7. No evidence has been obtained to indicate the existence of a barium phosphate more basic than tribarium phosphate.

8. The isotherm for the adsorption of calcium hydroxide shows that in most concentrated solutions approximately one-third of a mol of calcium hydroxide was adsorbed per mol of basic phosphate. Comparison of the curves for the three days' and six months' period indicates that either the calcium hydroxide penetrates the interstices of the solid phase very slowly or solid solutions are formed.

9. The adsorption of calcium hydroxide by tricalcium phosphate is slightly greater than by the basic phosphate.

10. The strong adsorption of calcium hydroxide by tricalcium phosphate and by basic calcium phosphate affords a basis for an explanation of many statements in the literature regarding basic phosphates of calcium.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF VERMONT]

# THE EQUILIBRIUM IN AQUEOUS SOLUTION BETWEEN AMMONIUM ACETATE, ACETAMIDE AND WATER

BY EDGAR E. LINEKEN AND GEORGE H. BURROWS

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## Introduction

The general reaction between ammonium salts of organic acids, the corresponding amides and water, though complicated by ionization and hydrolysis phenomena, in many instances runs smoothly and is adapted to studies in equilibria. In particular, it permits a comparison in equilibria among members of a homologous series.

E. E. Reid[1] has measured the benzamide formed upon heating until establishment of equilibrium of solutions of ammonium benzoate. Menschutkin[2] has studied the formation of amides on heating in closed glass tubes the pure ammonium salts of acids from formic to caproic, and also of benzoic and anisic acids. Other studies have been made purely from the standpoint of amide preparation.

E. A. Brodie, in this Laboratory, has measured the equilibrium between ammonium acetate and acetamide in aqueous solutions of several concentrations and at two temperatures. He heated the solutions to be brought to equilibrium in sealed pyrex glass tubes and analyzed the equilibrium mixtures through determination of their refractive indices. The present experiments are essentially repetitions of those of Brodie, substituting, however, for index of refraction, electrical conductance, thus lessening errors of analysis.

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[1] Reid, *Am. Chem. J.*, **44**, 76 (1910).

[2] Menschutkin, *J. prakt. Chem.*, [2] **29**, 422, 436, (1884).

## Experimental

The acetamide used was twice crystallized from benzene, with centrifugal draining, and was dried at 50–70°, yielding odorless crystals.

The ammonium acetate was crystallized from absolute alcohol, centrifuged, washed with absolute ether, or alcohol, and dried for several hours at 40° in an atmosphere of dry ammonia gas. The crystals were kept in well-filled, tightly stoppered bottles.

Conductivity water of uniform quality was used in preparing all solutions. In the work of Mr. Brodie equilibrium was approached from both sides, and shown to be attained within two days, at 184 and at 193°. In most of the present experiments equilibrium was approached from the amide side only, this substance being less subject to change during weighing.

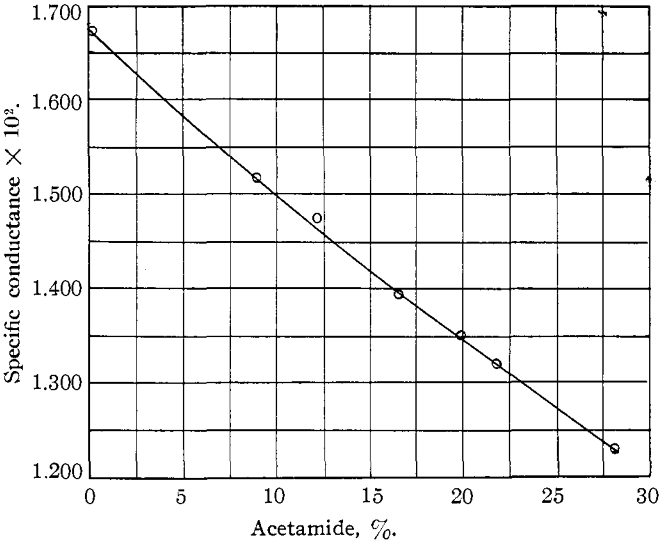

Fig. 1.

To attain equilibrium, solutions of acetamide were sealed in pyrex glass tubes of 5–10-cc. content, so that when hot the tubes would be closely full, and were heated in vapor-baths of dimethylaniline (193°), aniline (184°) or secondary butylbenzene (172°), for the necessary length of time. After this they were plunged into cold water, opened and the contents of each tube, if not already of this concentration, were brought to a concentration of 0.2 mole of total solids (amide plus acetate) to 1000 g. of solution. Analysis was then effected by measuring the specific conductance of the solution and referring this to a curve (Fig. 1) plotted from conductance measurements on synthetic mixtures. The plot permitted reading to the nearest 0.1% of amide.

The data for the curve plotted are given in Table I. In this table the specific conductances are those of a series of synthetic solutions of ammonium acetate and acetamide, each of which holds the same total solute concentration of 0.2 mole of acetate plus amide to 1000 g. of solution.

TABLE I

DATA FOR CURVE

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Solute as amide, % | 28.35 | 21.99 | 20.00 | 16.92 | 12.32 | 10.51 | 9.16 | 0.00 |
| Specific cond. × $10^2$ | 1.227 | 1.318 | 1.346 | 1.392 | 1.473 | 1.494 | 1.514 | 1.670 |

The results of the analysis of the equilibrium mixtures studied are given in Table II. They are shown graphically in Fig. 2

TABLE II

RESULTS OF ANALYSES

| Tube | Concn. (moles amide + acetate in 1000 g. soln.) | Temp., °C. | Time of heating, days | Spec. cond. at 0.2 *M* concn. | Total solute in form of amide, % |
|---|---|---|---|---|---|
| 14 | 0.5 | 172 | 5 | $1.527 \times 10^{-2}$ | 8.4 |
| 15 | 0.5 | 172 | 5 | $1.521 \times 10^{-2}$ | 8.7 |
| 6 | 1 | 172 | 5 | $1.474 \times 10^{-2}$ | 11.6 |
| 7 | 1 | 172 | 6 | $1.474 \times 10^{-2}$ | 11.6 |
| 18 | 2 | 172 | 5 | $1.356 \times 10^{-2}$ | 19.3 |
| 19 | 2 | 172 | 5 | $1.356 \times 10^{-2}$ | 19.3 |
| 10 | 0.5 | 184 | 2 | $1.514 \times 10^{-2}$ | 9.2 |
| 11 | 0.5 | 184 | 2 | $1.514 \times 10^{-2}$ | 9.2 |
| 4 | 1 | 184 | 2 | $1.441 \times 10^{-2}$ | 13.8 |
| 5 | 1 | 184 | 2 | $1.437 \times 10^{-2}$ | 14.0 |
| 1 | 2 | 184 | 2 | $1.305 \times 10^{-2}$ | |
| 2 | 2 | 184 | 2 | $1.319 \times 10^{-2}$ | 21.9 |
| 3 | 2 | 184 | 2 | $1.319 \times 10^{-2}$ | 21.9 |
| 16 | 0.5 | 193 | 2 | $1.470 \times 10^{-2}$ | 11.9 |
| 17 | 0.5 | 193 | 2 | $1.467 \times 10^{-2}$ | 12.1 |
| 8 | 1 | 193 | 2 | $1.407 \times 10^{-2}$ | 15.9 |
| 9 | 1 | 193 | 2 | $1.407 \times 10^{-2}$ | 15.9 |
| 12 | 2 | 193 | 2 | $1.289 \times 10^{-2}$ | 24.0 |
| 13 | 2 | 193 | 2 | $1.289 \times 10^{-2}$ | 24.0 |

Identity in composition of Tubes 6 and 7 indicates that equilibrium was established within about five days at 172°, a temperature not used by Mr. Brodie.

For comparison, part of the data obtained by Mr. Brodie, through use of the refractometer as a means of analysis, are quoted. He determined the percentage of amide and of ammonium acetate at equilibrium by comparing the refractive index of the mixture with those of pure amide and pure acetate solutions of the same concentration. A refractive index-concentration curve for acetamide solutions and for ammonium acetate solutions, each plotted in the same coördinate frame, gave two converging and almost straight lines. The value for any mixture, of

TABLE III

DATA FOR PURE SOLUTIONS

| Amide | | Acetate | |
|---|---|---|---|
| Moles in 1000 g. of soln. | $n_D^{25}$ | Moles in 1000 g. of soln. | $n_D^{25}$ |
| 0.0000 | 1.33260 | 0.2700 | 1.33567 |
| 0.5000 | 1.33590 | 1.0147 | 1.34396 |
| 1.0000 | 1.33929 | 1.1242 | 1.34538 |
| 1.9924 | 1.34589 | 1.9924 | 1.35482 |
| 2.4410 | 1.34880 | 2.3102 | 1.35828 |
| | | 2.6956 | 1.36270 |
| | | 0.0000 | 1.33260 |

course, lay between these lines. The data for the pure solutions, and the curves plotted from these, are given in Table III and Fig. 3, respectively.

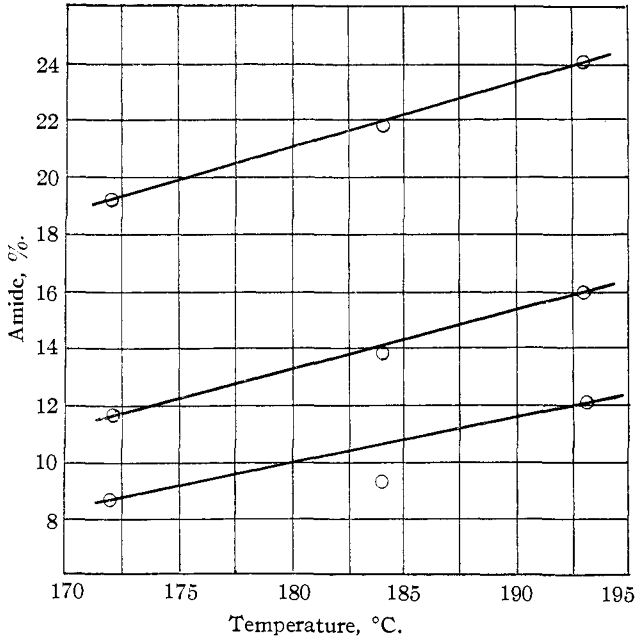

Fig. 2.

A summary of Mr. Brodie's analyses of equilibrium mixtures is given in Table IV.

TABLE IV

SUMMARY OF ANALYSES

| | | | |
|---|---|---|---|
| Concn., moles solute/1000 g. soln. | 2 | 2 | 1 |
| Temperature, °C. | 184 | 193 | 184 |
| Soln. in form of amide, % | 19.7 | 24.9 | 11.7 |

Approached from opposite sides, solutions of the same total solute concentration and at the same temperature always gave, at equilibrium, identical refractive readings, giving confidence in the purity of the amide and acetate used, and in the absence of side products.

Full treatment of the system under consideration would involve a knowledge of the ionization and of the hydrolysis of ammonium acetate at the concentrations and temperatures used. A. A. Noyes and coworkers[3] have determined such data for ammonium acetate in less concentrated solutions, at highest, approximately 0.01 molar.

An attempt was made to measure the equilibrium at this lower concentration. This failed, the results being quite irregular. In this attempt, refinements were made in the method of attaining equilibrium that will be mentioned.

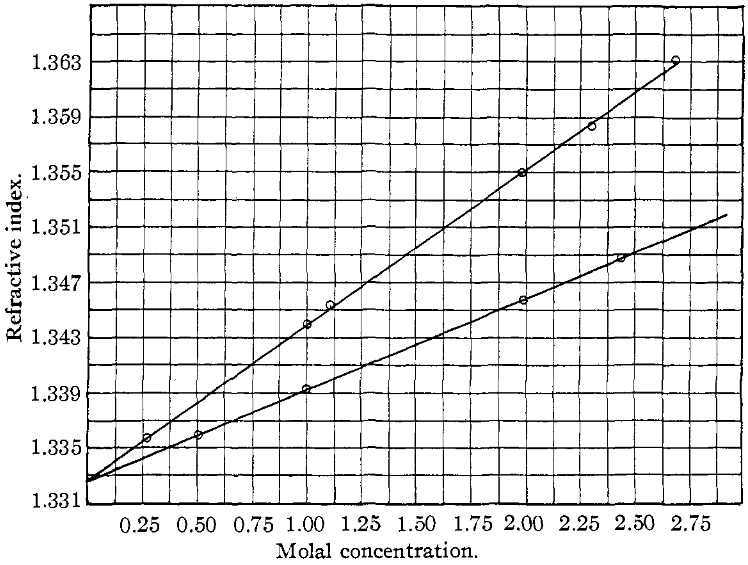

Fig. 3.

Though nothing of quantitative sort is known of the effect of the dissolved glass on the reaction itself, or of the effect of the reacting substances on the solubility of the glass, a brief study was made of the change

TABLE V

CHANGE IN CONDUCTANCE OF WATER WHEN HEATED IN PYREX GLASS

| 184° | | 193° | |
|---|---|---|---|
| Time | Incr. in spec. cond. × $10^{-5}$ | Time | Incr. in spec. cond. × $10^{-5}$ |
| 1 Hour | 2.101 | 1 Hour | 3.632 |
| 5 Hours | 1.50 | 4 Hours | 3.58 |
| 4 Days | 9.556 | 7 Hours | 5.80 |
| 5 Days | 7.758 | 5 Days | 12.626 |

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[3] A. A. Noyes, "The Electrical Conductivity of Aqueous Solutions," Carnegie Institute, **1907**.

in conductivity of water when sealed in pyrex glass tubes of 5 to 10 cc. capacity and heated. The results are given in Table V.

The errors in the results due to this glass solubility at such concentrations as those recorded in Table II would be small, and likely within other errors of the method.

To minimize the effect of the solvent action on the glass, and that of the necessary residual gas space in the reaction tube, a different form of tube was designed, shown in Fig. 4. The glass tube A contains the loosely covered platinum cylindrical vessel D. The cover is kept in place by the platinum wire E. Tube A is connected to Tube B, and Tube B to Tube C by capillary tubing. The solution fills the apparatus to a suitable level in C, thus limiting to C any change in concentration due to evaporation into the gas space. The portion of the solution subjected to analysis is that contained in the platinum vessel. These precautions did not avail to give consistent results with solutions as dilute as 0.01 molar. A 2 molar solution of amide heated for two days at 184° in such a tube, then diluted to 0.2 molar, had at 25° a specific conductance of $13.36 \times 10^{-4}$, corresponding to 20.7% of amide remaining, and agreeing fairly well with the 21.9% of Table II.

Examination of the data of Table II brings out that the ratios of the equilibrium concentrations of amide to those of ammonium acetate, including in the latter its dissociation and hydrolysis products, show, at a given temperature, no tendency to constancy. Such tendency is shown when the concentrations of amide are divided by the squares of the acetate concentrations (Table VI), indicating that the amide is formed through the interaction of the ammonium and the acetate ions.

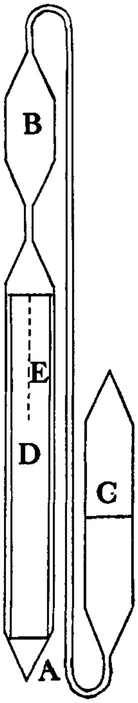

Fig. 4.

TABLE VI

RELATIONS OF AMIDE AND ACETATE CONCENTRATIONS

| Temp., °C. | Concn. of amide | Concn. of acetate | $\frac{\text{Concn. of amide}}{(\text{Concn. of acetate})^2}$ |
|---|---|---|---|
| 172 | 0.043 | 0.457 | 0.200 |
| 172 | .116 | .884 | .148 |
| 172 | .386 | 1.614 | .148 |
| 184 | .046 | 0.454 | .2231 |
| 184 | .139 | .861 | .1875 |
| 184 | .438 | 1.562 | .1795 |
| 193 | .06 | 0.44 | .31 |
| 193 | .159 | .841 | .225 |
| 193 | .48 | 1.52 | .208 |

In Table VI the compositions are in moles per 1000 moles of solution.

Owing to the small concentration of amide, the first value for each temperature is the least accurate.

The conclusion that the amide is formed through the ions is in accord with such results as those of Walker and Hambly,[4] who show that the transformation of ammonium cyanate into urea is bimolecular

## Summary

Results are given of measurements of the equilibrium between ammonium acetate, acetamide and water in aqueous solution at several temperatures and at several concentrations.

Evidence is presented that the amide is formed through the ions of the salt.

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[CONTRIBUTION FROM THE PHYSICO-CHEMICAL LABORATORY OF THE POLYTECHNICAL INSTITUTE OF COPENHAGEN]

# THE ACTIVITY COEFFICIENTS OF IONS IN VERY DILUTE METHYL ALCOHOL SOLUTIONS[1]

BY JOHN WARREN WILLIAMS[2]

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The fundamental equations of the activity theory of Debye and Hückel[3] have been amply verified in solutions in which pure water was used as the solvent. The validity of the fundamental equations with respect to the effect of the variation of the dielectric constant of the medium has not been sufficiently investigated, although it has been attempted in a number of cases.[4] For the work to be reported in this article the papers by Kraus and Seward[4e] and by Robinson[4f] are perhaps of greatest interest because they have used the same method to determine their activity coefficients and have used non-aqueous solvents. The purpose of these articles, as well as of the present one, is to attempt a verification of the

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[4] Walker and Hambly, *J. Chem. Soc.*, **67**, 753 (1895).

[1] The work reported in this article was carried out during the months of November and December, 1927, under the direction of Professor J. N. Brönsted. At that time the work could not be continued and extended; therefore, it was withheld from publication. In the meantime articles by Kraus and Seward and by Robinson, to which references will be made, have appeared which make it desirable to publish the results to date. The continuation and extension of the work has now been begun at the University of Wisconsin.

[2] National Research Council Fellow in Chemistry.

[3] Debye and Hückel, *Physik. Z.*, **24**, 185 (1923).

[4] (a) Scatchard, THIS JOURNAL, **47**, 2098 (1925); (b) Noyes and Baxter, *ibid.*, **47**, 2122 (1925); (c) Nonhebel and Hartley, *Phil. Mag.*, **50**, 729 (1925); (d) Baxter, THIS JOURNAL, **48**, 615 (1926); (e) Kraus and Seward, *J. Phys. Chem.*, **32**, 1294 (1928); (f) Robinson, *ibid.*, **32**, 1089 (1928); (g) Brönsted and Williams, THIS JOURNAL, **50**, 1338 (1928).