THE ACTIVITY OF AMMONIA

IN WATER AND IN AQUEOUS AMMONIUM CHLORIDE

BY

PARTITION COEFFICIENT METHOD

BY

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MAY, 1932.
ABSTRACT

from the thesis
THE ACTIVITY OF AMMONIA IN WATER
AND IN AQUEOUS AMMONIUM CHLORIDE
BY PARTITION COEFFICIENT

METHOD

H. E. LATHRES.

A short historical review is given of the work of previous investigators upon the distribution of ammonia between water and chloroform and the influence of ammonium chloride upon this distribution.

An experimental procedure is described for the accurate determination of the partition coefficient of ammonia: results are given for its value using chloroform and pure water, chloroform and aqueous solutions of ammonium chloride.

From these determinations, the activity coefficient of the undissociated portion of ammonia in aqueous solution and in aqueous ammonium chloride solution, is calculated. The variation of this function with ionic strength is discussed and its behaviour compared with that indicated by recent activity theories.
The phenomenon of the distribution of a substance between two non-miscible liquids has numerous applications of both a theoretical and practical nature. Distribution experiments may shed light on a variety of chemical equilibria including association and dissociation of simple compounds, formation of complexes, various types of hydrolysis and reversible reactions, whilst the common use of the distribution principle in the process of extraction as used in ordinary laboratory practice makes it a factor of paramount importance in the realms of organic chemistry.

The first investigation of the laws governing such distribution was made by William Henry and was concerned only with the equilibrium existing between a gas and its solution in a liquid. The fact that the mass of gas absorbed or dissolved by a given volume of liquid is proportional to the pressure of the gas, at constant temperature, became known as Henry's law and its applicability to the distribution of a dissolved substance between two liquid phases subsequently became realised as a result of further experimental work. It follows that if the vapour is in equilibrium with separate solvents the ratio of the concentrations in the two solvents will be constant.

There have been numerous cases where experimental results and the requirements of the distribution law are
not in agreement. These deviations are due to at least two causes, the first being the neglect of the important restriction enunciated by Nernst that a constancy in the distribution ratio can exist only between those molecules of the distributed substance which are in the same state of aggregation in both phases and, secondly, that, if the distribution ratio is to be constant in systems consisting of two liquids, the latter must be mutually insoluble or must not have their mutual solubility altered by the presence of the distributed substance. In actual practice such a state of affairs is not realisable, the distributed substance does have an effect upon the mutual solubility and this effect may vary both in amount and direction.

The earliest reported observations upon the distribution of ammonia between chloroform and water appear to be those of Hantzsch and Sebaldt (1) who were investigating the molecular state of ammonia and of amines in aqueous solutions. The calculation of the partition ratio was made on the assumption that the hydroxide itself is insoluble in chloroform and as the concentration of the gaseous ammonia in the aqueous phase is proportional to that of the hydroxide, the total concentration may be, and is, employed instead of that of the gaseous ammonia only. A value of 25.1 as the mean of five determinations varying over a

(1) Zeit. für Phys. Chem. 1899, 29, 258.
concentration range 0.00275 to 0.04425 molar in the aqueous phase, was obtained at 25°C, leading the authors to conclude that the distribution ratio remained constant for varying concentration. Determinations at 2°C gave a value 39.53 showing that the partition coefficient increased with fall of temperature. The addition of ammonium chloride, according to their report, did not affect the distribution, a result they considered surprising, although, they continue "in view of the slight electrolytic dissociation of ammonium hydroxide it might have been expected." These experiments were the first of their kind and were not attended by the experience and accuracy necessary to detect the variations produced by the addition of salts, but the constancy of the partition ratio indicated that the molecular complexity of the ammonia in both solvents was the same.

The initial experiments of Dawson and McRae carried out at 20°C gave a mean value 26.3 for the partition ratio. The concentration of ammonia in the chloroform layer ranged from 0.2317 to 0.5431 grms. per litre and the maximum variation from the mean value exhibited by the results was 0.6. The units of concentration used were grammes of ammonia per litre of solution and the accuracy of the results did not warrant the correction due to the dissociation of the ammonia in the aqueous phase. They concluded that the deviations from the mean value shown by their results

(2) J.O.S. 1909 77, 1242
were quite irregular and no regular variation of the distribution coefficient with concentration was observable. Determinations carried out at 25°C and 30°C gave average values 24.9 and 23.2 respectively for the distribution ratio, indicating the inverse effect of temperature rise.

Dawson and McRae's (3) second series of determinations at 20°C led them to the conclusion that the ratio of distribution of ammonia between water and chloroform is not quite independent of ammonia concentration. These determinations were made over a slightly wider concentration range (0.1958 to 0.6780 gms. of ammonia per litre of chloroform solution) and were corrected for the dissociation of the ammonia. The distribution coefficient appeared to diminish with increased ammonia concentration following very nearly a linear law. As the concentration decreased, experimental difficulties of determining accurately the value of the distribution ratio increased but the results obtained at concentrations below half normal in the aqueous phase appeared to give a constant value.

These conclusions were substantiated by further experiments (4) carried out at 10°C and 30°C. The results showing very much the same relationship as those previously obtained at 20°C, namely, solutions less than half normal with respect to ammonia exhibited a constant distribution

(3) J.C.S. 1901 79 493
(4) J.C.S. 1901 79 1869
coefficient while with more concentrated solutions this coefficient diminished with increasing concentration. Moreover, the variation of the distribution coefficient within the same limits of ammonia concentration seemed very nearly the same at the three temperatures whereas the distribution coefficient at constant ammonia concentration was not a linear function of the temperature.

Dawson, in his 'Nature of Ammoniacal Copper Solutions', endeavoured to investigate more accurately the distribution ratio at concentrations of ammonia below half normal. To this end certain experimental improvements were adopted; temperature was controlled more carefully and larger samples of the aqueous and chloroform layers were employed in analysis. Experiments were carried out at 19·5°G. and the results lay, very approximately, on a straight line corresponding to the equation:

$$k = 25·16 - 34·14c$$

$k$ being the distribution coefficient at concentrations of ammonia less than half normal while $c$ is the molar concentration of ammonia in the chloroform. No doubt, if these results were corrected for ammonia dissociation, the graph obtained would lose much of its former curvature and enable a better representative line to be drawn.

Abbot and Bray, in their determinations, experienced the difficulty arising from the fact that the aqueous

(5) J.C.S. 1906 89 1666
(6) J.C.S. 1909 51 729
solutions formed emulsions with the chloroform layer, the latter remaining turbid even after standing several hours in the thermostat. Minute drops of the aqueous solution remained suspended in the chloroform layer making it impossible to obtain concordant results when different samples were analysed. The difficulty was eliminated, however, by rotating the solutions within the thermostat for a period of one to three hours when the two phases separated with a sharply defined bounding surface. Samples of the layers were removed by means of syphon tubing and air pressure while the distribution apparatus was still within the thermostat. In the experiments of previous workers the distribution apparatus was removed from its constant temperature surroundings before portions of the layers were extracted extracted for analysis. This is quite an important point and will be discussed more fully in the experimental section of this paper. Their results, determined at 19° C and varying over the small concentration range of 0.0007067 to 0.001784 grm. mols. of ammonia per litre of chloroform solution, gave a mean value 27.45 for the distribution coefficient after correction for the ionisation of ammonia in the aqueous phase.

Dawson, during his work upon ammoniacal copper solutions, investigated the variation of the distribution coefficient with concentration of ammonia over a higher
concentration range than had previously been attempted. His results, extending to 4·3 normal solution, at 19°C, are shown in Fig. 1 and are seen to lie upon a smooth curve.

This work was extended by Bell and Field (8) who determined the distribution at 23°C over a concentration range extending to 12 normal. These results were plotted and approximately formed a curve which, upon extrapolation, gave 24 as the value for the distribution coefficient at limiting dilution. Such extrapolation is not strictly legitimate for it does not take into account the effects of the dissociation of the ammonia. This would not greatly affect the actual experimental values, for the lowest concentration was normal with respect to the aqueous layer, but the effect becomes considerable at high dilution. These curves depicting high concentration values are of little use for deductive purposes. The multitude of factors which come into play at these concentrations make the problem of analysis one of great complexity.

The effect of ammonium chloride upon the ionisation of the ammonia was also investigated. Quoting from Bell and Field's paper - "As ammonia is a weak base it is but slightly ionised even at great dilution and consequently the addition of an ammonium salt would increase the number of undisassociated molecules very slightly, while the percentage decrease in ionisation would be greatly
diminished. If the unionised portion of the substance is distributed than the presence of ammonium chloride should affect the distribution very slightly and then only on account of the 'salting out effect'. If, on the other hand, the ionised portion were distributed, the presence of the highly ionised salt would affect the distribution very greatly. The following results were obtained using three normal ammonium chloride; the first column gives the estimated aqueous concentrations, the second the calculated concentrations in the chloroform layer using the previously obtained data, and the last column the concentrations in the chloroform as determined experimentally.

NH₄Cl 3N.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>0.04</td>
<td>0.037</td>
<td>0.037</td>
</tr>
<tr>
<td>4.32</td>
<td>0.226</td>
<td>0.228</td>
</tr>
<tr>
<td>7.72</td>
<td>0.434</td>
<td>0.512</td>
</tr>
<tr>
<td>10.16</td>
<td>0.637</td>
<td>0.829</td>
</tr>
</tbody>
</table>

The differences between the last two columns are seen to be very small as would be expected using such high concentrations of ammonia.

Moore and Winmill (9) emphasize the necessity for the removal of samples from the aqueous and non-aqueous layers whilst the partition bulb is still within the thermostat. Their determinations were carried out at three temperatures 18°C, 25°C and 32-35°C but over such a small
concentration range that the results exhibited nearly constant values.

<table>
<thead>
<tr>
<th>TEMPERATURE</th>
<th>CONC: IN CHCl₃ (Molar)</th>
<th>P.C.</th>
</tr>
</thead>
<tbody>
<tr>
<td>18°C</td>
<td>0.00201</td>
<td>27.42</td>
</tr>
<tr>
<td>25°C</td>
<td>0.00437</td>
<td>27.44</td>
</tr>
<tr>
<td>32-35°C</td>
<td>0.00618</td>
<td>24.23</td>
</tr>
<tr>
<td></td>
<td>0.00819</td>
<td>24.86</td>
</tr>
<tr>
<td></td>
<td>0.00471</td>
<td>21.20</td>
</tr>
<tr>
<td></td>
<td>0.01143</td>
<td>21.17</td>
</tr>
</tbody>
</table>

The value at 18°C is in good agreement with that obtained by Abbott & Bray (6) viz. 27.43 at a similar ammonia concentration.

Dietrich (10) investigated the possibility of stock samples of chloroform from varying sources giving differing results on account of the presence of traces of stabilisers introduced by the manufacturers to minimise decomposition.

For this purpose three samples of chloroform: -

1. Mallinckrodt's C.P. quality;
2. Merck's U.S.P.X. and Baker's C.P. were each distilled and used for distribution measurements. Determinations were carried out at 25°C the partition bottles being rotated, as recommended by Abbott & Bray, for a period of four hours. After this time, however, the chloroform layer was still cloudy and, in order to eliminate the emulsion, it was found necessary to filter the chloroform by forcing it, using air pressure, through a cotton-wool filter.

(10) - J. Phys. Chem. 1929 33 98
The results for the distribution coefficient, using a particular stock sample of chloroform, showed no regular variation and Dietrich contents himself by stating:

"as the distribution of ammonia is between water and aqueous chloroform and as the solubility of water in chloroform is influenced by the presence of ammonia, the value of the distribution co-efficient tends to decrease with increase in concentration of ammonia in the water phase; this change however, is pronounced only in the range of high concentrations of ammonia in the aqueous layer and for the lower concentrations employed in this investigation, in general 'less than 0.1 Molar, comes within the experimental error involved in carrying out the analyses."

As will be seen, concentrations are expressed in gram molecules of ammonia per thousand grammes of solution. Estimations by weight, besides leading themselves to greater accuracy than volumetric determinations, have the additional advantage of allowing correction to be made, if the concentrations used are high, for the weight of dissolved ammonia - a refinement that is not possible using a volumetric basis. Thus, the distribution ratio is able to be expressed as the ratio of the molar concentrations of ammonia per thousand grammes water to that per thousand grammes chloroform as opposed to the ratio molar concentration of ammonia per litre of aqueous ammonia solution to that per litre of ammoniacal chloroform. Obviously, the former basis gives more accurate results, especially when
a large concentration range of ammonia is used, in enabling the determinations to be correct relatively to each other. This correction would not, however, materially affect Dietrich's results - which are presumably expressed in concentrations per thousand grammes solution - the concentration range being so small and the dilution high.

Upon comparison of the mean values for the distribution ratio of the three different samples of chloroform, a discrepancy greater than that accounted for by experimental error manifests itself when chloroform of Baker's stock is used, as the following results (which are corrected for ammonia dissociation) show:

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Sample</th>
<th>Concentration in CHCl₃</th>
<th>F.C.</th>
</tr>
</thead>
<tbody>
<tr>
<td>23°C</td>
<td>Mallinckroit's</td>
<td>0.00025236</td>
<td>35.71</td>
</tr>
<tr>
<td></td>
<td>C.P. Quality</td>
<td>0.00028735</td>
<td>35.80</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.001263</td>
<td>35.77</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.001361</td>
<td>35.92</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.001631</td>
<td>35.81</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.002772</td>
<td>35.89</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Mean</td>
<td>35.83</td>
</tr>
<tr>
<td></td>
<td>Henley's</td>
<td>0.00025495</td>
<td>35.31</td>
</tr>
<tr>
<td></td>
<td>U.S.P.X.</td>
<td>0.001216</td>
<td>35.39</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.001555</td>
<td>35.36</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.001919</td>
<td>35.63</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.002573</td>
<td>35.60</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Mean</td>
<td>35.62</td>
</tr>
<tr>
<td></td>
<td>Baker's</td>
<td>0.0007165</td>
<td>35.66</td>
</tr>
<tr>
<td></td>
<td>C.P.</td>
<td>0.001302</td>
<td>35.87</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.001523</td>
<td>35.49</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.001986</td>
<td>35.40</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.002322</td>
<td>35.42</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.003671</td>
<td>35.41</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Mean</td>
<td>35.40</td>
</tr>
</tbody>
</table>
Dietrich suggests that "this factor of dissolved impurities in the chloroform probably accounts for the differences existing between the distribution coefficients determined on the volumetric basis by different investigators and for the discrepancies in individual investigators" This certainly does seem a reasonable theory, not only from a consideration of Dietrich's own results, but from the differing results reported by investigators in the past. For instance, in Dawson & McRae's first paper (2) the following results are given at 30°C.

<table>
<thead>
<tr>
<th>Concentration in CHCl₃ (grms/litre)</th>
<th>Concentration in Aq. (grms/litre)</th>
<th>P.C.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2037</td>
<td>6.245</td>
<td>23.2</td>
</tr>
<tr>
<td>0.3375</td>
<td>7.815</td>
<td>23.2</td>
</tr>
</tbody>
</table>

whereas in a later paper (4) these results appear at 30°C.

<table>
<thead>
<tr>
<th>Concentration in CHCl₃ (grms/litre)</th>
<th>Concentration in Aq. (grms/litre)</th>
<th>P.C.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2949</td>
<td>6.565</td>
<td>22.57</td>
</tr>
<tr>
<td>0.3751</td>
<td>8.427</td>
<td>22.65</td>
</tr>
</tbody>
</table>

Dawson and McRae in this latter paper say they wish to ignore the earlier figures because "considerable experience in the carrying out of the determinations has enabled us to attain a much greater degree of accuracy than can be attached to the numbers referred to above, which were obtained at the commencement of our inquiry into the subject." Nevertheless a discrepancy of 0.6 is a very large experimental error and could easily be used as an argument for the above theory. Again the later results of
Dawson and McRae (3) at 20°C, and the results of Dawson (5) himself at 19.5°C may be contrasted. When plotted, both series of determinations lie approximately on two straight lines—thus eliminating the argument of experimental error—but the ordinates of the graph representing values at 20°C are greater than the corresponding ordinates of the graph at 19.5°C by approximately 0.5 (as shown in fig. 3) whereas combined experimental evidence and the conclusions of Dawson and McRae themselves have definitely proved that increase in temperature causes decrease in the value of the distribution coefficient.

The experiments of Oolleshaw (11) were the first to take into consideration the influence of carbon dioxide, present in the atmosphere, upon the distribution of ammonia between water and chloroform. Precautions were taken to eliminate, as far as possible, the presence of carbon dioxide during the actual distribution. To this end, the stock ammonia was initially distilled over baryta and collected in air-free water, the chloroform was shaken with concentrated sulphuric acid and water, distilled, washed with dilute ammonia solution, dilute sulphuric acid and redistilled. After the chloroform had been added to the partition funnel, the air was displaced by hydrogen and the ammonia solution aided out of contact of air.

Oocleshaw’s results show that at 25°C, over a concentration range 0.1388 to 1.022 molar in the aqueous layer,
the distribution coefficient, not corrected for ammonia
dissociation, may be represented by the linear equation

\[ k = 24.10 - 23.45c' \]

where \( c' \) is the molar concentration of ammonia in the non-
aqueous layer. If the results, corrected for ammonia
dissociation, are plotted, the equation becomes approximately

\[ k' = 23.85 - 24.53c' \]

The precise effect of temperature variation upon the
distribution coefficient, at constant ammonia concentration
in any one layer, has not yet been defined beyond the
general statement that the law is an inverse one, increase
in temperature causing decrease in the distribution
coefficient. In the following table a selection of results
of observers, who have used a volumetric basis of analysis,
are given. These readings are obtained by correcting results
for dissociation of ammonia, plotting and extrapolating to
infinitely small ammonia concentration.

<table>
<thead>
<tr>
<th>TEMP. °C</th>
<th>PARTITION COEFFICIENT</th>
<th>OBSERVER</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>25.55</td>
<td>HANTZSCH &amp; SEBALDT (ref. 1)</td>
</tr>
<tr>
<td>13</td>
<td>27.45</td>
<td>ABBOT &amp; BRAY (ref. 6)</td>
</tr>
<tr>
<td>18</td>
<td>27.59</td>
<td>DAWSON</td>
</tr>
<tr>
<td>20</td>
<td>25.40</td>
<td>DAWSON &amp; MORAY (ref. 3)</td>
</tr>
<tr>
<td>25</td>
<td>25.10</td>
<td>HANTZSCH &amp; SEBALDT (ref. 1)</td>
</tr>
<tr>
<td>26</td>
<td>24.69</td>
<td>BELL &amp; FIELD (ref. 8)</td>
</tr>
<tr>
<td>25</td>
<td>25.65</td>
<td>COOLESHAW (ref. 11)</td>
</tr>
</tbody>
</table>

(Note - a similar table may be found in the report of
Bell & Field, consisting, however, of a mixture
of results corrected and uncorrected for ammonia
dissociation)

Theoretically, of course, the distribution coefficient
at infinite dilution is indeterminate, the solute having
completely dissociated, but these results represent values obtained if the experimental distribution curves are extrapolated and they serve as an arbitrary basis for comparison. Little information can be obtained by plotting these values; in the first place there are not sufficient of them and, secondly, one would hardly expect a regular variation of distribution coefficient with temperature change for at least three reasons. Firstly, the results are not comparable owing to the mutual solubility of the chloroform and water altering with temperature; secondly, the varying dissociation of the ammonia with temperature will affect the results; and, finally, there is the objection raised by Dietrich that the results were not obtained using one specific sample of chloroform.
Having briefly reviewed the work of previous investigators, an experimental procedure for the determination of the partition coefficient of ammonia will now be described which, it is claimed, will yield the most accurate results. It has, as its main feature the entire elimination (as far as possible) of carbon dioxide of the atmosphere from all re-agents and from the distribution bulb itself.
PREPARATION AND ESTIMATION OF STANDARD ACID

The concentrations of ammonia in the aqueous and non-aqueous layers were estimated with standard acid. For this purpose solutions were prepared of approximately 0.7 and 0.3 Normal Sulphuric Acid together with approximately 0.02 and 0.002 normal caustic soda. The alkali was stored in Winchester bottles which, together with their glass leads were coated with a thin layer of paraffin wax to prevent interaction with the glass, and were protected from the carbon dioxide of the atmosphere by soda lime guard-tubes. The relatives strengths of the acid in terms of the alkali were first determined by weighing out about 2 grammes of acid and titrating with the alkali, using methyl red as indicator. All titrations were performed by weight and the number of grammes of alkali equivalent to one gramme of acid, for the two sets of solutions, was determined.

Standardisation of the stronger (0.7N) Sulphuric acid. Pure sodium carbonate was prepared by heating A.R. sodium bicarbonate in a porcelain dish until constant weight was obtained. About 0.5 to 0.8 grammes of carbonate was then weighed into a small tube and added to a known weight of acid - sufficient of the latter being present to provide a small excess. (This necessary weight of acid is very readily calculated from the results of a preliminary titration of the acid against a known weight of carbonate).
Care was taken on the addition of the carbonate, to avoid loss of liquid by splashing or spraying. The excess acid was then back titrated with the 0.02 N alkali, enabling the weight of acid which is equivalent to the carbonate to be calculated; hence follows the strength of the acid. In this titration methyl orange had to be employed since methyl red gives an indefinite end-point in the presence of carbon dioxide. In the standardisation which follows, the use of methyl red was resumed, this indicator being much more sensitive at high dilution than methyl orange.

**Standardisation of the Weaker (0.03 N) Sulphuric acid.**

About 10 grammes of the 0.03 N alkali were weighed out and neutralised, to a small excess, with 0.03 N acid. This excess was then back titrated with the 0.062 N alkali; a simple calculation gives the value of the acid in terms of the 0.03 N alkali and, as this is known with reference to the standard 0.7 N acid, the required strength of the weaker acid easily follows.

This method of standardisation possesses the advantage of not only giving the absolute values for the strengths of the acids but also provides a double check ensuring that they are correct relatively to each other.

The values of the alkalis in terms of their complementary acids were kept periodically in check and, in order to be consistent, were carried out using bromo-cresol purple as indicator, for this was the selected indicator adopted in determining distribution coefficients.
The Thermostat

The thermostat consisted of a rectangular tank insulated upon a wooden stand and covered with a thick layer of felt, to prevent loss of heat by radiation. Constant temperature control was effected by a mercury-toluene regulator of the spiral type. The toluene had been purified by shaking with mercury, (thus removing thiophene impurity as a black precipitate); separating and distilling - the first fraction containing any remaining thiophene being neglected -. This process was continued until addition of mercury showed complete absence of impurity. Purification of the mercury consisted in preliminary filtration and then in allowing it to fall repeatedly in tiny droplets from a funnel (drawn out to a fine point) through a solution of mercurous nitrate in 50% nitric acid contained in a burette. Finally the mercury was warmed to about 100°C. in an evaporating dish and then filtered.

The regulator operated a relay of the usual electromagnetic type, the latter being supplied with current by a 6-volt accumulator and working a mercury contact, making or breaking the current in the heating circuit according to the fall or rise in temperature of the thermostat.

The water was carefully maintained at a constant level and was efficiently stirred by a two-blade paddle worked by an electric motor. The temperature was set at 25°C. by means of a standard thermometer and did not vary more than ± 0.02°C.
To maintain the sensitivity of the thermostat, sparking at the mercury surface in the regulator was prevented by connecting a four microfarad condenser and an electrolytic condenser across the terminals. The electrolytic condenser consisted of two aluminium foil plates immersed in soap solution. Upon any scum forming on the mercury - causing fall of sensitivity - the surface was cleaned by means of an ordinary pipe cleaner moistened with benzene.

**SUPPLY OF CARBON-DIOXIDE-FREE AIR ("PURE" AIR)**

This supply of air was also used for conductivity purposes and consequently, in addition to being free from carbon dioxide, was washed free from ammonia.

A constant stream of air was obtained by means of a filter pump in conjunction with a Wolst's bottle and syphon tube. After passage through a reservoir, the air travelled up a vertical glass column packed with small pieces of pumice stone over which flowed a stream of strong caustic soda. A second similar column, containing Nessler Solution, removed any traces of ammonia present. Filtration was then accomplished by first passing the air through glass wool and then through an adapted Buchner flask fitted with filter paper.

The normal pressure of the air stream was equivalent to about 15 inches of water, but, if necessary, considerably higher pressures - in the neighbourhood of 2ft. of water -
could be obtained by tightening the screw clip on the syphon tube. With these higher pressures, washing was obviously not so efficient, so that slow streams of air were always used, except in such cases as did not permit their use. The purity of the air stream was tested, from time to time, by means of baryta solution.

**PREPARATION OF CARBON-DIOXIDE-FREE WATER**

Carbon-dioxide-free water was obtained from a conductivity still of the type recommended by Bengough, Stuart and Lee\(^{(12)}\) the essential parts of which were composed of pure tin. Ordinary laboratory distilled water, together with a quantity of potassium bi-sulphate, was boiled in a copper boiler. The steam passed down a coiled tube into a water-trap chamber - entering this chamber by a tangential opening and thus having a spiral motion. Any carbon dioxide present was swept away by an upward stream of 'pure' air in the main part of the still, while the steam, condensed by a surrounding cold water jacket, collected in the reservoir and was syphoned out when required.

After working for about two months, the still gave water of specific conductivity \(k = 0.5 \times 10^{-5}\) or less, at the rate of three-quarters of a litre per hour, provided that reasonable care in maintenance was observed.

**PURIFICATION OF THE CHLOROFORM.**

The chloroform used was a sample of May & Baker's R.P. It was first shaken with very dilute \((\text{H}_2\text{O})_{100}\) caustic soda

12 - J.C.S. - 1927 - 2156
to remove any dissolved carbon dioxide or other acid impurities, then separated and fractionally distilled in a current of 'pure' air. The distillate was collected in a yellow Winchester bottle fitted with syphon tube and soda lime guard tube.

From time to time a stream of 'pure' air was passed through the stock solution and it was periodically tested for acidity.

PURIFICATION OF THE AMMONIA SOLUTION.

A. 0.083 ammonia solution was distilled in a Kjeldahl apparatus - previously flushed out with 'pure' air - the ammonia being collected in a paraffin waxed Winchester bottle containing conductivity water. Any initial ammonium carbonate present was converted to barium carbonate by the addition of a few drops of baryta solution to the distilling flask. Any tendency towards back suction was eliminated by having the leading-in tube just below the surface of the water in the receiver.

An approximate subsequent analysis of this stock ammonia solution proved the strength to be approximately eight normal.

THE DISTRIBUTION APPARATUS AND ITS METHOD OF USE

The distribution bulb was a modification of that used by BROWN & BURY (13) in their distribution measurements and

(13) - J.O.S. 1923 - 129 - 2430.
consisted of a pyrex glass bulb of 250 cc. capacity fitted with capillary tubes of 1 mm. bore as shown in the diagram. The apparatus was designed and its method of use such that contact of the outside air with the reagents was prohibited; so that, as far as was possible, no carbon dioxide was allowed to be present either in the apparatus or in the liquids contained therein during the distribution measurements. In order to transfer solutions from their respective stock bottles to the partition bulb, an intermediate vessel was necessary, and this took the form of a measuring cylinder. This measuring cylinder was fitted with two tubes having rubber extremities and pinch clips so that definite quantities of reagents could be measured out for use.

The method of filling was conducted as follows:—

The partition bulb was cleaned thoroughly and then rinsed out with conductivity water. A stream of 'pure' air was then led through both the bulb and the measuring cylinder to flush out all carbon dioxide. When this had been completed, the various clips were closed, the last one to be so closed being the one for admitting the 'pure' air current. This procedure had the effect of creating a small pressure within the apparatus and thus ensured that, when the clips were subsequently released, the air motion was outwards.

Reference is now made to the accompanying diagrams.
In these diagrams: the tube $g$ is connected to the delivery tube, $f$ of the conductivity still and, on releasing the clips on the tubes $g$ and $g'$ (in that order) the required amount of water is allowed to run in. The tube $a$ is now connected to the syphon tube, $e$, of the ammonia bottle, and the tube $a'$ to the suction pump, $d$. Sufficient ammonia is sucked in to give approximately the desired concentration; the amount being readily calculated from a knowledge of the strength of the ammonia stock solution and the volume of water already in the cylinder. The vacuum existing inside the measuring cylinder is released by flushing out the cylinder with 'pure' air from the supply, $e$. The tube, $a$, is now joined to the tube, $b'$, the tube, $o$ to the tube $a'$, and the suction pump, $d$ to the tube, $b^2$. In this way the aqueous ammonia is transferred from the cylinder to the bulb. After eliminating the vacuum in the bulb with 'pure' air, the tube, $b$ is connected to the chloroform supply, $g$; the suction pump $d$ is connected to the tube, $b^2$ and sufficient of the non-aqueous solvent thus added. A final stream of 'pure' air is admitted through the tube, $b$ and the clips then closed in the order $b'$, $b^2$, $b$.

It was unnecessary, in this first series of experiments, to have any definite ratio existing between the volumes of the aqueous and non-aqueous layers. The chloroform was therefore sucked directly from the stock solution. The use of the measuring cylinder, in the first instance, was for
- 26 -

diluting the stock ammonia to the required concentration.

This, in brief, was the method used for filling the distribution bulb; many minor details and refinements have been purposely omitted as they would only serve to complicate the description of the process.

The method may seem lengthy and the process fastidious but the required conditions are only satisfied in the manner set out. Hence no apology is offered for the space devoted to the description.

After thoroughly shaking, the bulbs were placed in the thermostat; two or three subsequent and violent shakings were given to the bulbs at hourly intervals after which they were allowed to remain undisturbed for a period of at least 18 hours. ABBOB & ESRAY and later DIMINICH - as has previously been mentioned - experienced the difficulty of emulsified non-aqueous layers. The former advocated rotating the bulbs for from one to three hours; while the latter adopted a filtration method to overcome the difficulty. In the present series of experiments, however, after the stated period of 18 hours both the aqueous and the non-aqueous layers were quite clear. On removing the bulb from the thermostat however emulsification did take place: a natural result of the fall in temperature affecting the mutual solubility of the two solvents.

The absence of emulsification may have been due to a different sample of chloroform having been used or to the different method of initial purification or again, and
more probably, to the longer period given in the thermostat. No doubt equilibrium between the two layers, as far as the distribution of ammonia is concerned, was reached in much less time. NOONAN & WIMMILL as well as COOLESHAW recommend two hours. DIETRICH uses four hours as periods necessary for definite equilibrium; no doubt two hours may be given as a conservative estimate.

**CHOICE OF INDICATOR FOR THE ANALYSIS**

The indicator selected for use must fulfil three conditions, viz:

1. It must be insoluble in chloroform
2. It must be sensitive and give a distinct colour change.
3. It must not be affected by carbon dioxide.

Dawson & Naife, Abbot & Bray, and Cooleshaw all used methyl orange in their determinations in which the weakest standard solution employed was Abbot & Bray's 0.02N hydrochloric acid. In the present experiments 0.002N. alkali was employed, so that the use of methyl orange was out of the question owing to its insensitivity at this concentration. Moore & Wimmill support the use of methyl red, and, in all respects - save that it is soluble in chloroform - it would have been an admirable indicator to use. This solubility in chloroform, however, involved such difficulties and uncertainties that its use was abandoned. Dietrich advocates Sodium Alizarin Sulphonate as a suitable indicator and uses it in conjunction with 0.02N. acid;
judging from his results, it seemed satisfactory.

The indicator finally decided upon was Bromo Cresol Purple (pH 5·2 - 6·0); this was not the ideal indicator for the work by any means - such an indicator has yet to be discovered - but it possesses the qualities of being insoluble in chloroform, of giving a very decided colour change (yellow to purple) and of being very sensitive. It possessed the disadvantage of being affected, to some extent, by carbon dioxide; this was guarded against, however by using only conductivity water in titrations. It was possible to back titrate with NaOH, alkali and to obtain the end-point to the nearest drop (0·03 cc)

WITHDRAWAL AND ANALYSIS OF LAYERS

It is imperative that samples of the individual layers should be withdrawn whilst the partition bulb is still within the thermostat. This point does not appear to have been stressed in the reports of previous investigators, although it is one which is certain to influence the accuracy of the results obtained. If the partition apparatus is removed from its constant temperature surroundings, some of the water dissolved in the chloroform will be eliminated in tiny droplets and, from density considerations, slowly migrate to the upper regions of the layer. Moreover, each droplet will abstract from the chloroform a certain quantity of ammonia so that estimated concentrations of ammonia in the chloroform layer will be too high or too low.
according as to whether the sample is removed from the top
or from the bottom of the layer.

Samples of the layers were removed by pressure of a
stream of 'pure' air through a three-way tap connected to
the tube, \( E^2 \) in the diagram already given (facing p.24).
The existing pressure within the apparatus was first
released by opening this tap - which was closed as soon as
the hiss of outrusting gas had ceased. The rubber tubing
and clip at \( E \) were then removed and the capillary tube
washed by blowing over a small quantity of the aqueous layer,
control being effected by the three-way tap. After drying
the end of the capillary tube with a piece of filter paper,
weighed conical flasks - containing indicator - were
allowed to receive samples. The rubber tubing and clip
were then replaced. A similar procedure is followed in
removing samples from the chloroform layer: the receiving
flasks containing, in addition to indicator, a few cubic
centimetres of conductivity water.

In this way, two or three samples of each layer were
simultaneously removed for analysis. The bulb was then
well shaken, allowed to remain in the thermostat for another
period of three or four hours, and again analysed. The
quantities removed for analysis depended on the concentration
of ammonia present, varying from approximately 20 grammes
at the smallest concentration to five grammes at the highest.

After the removal of samples, the flasks with their
contents were weighed, neutralised to a small excess with
standard sulphuric acid and weighed again. The excess acid was then back titrated with the standard caustic soda and the amount required determined by a final weighing of the flasks. The stronger acid and alkali were used in estimating the aqueous layer, whilst the weaker solutions determined the concentrations in the chloroform layer.

-------------------------------------------------------------------

EXPERIMENTAL - PART II

-------------------------------------------------------------------

In making up solutions of ammonium chloride the same precautions were observed with regard to carbon dioxide, i.e., contact of the liquid with the atmosphere was reduced to a minimum. To this end a German standard litre flask, calibrated at 25°C, was fitted with syphon tubing. This flask was first flushed out with 'pure' air, then connected to the still and some conductivity water added. The necessary amount of salt was then weighed out - the weights having been previously calibrated by Richards' Method (14) - the syphon tube removed from the flask and the salt washed into the flask as rapidly as possible. The wash bottle used contained conductivity water and was operated by pressure from the 'pure' air supply. Any carbon dioxide that may have entered the flask while

(14) - J.A.C.S., 1906, 28, 144
adding the salt was swept out and the necessary quantity
of stock ammonia solution was added to obtain any desired
concentration. This was accomplished by first sucking
into the measuring cylinder, described in Part I - the
volume of ammonia solution required; connecting the cylinder
to the flask and transferring the solution from the one to
the other. More conductivity water was then admitted until
the level was just below the graduation mark and the flask
placed in the thermostat. When the solution had attained
the temperature of the thermostat, sufficient conductivity
water was added to make the volume of the solution up to
one litre and it was then rapidly transferred for storage
and use into a Winchester bottle fitted with syphon tube
and soda lime guard tube.

The proportions present of chloroform and water in the
partition bulb cannot be selected at random - in view of
their mutual solubility - as was the case in the first series
of determinations, for the ionic strength of the salt solu-
tions must be preserved. To obtain perfect constancy of
the ionic strength of the aqueous solution after the addition
of the chloroform, it would be necessary to know the effects
of the dissolved salt and of the ammonia upon the mutual
solubilities of water and chloroform at 20°C. Approximate
results, however, may be procured by using the data supplied
by Dawson (5) who gives the relative solubilities at 20°C
as follows:—
100 cc. water dissolve 0.42 cc Chloroform giving 100.39 cc Soln: 
100 cc. Chloroform dissolve 0.152 cc Water giving 99.62 cc Soln:

It was decided, however, in these experiments to use 
a constant ratio of 60 cc aqueous layer to 50 cc. chloroform 
layer—these volumes of liquid being suitable, when in the 
partition bulb, for the removal of samples by the method 
already described. The error involved may be approximately 
computed by using the above data; it will be a maximum 
for the weakest salt solution—the 0.02 Normal—and will 
amount to approximately 0.25%.

The general experimental procedure was similar to 
that described in Part I; the volumes of chloroform and of 
ammoniacal salt solution were measured out by means of the 
measuring cylinder and introduced into the partition bulb 
after the latter had been carefully dried.
RESULTS

The following results were obtained for the distribution of ammonia between pure water and chloroform at 25°C.
The first two columns show the measured concentrations of ammonia in chloroform and water respectively and are expressed in gramme equivalents of ammonia per thousand grammes solvent. Column three gives the 'uncorrected' partition coefficient obtained by dividing column two by column one; the degree of dissociation ($\alpha$) of the ammonia is then calculated from the dissociation constant $k = 1.8 \times 10^{-5}$, finally column five shows the true partition coefficient given by multiplying the 'uncorrected' partition coefficient by the factor $(1 - \alpha)$.

TABLE I

<table>
<thead>
<tr>
<th>$\text{[NH}_3\text{]}$ in CHCl$_3$</th>
<th>$\text{[NH}_3\text{]}$ in water</th>
<th>P.C. = $\frac{b}{a}$</th>
<th>Degree of Dissociation ($\alpha b$) of Ammonia</th>
<th>P.C. = $\frac{b}{a}(1 - \alpha)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Gm: Mols. per 1000 gns.}$</td>
<td>$\text{Gm: Mols. per 1000 gns.}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.003597</td>
<td>0.12990</td>
<td>35.934</td>
<td>0.01190</td>
<td>35.597</td>
</tr>
<tr>
<td>0.01988</td>
<td>0.49757</td>
<td>35.333</td>
<td>0.00690</td>
<td>35.121</td>
</tr>
<tr>
<td>0.02229</td>
<td>0.77957</td>
<td>34.981</td>
<td>0.00475</td>
<td>34.817</td>
</tr>
<tr>
<td>0.02735</td>
<td>0.95192</td>
<td>34.832</td>
<td>0.00433</td>
<td>34.651</td>
</tr>
<tr>
<td>0.03957</td>
<td>1.0284</td>
<td>34.707</td>
<td>0.00418</td>
<td>34.561</td>
</tr>
<tr>
<td>0.03513</td>
<td>1.2129</td>
<td>34.523</td>
<td>0.00388</td>
<td>34.391</td>
</tr>
<tr>
<td>0.04762</td>
<td>2.2578</td>
<td>33.533</td>
<td>0.00275</td>
<td>33.446</td>
</tr>
<tr>
<td>0.0233</td>
<td>3.0249</td>
<td>32.858</td>
<td>0.00245</td>
<td>32.788</td>
</tr>
</tbody>
</table>

The results for the third determination are given below, in full detail, as an example of experimental data and its treatment.
Analysis of Aqueous layer (two simultaneous withdrawals)

(a) $16.3998\text{ grms.}$ neutralised to excess with $18.9209\text{ grms.}$ of $0.66776\text{N H}_2\text{SO}_4$ and back titrated with $1.9417\text{ grms.}$ of $0.017312\text{N NaOH}$.

$16.3998\text{ grms.}$ therefore require $19.3087\text{ grms.}$ of acid for neutralisation.

$1000\text{ grms.}$ of aqueous layer hence contain $0.76984$ equiv. of ammonia; i.e. $13.113\text{ grms.}$ of $\text{NH}_3$.

$0.76984$ equiv. of ammonia are therefore present in $965.89\text{ grms.}$ pure water; Hence

$0.76984$ equiv. of ammonia are therefore present per $1000\text{ grms.}$ pure water.

(b) $6.4640\text{ grms.}$ neutralised to excess with $7.4919\text{ grms.}$ acid and back titrated with $1.9324\text{ grms.}$ alkali.

$6.4640\text{ grms.}$ therefore require $7.4428\text{ grms.}$ acid for neutralisation.

$1000\text{ grms.}$ aqueous layer hence contain $0.76337$ equiv. of ammonia; i.e. contain $13.097\text{ grms.}$ of $\text{NH}_3$.

$0.76337$ equiv. of ammonia are therefore present in $963.90\text{ grms.}$ pure water; Hence

$0.76337$ equiv. of ammonia are therefore present in $1000\text{ grms.}$ pure water.

Analysis of Non-Aqueous layer (two simultaneous withdrawals)

(a) $21.6358\text{ grms.}$ neutralised to excess with $16.2917\text{ grms.}$ of $0.66776\text{N H}_2\text{SO}_4$ and back titrated with $0.2934\text{ grms.}$ of $0.0027177\text{N NaOH}$.

$21.6358\text{ grms.}$ therefore require $16.2546\text{ grms.}$ acid for neutralisation.

$1000\text{ grms.}$ chloroform solution contain $0.628257$ equiv. of ammonia, i.e. contain $0.37912\text{ grms.}$ of $\text{NH}_3$.

$0.628257$ equiv. of ammonia are therefore contained in $999.62\text{ grms.}$ pure chloroform; Hence

$0.628257$ equiv. of ammonia are contained in $1000\text{ grms.}$ pure chloroform.
(b) 21.6564 grms. neutralised to excess with 16.3299 grms. of acid and back titrated with 0.4058 grms. alkali

21.6564 grms. require therefore 16.2817 grms. acid for neutralisation

1000 grms. chloroform solution contain 0.022287 grms. equivs. of ammonia, i.e. 0.37962 grms. NH₃

0.022287 equivs. of ammonia are therefore contained in 999.62 grms pure chloroform; hence

0.022287 equivs. of ammonia are therefore contained in 1000 grms pure chloroform

AQUEOUS LAYER

\[
\begin{align*}
\text{Average of } & \{ 0.73508, 0.77957 \} \\
\text{gives } & 0.77957 \text{ equivs. per 1000 grms. Water}
\end{align*}
\]

NON-AQUEOUS LAYER

\[
\begin{align*}
\text{Average of } & \{ 0.622266, 0.622268 \} \\
\text{gives } & 0.62227 \text{ equivs. per 1000 grms. Chloroform}
\end{align*}
\]

PARTITION COEFFICIENT \( \frac{0.77957}{0.62227} = 34.921 \)
The distribution of ammonia between ammonium chloride solution and chloroform at 25°C gave the following values:

<table>
<thead>
<tr>
<th>CONC: of NH₄Cl</th>
<th>[H₃] in CHCl₃ Grm. Nols. per 1000 gms (a)</th>
<th>[H₃] in aq. Grm. Nols. per 1000 gms (b)</th>
<th>P.C. = b/a</th>
<th>Degree of Dissociation (α₄) of Ammonia</th>
<th>P.C. = b/(1 - α₄)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.02 M.</td>
<td>0.01343</td>
<td>0.47332</td>
<td>35.252</td>
<td>0.000381</td>
<td>35.220</td>
</tr>
<tr>
<td></td>
<td>0.01493</td>
<td>0.52519</td>
<td>35.183</td>
<td>0.000379</td>
<td>35.167</td>
</tr>
<tr>
<td></td>
<td>0.03580</td>
<td>1.2493</td>
<td>34.508</td>
<td>0.000354</td>
<td>34.479</td>
</tr>
<tr>
<td></td>
<td>0.07320</td>
<td>2.6972</td>
<td>33.341</td>
<td>0.000313</td>
<td>33.311</td>
</tr>
<tr>
<td>0.05 M.</td>
<td>0.07419</td>
<td>2.4854</td>
<td>33.439</td>
<td>0.000266</td>
<td>33.438</td>
</tr>
<tr>
<td>0.2 M.</td>
<td>0.01678</td>
<td>0.57935</td>
<td>34.522</td>
<td>0.000309</td>
<td>34.519</td>
</tr>
<tr>
<td></td>
<td>0.03541</td>
<td>1.2494</td>
<td>34.066</td>
<td>0.000295</td>
<td>34.063</td>
</tr>
<tr>
<td></td>
<td>0.07463</td>
<td>2.6999</td>
<td>33.093</td>
<td>0.000262</td>
<td>33.093</td>
</tr>
<tr>
<td>1.0 M.</td>
<td>0.07633</td>
<td>2.5330</td>
<td>33.263</td>
<td>0.000232</td>
<td>33.263</td>
</tr>
</tbody>
</table>
DISCUSSION

The Partition Coefficients given in columns three and five of Table I are shown in Fig. 5 plotted against concentration of ammonia in chloroform. The corrected results lie on a smooth curve which on extrapolation yields 35.64 as the limiting value at infinite dilution of ammonia. For concentrations of ammonia (in the aqueous phase) extending to approximately one molar, the determinations may be said to lie on a straight line corresponding to the equation

\[ k(25^\circ C) = 35.64 - 36.5 \cdot c \]

where \( k \) is the partition coefficient, \( c \) is the concentration of ammonia (by weight) in chloroform.

The only other results on a weight basis, and therefore capable of direct comparison are those of Dietrich (see page 11) whose value of 35.62 at high dilution is given by a series of estimations having an average deviation of \( \pm 0.07 \). It is possible, however, to reduce values from a weight basis to a volumetric basis by employing a knowledge of the densities of chloroform and water at 25\(^\circ\)C. If we multiply the ratio of concentration per 1000 grams water by the ratio of density of water at 25\(^\circ\)C, we shall obtain a good enough approximation for the distribution coefficient on a volumetric basis. The densities of water and of chloroform at 25\(^\circ\)C, are 0.99708 and 1.4843 respectively and, on multiplying 35.64 - the 'infinite dilution' result -
by the ratio of these densities, the value of 23.94 is obtained. If this be compared with the extrapolated values of other investigators (obtained from Table on page 14) the agreement is seen to be fairly close.

25°C.

<table>
<thead>
<tr>
<th>PARTITION COEFFICIENT AT INFINITY DILUTION OF AMMONIA</th>
<th>OBSERVER</th>
</tr>
</thead>
<tbody>
<tr>
<td>23.85</td>
<td>O'COOLEY</td>
</tr>
<tr>
<td>23.94</td>
<td>MATTHEWS</td>
</tr>
<tr>
<td>24.00</td>
<td>BELL &amp; FIELD</td>
</tr>
<tr>
<td>24.06</td>
<td>DISTRICH</td>
</tr>
</tbody>
</table>

Those values for the distribution ratio in the presence of 0.02 and 0.2 Molar ammonium chloride are also found to lie upon straight lines, the three curves being exhibited together in fig. 6.

Distribution measurements give a ready method of calculating an important function, namely, the activity coefficient of the undisassociated portion of the ammonia. The activity or 'thermodynamic' concentration of a substance in solution divided by the actual concentration gives the activity coefficient - a quantity that will now be studied with the limited data available. In a perfect solution, i.e. one which follows the ideal gas laws, the activity coefficient of a solute will be unity, but, in actual practice, such a state of affairs is not obtainable even at high dilution. The deviation of the activity coefficient
from unity will, however, give us a measure of the deviation
of behaviour of the substance from the laws of the ideal
solution.

Let us first of all see how this activity coefficient
may be derived from the distribution data. By definition
the partition coefficient \( k \) at any concentration \( c \)
is given by the ratio concentration of undissociated ammonia
in water to that in chloroform

\[
k_c = \frac{N_c}{m_c} \quad \ldots \ldots \ldots \ldots (1)
\]
a ratio that is observed to vary with change in total
ammonia concentration. When, however, we use the ratio \( \frac{A}{a} \)
of the activities of the undissociated ammonia in water and
in chloroform, an 'ideal' partition coefficient is obtained
that remains constant for all ranges of concentration and
which is equal in value to the ordinary partition coefficient
\( k_o \) at infinite dilution of ammonia. This is necessarily
true from the concept of activity and from the fact that, at
infinite dilution, activity and concentration become
identical. Hence at the concentration \( c \), we shall also
have

\[
k_o = \frac{A_o}{a_o} \quad \ldots \ldots \ldots \ldots (2)
\]

If, now, we make the assumption that in the non-aqueous
layer the activity of the ammonia is equal to its concen-
tration, then, on dividing (2) by (1) we obtain:
The right hand side of this equation is, by definition, the activity coefficient \( f_{NH_3} \) of the undissociated ammonia at concentration \( c \), so that we have

\[
\frac{k_o}{k_c} = \frac{A_c}{M_o}
\]

The same equation holds, not only for changes in ammonia concentration but also when salt solutions are employed in place of pure water, the activity coefficient being given by the ratio of \( k_o \) to the measured partition coefficient. In taking the activity of the ammonia as equal to its concentration in the non-aqueous layer, we are assuming that salt does not pass from the aqueous to the non-aqueous phase and that the amount of water present in the latter is not sufficient to materially alter the activity coefficient of the ammonia.

In the following table (Table III) is shown how the activity coefficient of the undissociated ammonia in pure water varies with the concentration of ammonia present.
It has been stated in the past, and it has been customary to assume, that the logarithm of the activity coefficient of a non-electrolyte is proportional to its concentration. Thus, the formula \( \log f_a = km \), where \( k \) is a constant and \( m \) the molality, can be immediately derived from the empirical formula of Lewis and Randall and has been widely used by Randall & Failey. The formula rests, however, on fragmentary and not very accurate data.

Fig. 7 shows the values of \( f_{ma} \), taken from Table III above plotted against the molality, and also the values of \( \log f_{ma} \). It will be seen that \( f_{ma} \) follows a linear relation very much more closely than \( \log f_{ma} \), so that the equation

\[
f_{ma} = 1 + k'm
\]

is to be preferred.

(15) - 'Thermodynamics' equation XXIII, 31st., p. 288
Of more interest is the variation of \( f_{\text{H}_3\text{O}} \) in presence of ammonium chloride, particularly at infinite dilution of ammonia. The two curves depicting the partition coefficients in presence of 0.02 and 0.2 Molar ammonium chloride on extrapolation give values 35.67 and 34.98. Table IV below shows the calculated activity coefficients.

### Table IV

<table>
<thead>
<tr>
<th>[( \text{NH}_3 )] IN AQUEOUS PHASE</th>
<th>PARTITION COEFFICIENT ( k_a )</th>
<th>ACTIVITY COEFFICIENT ( f_m )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grm. Mois. per 1000 grms NH(_4)Cl solution</td>
<td>( \text{NH}_3 )</td>
<td></td>
</tr>
<tr>
<td>( 0.02 \text{ H. NH}_4\text{Cl} )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.47332</td>
<td>35.67</td>
<td>0.99916</td>
</tr>
<tr>
<td>0.52519</td>
<td>35.220</td>
<td>1.0119</td>
</tr>
<tr>
<td>1.2493</td>
<td>35.157</td>
<td>1.0137</td>
</tr>
<tr>
<td>2.6072</td>
<td>34.479</td>
<td>1.0337</td>
</tr>
<tr>
<td>33.311</td>
<td></td>
<td>1.0700</td>
</tr>
<tr>
<td>( 0.2 \text{ H. NH}_4\text{Cl} )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.57935</td>
<td>34.38</td>
<td>1.0189</td>
</tr>
<tr>
<td>1.2494</td>
<td>34.519</td>
<td>1.0325</td>
</tr>
<tr>
<td>2.4698</td>
<td>34.063</td>
<td>1.0463</td>
</tr>
<tr>
<td>33.093</td>
<td></td>
<td>1.0711</td>
</tr>
</tbody>
</table>

Before discussing these results, it will be necessary, very briefly, to review some of the conclusions induced by both theoretical and practical considerations of activity coefficients.

That the deviation of behaviour of substances in solution from the ideal gas laws is due to the ultimate electrical nature of matter has been realised since the time of Arrhenius, but the theoretical explanation of
experimental results is still very incomplete. In the case of strong electrolytes, where abnormality is most marked, modern chemistry has provided an adequate explanation. Here we are dealing with the interaction of particles possessing an excess charge of positive and negative electricity, and, from a knowledge of this ionic charge, the dielectric constant of the solvent and the distance between ions, we can predict changes in the activity coefficient. This was accomplished by Debye \(^{(16)}\) in 1923, when he evolved the expression, for dilute solution:

\[ -\log f = \alpha \sqrt{\mu} \]

\(\mu\) being the ionic strength of the solution and \(\alpha\) a constant.

Besides the primary ionic interaction developed by Debye, there exists a secondary effect of a similar nature to that produced upon non-electrolytes by the presence of salts, and which results in an increase in activity coefficient. This is taken into account in Brønsted's formula \(^{(17)}\)

\[ -\log f = \alpha \sqrt{\mu} - \beta \mu \]

the second term on the right hand side of the equation including the so-called "salting-out" effect in which the constant \(\beta\) is characteristic for individual salts. In very dilute solution, the salting out effect becomes negligible and the expression then reduces to that given by Debye. It will be seen from the equation, that, if the ionic effect predominates, then increase in ionic strength will cause a decrease in the activity coefficient and this is

\(^{(16)}\) - Debye & Hückel, Phys. Z. 1923, 24, 183
precisely what is observed by the experimental determination of \( f \) for strong electrolytes.

Whereas the behaviour of strong electrolytes in the presence of salts is fairly well understood, the empirical laws which govern the variation of activity coefficient of non-electrolytes in presence of salts are still indefinite; neither has a satisfactory theoretical explanation been advanced for the mechanism involved. The commonly adopted empirical formula for the variation of \( f \), for a non-electrolyte, with ionic strength, is

\[
\log f = B \mu.
\]

\( B \) being a constant: since, in general, the activity coefficient increases with increasing ionic strength.

An interesting modification of this expression is given by Rørdam in his 'Studies on activity' in which he assembles the data for the solubility of various non-electrolytes in salt solutions and proceeds to calculate the activity coefficients. On plotting the activity coefficients against ionic strength, he finds that, although as a general rule the value of \( f \) increases with the addition of salt, for a number of curves at low ionic strength, the \( f \) curve lies below unity, subsequently rising more or less rapidly.

The curves using phenylthiocarbamide, for which data was available at low ionic strength, showed this effect most markedly. These results cannot be considered remarkable when compared with the data for trinitrotriamine cobalt.
which, although a typical non-electrolyte, yet shows activity coefficient curves similar to those of electrolytes. Björnsted therefore concludes that there are two effects present in the case of non-electrolytes; first, the ordinary salting out effect resulting from increase in \( f \) due to the presence of ions; and, second, a decrease in \( f \) due to the molecule, with its separate positive and negative charges, possessing an electrical moment and thus behaving in a manner similar to ampho ions. He then extends Björnsted's equation for the activity coefficient of electrolytes to the activity coefficient of non-electrolytes in salt solutions, obtains

\[
-\log f = A\sqrt{\mu} - B\mu.
\]

and thereby advocated that "the activity coefficient curves of electrolytes and non-electrolytes in salt solutions belong to the same family of curves, the differences only arising from whether one or other of the two influences, which ever seem to be present simultaneously, predominates." It is assumed that those \( f \) curves which apparently do not show the interval where \( f \) is below unity, have, in reality, this feature but that it is too small to be shown by experiment.

Finally Björnsted has also shown, by solubility measurements of weak organic acids, that the undisassociated part of weak electrolytes behaves as a typical non-electrolyte; quoting from his thesis: "The results show that the activity of the non-ionized molecules of a weak electrolyte
Fig. 8.

\[ f \text{ INFINITE DILUTION} \]

\[ \text{OF AMMONIA} \]

\[ \frac{f}{\text{NH}_3} \]

1.02

1.01

1.00

0.99

0.98

0

\[ \mu \]

0.1

0.2
follow the same law as does the activity of non-electrolytes; especially in several cases the interesting effect could be substantiated which had been pointed out for several non-electrolytes that the activity coefficient by addition of salts is first slightly decreased, then increases."

Having outlined these theories upon the nature of the variation of the activity coefficients for the three classes of compounds, we may now enquire how far the above results for the activity coefficient of the undisassociated portion of ammonia - a typical weak electrolyte - support these views. The three values for \( f_{\text{Mi}} \) at infinite dilution of ammonia are:

<table>
<thead>
<tr>
<th>( \mu )</th>
<th>( f_{\text{mi}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>1.0000</td>
</tr>
<tr>
<td>0.02</td>
<td>0.9992</td>
</tr>
<tr>
<td>0.20</td>
<td>1.0188</td>
</tr>
</tbody>
</table>

and, on plotting these results, the curve shown in Fig. 6 is obtained. It is observed that the activity coefficient appears first to decrease from unity and then to rise again with increase in ionic strength - a state of affairs which seems to support Rørdam's conclusions. If we assume the equation \(-\log f = A\sqrt{\mu} - B\mu\) to hold for this portion of the curve, then \( A \) and \( B \) have the values 0.01205 and 0.0672 respectively, and are comparable with the corresponding values given by Rørdam for phenylthiocarbamide.

Unfortunately, the remaining data obtained at other salt concentrations do not allow the value of \( f_{\text{Mi}} \)
at infinite dilution of ammonia, to be calculated, but we may explore the curve for higher values of \( \alpha \) by using the results of Bell & Field given on page 8. Their values for the partition coefficient in presence of 3-Normal ammonium chloride are shown in Fig. 9 and, even up to 10-N total concentration of ammonia, the graph only shows a small curvature. The extrapolated value, for infinite dilution of ammonia, 23.55 when divided into 24.0 - their limiting value for pure water - gives an activity coefficient of 1.010. This value hardly differs from that corresponding to 0.2 ionic strength \( \text{NH}_4\text{Cl} \) (1.0183) and would seem to indicate that, instead of a rapid increase in \( f_{\text{NH}_3} \) - as might have been expected - the activity coefficient apparently assumes a more or less constant value at high ionic strength.

That this is no idle suggestion may be shown by considering the variation of \( f_{\text{NH}_3} \) at a constant concentration of ammonia in the aqueous phase. Choosing the concentration of ammonia 2.539 Molar in the aqueous phase (the value for the single 1-N \( \text{NH}_4\text{Cl} \) determination) it is possible to obtain the corresponding partition coefficients from the distribution curve at other salt concentrations. The single value in presence of 0.05 N. \( \text{NH}_4\text{Cl} \) is not far removed from the desired ammonia concentration and may be corrected to a good enough degree of approximation by assuming it to lie on a curve of similar slope to the other three curves. The results of Bell & Field may be also incorporated after transforming the weight concentration 2.539 equivs: per
1000 grammes to a volumetric basis by multiplying by the density of aqueous ammonia at this concentration and obtaining the partition coefficient from their curve. The following table gives these results in calculated values for $f_{\text{NH}_3}$.

25°C. CONCENTRATION OF AMMONIA IN AQUEOUS LAYER
2.539 equiv. per 1000 grms.

<table>
<thead>
<tr>
<th>MOLAR CONCENTRATION of $\text{NH}_4\text{Cl}$</th>
<th>ACTIVITY COEFFICIENT $f_{\text{NH}_3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>1.0729</td>
</tr>
<tr>
<td>0.05</td>
<td>1.0681</td>
</tr>
<tr>
<td>0.25</td>
<td>1.0659</td>
</tr>
<tr>
<td>0.50</td>
<td>1.0757</td>
</tr>
<tr>
<td>1.00</td>
<td>1.0714</td>
</tr>
<tr>
<td>3.00 (Bell &amp; Field)</td>
<td>1.1439</td>
</tr>
</tbody>
</table>

These figures again exhibit an initial decrease in $f_{\text{NH}_3}$, the latter attaining a minimum value somewhere between $\mu = 0$ and $\mu = 0.2$, while the value at high ionic strength appears to remain fairly constant or at least only rises very slowly. Whether this latter phenomenon is due to the formation of any complex in solution or whether there is any other theory that will explain why the usual rapid increase in $f$ is not obtained, we can only at present surmise; for the experimental evidence on which the conclusion is based is so meagre that further assumption is not justifiable.
SUMMARY

1. A short critical account has been given of the work of previous investigators concerning the distribution of ammonia between water and chloroform.

2. The following list may be taken as representing the more reliable results, so far determined:

<table>
<thead>
<tr>
<th>TEMP:</th>
<th>[NH₃] in CHCl₃</th>
<th>RESULTS (corrected for dissociation)</th>
<th>OBSERVER</th>
</tr>
</thead>
<tbody>
<tr>
<td>18°C</td>
<td>0.0007 - 0.0028</td>
<td>k = 27.45 (average)</td>
<td>Abbot &amp; Bray (6)</td>
</tr>
<tr>
<td>18°C</td>
<td>Inf.Diln.of NH₃</td>
<td>k₀ = 27.50</td>
<td>Dawson (7)</td>
</tr>
<tr>
<td>18°C</td>
<td>0.0023 - 0.0044</td>
<td>k = 27.32 (average)</td>
<td>Moore &amp; Wimill (9)</td>
</tr>
<tr>
<td>19°C</td>
<td>Up to 0.035</td>
<td>k = 26.16 - 24.14 c</td>
<td>Dawson (8)</td>
</tr>
<tr>
<td>25°C</td>
<td>Inf.Diln.of NH₃</td>
<td>k₀ = 24.0 (approx.)</td>
<td>Bell &amp; Field (8)</td>
</tr>
<tr>
<td>25°C</td>
<td>0.005 - 0.020</td>
<td>k = 24.0 (average)</td>
<td>Moore &amp; Wimill (9)</td>
</tr>
<tr>
<td>25°C</td>
<td>Up to 0.045</td>
<td>k = 23.85 - 24.83 c</td>
<td>Colesaw (11)</td>
</tr>
<tr>
<td>25°C</td>
<td>Inf. Dil.of NH₃</td>
<td>k₀ = 24.06</td>
<td>Dietrich (10)</td>
</tr>
<tr>
<td>25°C</td>
<td>Inf. Dil.of NH₃</td>
<td>k₀ = 23.94</td>
<td>Matthews</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>VOLUMETRIC BASIS</th>
</tr>
</thead>
<tbody>
<tr>
<td>25°C  0.0005 - 0.0035</td>
</tr>
<tr>
<td>25°C  Up to 0.03</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>WEIGHT BASIS</th>
</tr>
</thead>
<tbody>
<tr>
<td>25°C  0.0035 - 0.0035</td>
</tr>
</tbody>
</table>

*Not corrected for dissociation of ammonia
Approximate computation from a weight to a volumetric basis for purposes of comparison.
3. - There seems a certain amount of evidence in support
of Dietrich's conclusion that the discrepancies between
the results of individual investigators are due to
varying samples of chloroform giving differing results
on account of traces of stabilisers present that have
been introduced by the manufacturers for preservative
purposes.

4. - That increase in temperature lowers the partition
coefficient is all that, at present, can be said with
regard to the influence of temperature change on the
distribution.

5. - An experimental procedure is described whereby, in
determining distribution ratios, the two following
important conditions may be satisfied:

(a) As far as possible, the presence of carbon dioxide
in all reagents and in the distribution bulb
itself must be prohibited.

(b) Samples of the layers, for analysis, must be
withdrawn from the distribution bulb while the
latter is still within its constant temperature
surroundings.

6. - A series of determinations of the partition coefficient
of ammonia between chloroform and solutions of ammonium
chloride have been made and thence the activity
coefficient of the undissociated ammonia calculated.
The values of $f_{NH_3}$ (at infinite dilution of ammonia)
at first decrease below unity with increase in ionic
strength and subsequently rise - thus supporting the
conclusions of Jørdan that, with non-electrolytes and
the undissociated portion of weak electrolytes, there are two influences at work.

(a) A 'salting out' effect tending to increase the activity coefficient.

(b) A second electrical effect, tending to decrease the activity coefficient, arising from the molecule being considered to possess an electrical moment.

The general formula

\[-\log f = A\sqrt{\mu} - B\mu\]

proposed by Björnand to represent both electrolytes and non-electrolytes, when applied to ammonia for low ionic strengths (up to \(\lambda = 0.2\)) gives values 0.01205 and 0.0672 for A and B respectively. At ionic strengths greater than 0.2 it would appear that the activity coefficient assumes a more or less constant value, or at least only rises slowly with increase in \(\lambda\); the slender nature of the experimental evidence upon which this conclusion is founded does not justify an explanation at this stage.