelfth and thirteenth experiment are the
same, the equilibrium pH's are considerably different. When
the corresponding equilibration periods are compared, it is seen
that of the exp. 13 is almost twice of that of exp. 12. So
it can be claimed that the equilibrium has not been reached in
the experiment No. 12 and consequently in Nos. 11 and 15.

In the 5 th columns of tables II and III the initial pH values
of the NH_4Cl solution are given. These values show either the
pH of the 1.00 m. NH_4Cl solution or that of the mixture obta-
ined by adding ammonia to the NH_4Cl solution of the same
concentration. By changing the initial pH it was checked that
the equilibrium was reached as can be seen from these tab·
les. These values were obtained with the solution taken from
the stock bottles since the pH change at first is very sudden
in the capillary vessel. For instance, if an NH_4Cl solution ha-
ving the original pH of 5.5 is led together with gas to the
capillary, the first portion to collect in the electrode vessel
shows a pH value of 7.5. This reading can be taken 1 to 3 mi-
nutes. Though it is not always possible to measure pH correctly
with such a small quantity of liquid, in this method the mixture
of gas and liquid emerging from just beneath the electrode can
surround the electrode [27]. The electrode vessel is protected
with a piece of cotton wool against the diffusion of air. The
increase in pH beyond 7.5 is much slower. For 1.00 m NH_4Cl
solution it can be seen from Fig. I that at 25°C. in this sensi-
tive region below pH = 7.5 the partial pressure of ammonia in
the gas is $2.10^{-4} - 10^{-5}$ atm. At 40°C, however, this zone
extends from 10^{-5} to 10^{-3} atm. as shown in Fig. 1' At 60.0°C.
this zone may be shifted towards 10^{-2} atm. It appears therefore,
that NH_3 can be estimated potentiometrically with sufficient ac-
curacy by the Kauko method at 40°C in gases containing 0.1
per cent or less, and at 60°C, those containing less than one
per cent ammonia.

TABLE III 40,0°C

a) With one capillary

Expt. No.	Conc. of NH$_3$ Mol lit.$^{-1}$ I.	Mean II.	$P_{NH_3}\cdot10^3$ Calc. atm.	$P'_{NH_3}\times10^3$ exptl. atm.	Initial pH	Equilibrium pH I.	II.	Vol of. solution ccs.	Total equilibration time, Mins	1st. stage equilibration time, Mins	Flow rate of liquid ccs/h	Flow rate of gas ccs/h	$\dfrac{P'_{NH_3}-P_{NH_3}}{P_{NH_3}}$	$-\log c$
19	0.0611				8.50	7.97		0.4	30	30	0.7	25		
		0,061	2.07	2.72			7.96						31.4	10.64
20	0.0609				8.50	7.95		0.2	30	30	0.4	23		
21	0.0578				8 50	8.25		0.7	60	15	3.0	25		
		0.057	1.97	2.72			7.96						31.4	10.66
23	0.0570				8.50	8.04		0.3	35	25	0.5	25		
24	0.0602				5.55	7.95		0.2	30	30	0.3	25		
		0.060	2.04	2.69			7.95						31.2	10.64
25	0 0600				5.55	7.93		0.3	70	52	0.3	25		

b) With two capillary

Expt. No.	Conc. I.	Mean II.	Calc.	exptl.	Initial pH	Equil. pH I.	II.	Vol	Total equil.	1st stage	Flow liquid	Flow gas	ratio	$-\log c$
11	0.0594		2.02		5.98	7.73	7.88	0.6	50	24	1.4	26		
12	0.0592		2.02		5.98	7.86	7.88	0.3	30	30	0.5	30		
13	0.0598		2.00		5.98	7.87		0.3	54	31	0.8	27		
		0.061	2.07	2.60			7.94						25.6	10.62
14	0,0615				5.98	7.94		0.6	39	39	1.3	30		
15	0.0604		2.06		5.98	7.86	7.86	0.2	20	20	0.6	30		
16	0.0588				8.50	8.04		0.5	144	70	0.4	30		
		0.059	2.01	2.66			7.95						32.3	10.65
17	0.0579				8.50	7.97		0.5	20	90	0.3	34		

For gas mixtures containing more than one percent ammonia
the other analytical methods can be used.

p'_{NH_3} values given in (table II and III column 4) are those
correspond to the equilibrium pH indicated by the straight lines
determined by the equation (III. 14) as shown in Fig. 2 and 2'.
The pH could be measured with an accuracy of ± 0.01 with
a Beckman pH-meter. The NH_4Cl solution was prepared with
an accuracy of ± 0.0005 in molality. The values of k_w, k_2 and
f_{NH_4} were taken from the literature. Their values are given in
table IV.

Table IV.

	25.0°C.	40.0°C.
k_w	$1.008 \cdot 10^{14}$ [26]	$2.917 \cdot 10^{-14}$ mol² lit.⁻² [26]
k_2	$1.07 \cdot 10^{-3}$	$5.82 \cdot 10^{-4}$ mol² lit⁻² atm.⁻¹
		(see table I)
f_{NH_4}	0 5797 [24]	C.5826 (see Fig. 6)

The values for k_w at 25.0°C, given in the literature vary from
$1.005 \cdot 10^{-14}$ to $1.29 \cdot 10^{-14}$ [26,28]; and at 40.0°C. from $2.917 \cdot
10^{-14}$ to $3.89 \cdot 10^{-14}$. mol.² lit.⁻². The values given for k_2 and
f_{NH_4} are also discordant as previously indicated. The relative
error in the calculated p_{NH_3} due to these uncertainties can be
estimated as follows :

At 25.0°C: $d \ln p_{NH_3} = 2.3 (d \log k_w + d \log k_2 + d \log f_{NH_4} + d \log pH)$

$$\frac{dp}{p} = 2.3 (0.06 + 0.02 + 0 01 + 0.01) = 2.3 \cdot 10 = \% \pm 23$$

At 40.0°C: $\frac{dp}{p} = 2.3 (0.06 + 0.01 + 0.01 + 0.01) = 2.3 \cdot 9 = \% \pm 21$

Taking these uncertainties into consideration the differences
$p'_{NH_3} - p_{NH_3}$ shown in table II and III column 12 do not appear
to be significant.

If the uncertainty due to the constants can be avoided, the
error in the determination of the partial pressure of ammonia
will only result from the pH determination. The pH is deter-
mined with an accuracy of ± 0.01. Therefore,

$$\frac{dp}{p} = 2.3 \ d \ \log \ \mathrm{pH} = 2\ 3 \cdot 0.01 = \% \pm 2.3$$

If the measurements are made with a Lindemann electrometer which secures an accuracy of ± 0.002 in pH, it is possible to determine the partial pressure of ammonia with an accuracy of

$$\frac{dp}{p} = 2.3 \cdot 0.002 = \% \pm 0.46$$

The influence of carbon dioxyde in the air can be neglected if the pH is 8 or less, because when carbon dioxide is dissolved in NH_4Cl solution, the concentration of salt increases and the equation (III. 13) becomes

$$\log \ p_{NH3} = \log \ \frac{k_w}{k_2} + \log \ (\overline{\overline{Cl'}} + \overline{\overline{HCO_3'}}) + \mathrm{pH}$$

At $\mathrm{pH} = 8$, $\overline{\overline{HCO_3'}} = 0.0003$, which is negligible compared to $\overline{\overline{Cl'}}$ in a solution of 1.00 m. NH_4Cl. Obviously it will be more so at $\mathrm{pH} < 8$

The concentrations of ammonia solution used for preparing gas mixtures containing ammonia are given in table II and III, column 2. The greatest difference in concentration is 0.0021 mol. lit.$^{-1}$. This corresponds to

$$\frac{dc}{c} = \frac{dp}{p} = \frac{0.0011}{0.0602} = \% \pm 1.7$$

A difference of $\% 2.3$ on $\frac{dp}{p}$ resulting from the error in pH determination corresponds to $dc = 0.0013$ mol. lit.$^{-1}$. Therefore, the fourth decimal in the values of NH_3 concentration is insignificant. For this reason the average values are given in column 2. II with three decimals. The equilibrium pH values corresponding to these average figures are also given in column 6. II. p_{NH3} given in column 3 are calculated from k_0 since at 25.0°C. Henry law is applicable to ammonia solutions up to a concentration of 0.3 mol. lit.$^{-1}$.[22]. As the temperature increases the range of applicability of this law becomes narrower.

Since $\overline{\overline{Cl'}}$ was constant in our experiments, if we define a constant c by

$$\log c = \log \frac{k_w}{k_2} + \log f_{Cl'} + \log \overline{Cl'}$$

the equ. (III. 13) becomes

$$\log p_{NH3} = \log c + pH$$

The partial pressures of ammonia and the average pH values for the calculation of log c, given in table II and III, column 13, are those given in columns 3 and 6. II, respectively.

Considering that the maximum deviation in these c values is $\dfrac{dc}{c} = \% \pm 0.31$ at 25.0°C. and $\dfrac{dc}{c} = \% \pm 0.19$ at 40.0°C, it is more clear that the differences $p'_{NH3} - p_{NH3}$ in column 12 are due to the uncertainties in the constants used in equation (III. 13). Thus as stated previously if the ammonia is to be determined potentiometrically using, an NH_4Cl solution of known molarity and a gas mixture of known composition, first the constant c should be determined experimentally to obtain more accurate results. Then the gas mixture of unknown composition is treated with the same NH_4Cl solution, and the partial pressure of ammonia is calculated from the equilibrium pH.

It is also possible to eliminate the errors resulting from the constants by using the differential method of Kauko [14]. In this method the following cell is used and the gas of known composition is let through one of the capillaries, while the gas of unknown composition is let through the other simultaneously with the same NH_4Cl solution.

Glass elec./NH_4Cl sol. NH_3/NH_4Cl sol./NH_4Cl sol.. NH_3/Glass elec.

             1.00 m. p_x 1.00 m.   1.00 m. p_1

After the equilibrium has been reached the e.m.f. of the cell is measured and the unknown partial pressure p_x is calculated from equ. (II. 8).

We intend to tackle this problem in the future with p_{NH3} of the order of 10^{-4} atm. paying more attention to pH to be in the more sensitive zone when the experiments will be repeated 60°C. to shorten the time of equilibration.

As described in Part I, an aeration method has been suggested by various authors to estimate ammonia in urine and soil, where the difficulties of this method was also stated. We believe that the present method can be used more satisfactorily

for this purpose. To perform such an estimation use can be
made of the apparatus designed by Kauko and Mantere [31] for
the determination of carbon dioxide in blood using NH_4Cl so-
lution and urine instead of $NaHCO_3$, solution and blood, res-
pectively, with the addition of an absorption vessel to exclude
CO_2.

Before concluding, we would like to mention the possibility
of adaptation of this method to the estimations of SO_2 and
H_2S in gas mixtures, as suggested by Ariola [17] and Pekkarinen [18].

S U M M A R Y

1) The potentiometric method of Kauko can be applied
accurately to the estimation of ammonia in gas mixtures of the
order of 0.001 per cent. In this method first the acid gases are
excluded by absorption in an alkaline medium, then the mixture
is brought into the equilibrium with 1.00 M. NH_4Cl solution,
the pH is measured and the corresponding partial pressure of
ammonia is calculated thermodynamically. The time of equilib-
ration at 25^0C is too long. At 40^0C, however, the equilibration
is reached in 30 minutes. Since the accuracy of the results
depends on the reliability of the equilibrium constants, a diffe-
rential method should be used when more accurate results are
required.

2) The value of $k_2^{\bullet} = (\overline{NH_4^{\cdot}} \cdot \overline{OH'})/p_{NH3}$, calculated ther-
modynamically from heat contents and entropies is not in
agreement with experimental k_2.

3) This method can be used to determine ammonia in solu-
tions such as urine and in soil.

4) The same method is also applicable to the estimation of
H_2S and SO_2 in gas mixtures.

A C K N O W L E D G M E N T

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