

A SIMPLE METHOD OF MEASURING HYDROLYSIS.

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Several methods of measuring the degree of hydrolysis of dissolved salts have been proposed from time to time; e. g., the measurement of the rate at which the solution saponifies an ester, such as ethyl acetate; the rate of hydration of milk sugar; and the measurement of the partial pressure of ammonia gas over solutions of its hydrolysed salts; but none of these methods is precise, and even under the most favorable conditions, they are far from satisfactory. The first is based upon the bold assumption that the rate of saponification is proportional to the concentration of the hydroxyl ions, and that it is unaffected by the presence of other molecular aggregates; the second method involves a similar assumption; while the last is of little if any practical value, owing to experimental difficulties.

The method about to be described was developed in the course of an extended research on the dissociation relations of Ortho and Pyro Phosphoric Acids and their salts, which will be published in detail elsewhere. It is simple and convenient, and should be capable of a fairly wide application to the ammonium salts of other weak acids; therefore it has seemed sufficiently interesting to justify a brief description at this time.

When an aqueous solution of ammonia is shaken up with chloroform, the ammonia distributes itself between the two non-miscible solvents, and the distribution ratio is constant at a given temperature. Fortunately this ratio is of a magnitude which makes it possible to determine the concentration of the ammonia in the aqueous solution by simply titrating a measured volume of the chloroform with which the solution is in equilibrium. It is obvious that we may take advantage of this fact to determine the concentration of the free ammonia in a solution of its hydrolysed salt, and thus determine the degree of hydrolysis. It is free from assumptions and is as direct as a chemical analysis itself.

But, simple in principle as the method appears, its successful application requires attention to certain experimental details. The chief difficulty arises from the fact that the ammoniacal solutions form emulsions with the chloroform layer which remain turbid even after standing several hours in

the thermostat. Drops of the aqueous solution of variable size thus remain suspended in the chloroform layer, making it impossible to obtain concordant results when different samples are titrated. Fortunately this difficulty may be easily overcome by merely rotating the solutions in glass-stoppered bottles in the thermostat. For this purpose the bottles are fastened to the axle of the rotary stirrer of the thermostat after the familiar method of making solubility measurements, and allowed to rotate several hours (one to three), when the two phases invariably separate perfectly clear, with a sharply defined bounding surface. In order to establish the equilibrium between the solution of the hydrolysed salt and the chloroform, the latter is vigorously shaken with the aqueous solution in a stoppered separatory funnel. The phases are allowed to separate, after which the water layer is removed as completely as practicable, and another portion of the solution is added. This process is repeated until three portions have been shaken up with the chloroform; a fourth portion is then rotated with the chloroform, at a constant temperature, as described above. It is important to remove the sample of chloroform for titration without contamination by any of the aqueous solution. This may be easily done by means of a syphon. The short limb of the glass tube is sealed in the flame, and a small thin bulb blown on the end. It may then be passed, closed, through the aqueous layer, and opened by breaking against the bottom of the bottle. The chloroform is syphoned into a clean, dry, vessel, measured, and titrated with 0.02 Normal hydrochloric, or nitric, acid, using methyl orange as indicator. Enough pure water should be added to make a layer of convenient depth to view the color of the indicator; since the latter does not enter the chloroform, and the stoppered vessel should be vigorously shaken at intervals during the titration.

The distribution coefficient of ammonia between chloroform and water was measured, at 18°, at concentrations 0.1, 0.05, and 0.02 Normal, and the mean of eight measurements gave 27.36. This is the ratio of the concentration of the undissociated ammonia in the aqueous solution to the concentration of the ammonia in the chloroform.

The method was applied to the measurement of the degree of hydrolysis of $\text{Na}_2\text{NH}_4\text{PO}_4$, at 18°, and concentrations 0.1, 0.05, and 0.02 molal, with the following results:

<i>Conc. Mols. per Litre.</i>	<i>Per Cent. Hydrolysis.</i>
0.1	95.39
0.05	95.44
0.02	95.65

That is, in a solution of $\text{Na}_2\text{NH}_4\text{PO}_4$, at the above concentration, only 5 per cent. of the ammonia is chemically combined. When the hydrolysis is large the method is accurate, and even when it is small the results are good, as shown by the following values for the salt $\text{NaNH}_4\text{HPO}_4$:

<i>Conc. Mols. per Litre.</i>	<i>Per Cent. Hydrolysis.</i>
0.1	2.98
	2.92
	2.98
	3.02
0.05	3.13
	3.02
	2.90
Mean, 3.0	

These values are corrected for the ionization of the ammonia at the different concentrations.