acid. The formation of $K(Cl.Na.Cl)$ would lower the value of the sodium ion fraction; so it would seem, as the only conclusion in harmony with the facts, that the preponderating complex formed is $Na(Cl.K.Cl)$, and that this ionizes somewhat to give Na^+ and $(Cl.K.Cl)^-$ ions.[1]

It might be objected that this explanation is not in harmony with the data in Table II, in which, though the total salt concentration of the mixed solutions varied only between the limits 1.25–1.50 N, the equivalent fractions, (NaCl) : (KCl), varied between the limits 0.1835 : 0.8165 and 0.8037 : 0.1963; and yet in which the values of the expression, $\frac{(KHg_m)(NaCl)}{(NaHg_n)(KCl)}$, are constant within the experimental error. This difficulty is removed, however, if we assume that the complex formation takes place only through the direct union of the non-ionized molecules,[2] according to the equation,

$$NaCl + KCl \rightleftarrows Na(Cl.K.Cl) \rightleftarrows Na^+ + (Cl.K.Cl)^-.$$

The law of mass action would then require a constant value for the expression,[3] $\frac{[NaCl]\,[KCl]}{[Na(Cl.K.Cl)\,]}$, and, so long as the total salt concentration remained approximately constant, a finite preponderance of either salt in the solution would lead to the same result.

URBANA, ILL., NOV. 15, 1912.

METHODS FOR THE PREPARATION OF NEUTRAL SOLUTIONS OF AMMONIUM CITRATE.

BY JAMES M. BELL AND CHARLES F. COWELL.

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The method at present approved by the Association of Official Agricultural Chemists[4] for the preparation of neutral solutions of ammonium

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[1] Other salts which would appear to form such complexes, in much more stable form, are the iodide of cadmium, $Cd(CdI_4)$ [cf. W. Hittorf, *Pogg. Ann.*, **106**, 545f (1859)], and mercuric chloride and cyanide, all of which, as is well known, are much less ionized than most other salts of the same type. Again, the fact that the pink color of aqueous solutions of $CoCl_2$ changes to a deep blue upon the addition of concentrated hydrochloric acid may be ascribed to the formation of complexes, such as $[CoCl_6]^{----}$ [cf. also Berthelot, *Ann. chim. phys.*, [5] **23**, 85–93 (1881)].

[2] Cf. Werner, "Zur Theorie der Basen," *loc. cit.;* cf. also in this connection the notable address on "Theories of Solution," by J. Walker; *Science*, **34**, 622–31 (1911). For example, after having pointed out strong evidence that in the case of the abnormal electrolyte, ammonium cyanate, the abnormality of the ionization equilibrium is to be attributed entirely to the non-ionized portion, he goes on to say (p. 629): "But ammonium cyanate differs in no respect, with regard to its electrolytic conductivity, from hundreds of other abnormal binary electrolytes with univalent ions; and I am therefore disposed to conclude that it is to the non-ionized portion in general of these electrolytes that the abnormality is to be attributed."

[3] The expressions inclosed in the brackets refer to the concentrations of the non-ionized portions of the substances in question.

[4] Bureau of Chemistry, *Bull.* **107** (revised), 1.

citrate requires the use of an alcoholic solution of corallin as indicator. It is common knowledge that this method is not accurate. The method proposed by Hand,[1] using purified litmus solution, has been thoroughly tried by Patten and Robinson[2] and like the corallin method has proven much less satisfactory than the conductivity method proposed by Hall and Bell.[3] By this conductivity method a series of solutions is prepared containing constant quantities of citric acid and variable quantities of ammonia in a constant volume. It was found that the solution just neutral has the highest electrical conductivity, the plot for conductivity and quantity of ammonia consisting of two curves intersecting at the neutral point. Up to that point the solutions consist of mixtures of ammonium citrate and free citric acid, and beyond the break the solutions consist of mixtures of ammonium citrate and free ammonia.

The conductivity method requires some temperature control, for the temperature coefficient of conductivity is large enough to cause serious errors in the final result unless the maximum variations in temperature are but very slight. Two further methods are here presented for the determination of the neutral point, neither of which requires careful temperature regulation. In one method there is an indirect determination of the excess of ammonia just past the neutral point by the use of chloroform as solvent. This method is called the "extraction method." The second method like the conductivity method is a physical method, depending on the great heat evolution when ammonia and citric acid solutions are mixed. This has been called the "temperature method."

I. Extraction Method.—Ammonia is soluble to a slight extent in chloroform; citric acid and ammonium citrate are insoluble in chloroform. This fact affords an accurate method of estimating the excess of ammonia in an aqueous solution of these substances. The distribution ratio of ammonia between chloroform and water has been shown by Bell and Feild[4] to be about 1–25 at ordinary temperatures; that is, between equal volumes of water and chloroform, free ammonia will distribute itself about 1/26 in the chloroform layer and 25/26 in the water layer.

A citric acid solution containing 370 grams per liter was prepared. To 100 cc. lots of this solution varying amounts of strong ammonia were added and the resulting solutions diluted to 200 cc. This addition was made through a narrow tube leading into the acid so as to avoid losses of ammonia by volatilization. Of this solution 100 cc. were shaken out with 125 cc. of chloroform and 50 cc. of this chloroform layer to which about 50 cc. of water were added was titrated against 0.1 *N* hydrochloric

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[1] Bureau of Chemistry, *Bull.* 132, 11.

[2] *J. Ind. Eng. Chem.*, 4, 443 (1912).

[3] THIS JOURNAL, 33, 711 (1911).

[4] *Ibid.*, 33, 940 (1911).

acid solution using methyl red as indicator. During this titration all the ammonia passed from the chloroform layer to the water layer as it was neutralized by the acid. In these determinations only a part of the total excess of ammonia is estimated, but knowing what fraction is taken, the total excess of ammonia may be estimated. For each gram of free ammonia left in 100 cc. of the water layer after shaking out, there is 0.04 gram in 100 cc. of the chloroform layer or 0.05 gram in 125 cc. of the chloroform layer. Hence, of the total excess of ammonia in the sample 1/21 is in the 125 cc. of chloroform. In 50 cc. there are 2/105 of the portion shaken out and as only half of the total is shaken out there is 1/105 of the total excess of ammonia actually titrated.

TABLE I.

Ammonium solution used. Cc.	0.1 *N* HCl required to neutralize 50 cc. chloroform extract. Cc.
40.5	1.50
40.2	0.97
40.0	0.47
39.8	0.22
39.5	0.00

The proportion in which the citric acid and ammonia solutions must be mixed to give a solution exactly neutral may be found by a graphic method. In Fig. 1 the number of cc. of ammonia added is abscissa and the number of cc. of acid required to neutralize the excess of ammonia in 50 cc. of the chloroform layer is ordinate. By extrapolating it is seen that 39.7 cc. of ammonia solution would just neutralize the amount of the citric acid solution employed. No trace of free ammonia was found in any of the solutions to which 39.5 or less of the ammonia solution had been added. When as much as 40.0 cc. had been added, the free ammonia could be detected by odor and these solutions showed increasing amounts of ammonia in the titrations. The solution containing 39.8 cc. of ammonia contained very little free ammonia, for 50 cc. of the chloroform extract required only 0.22 cc. of the acid. It will be seen that this method will indicate the proportions in which the solutions of ammonia and citric acid must be mixed with at least the accuracy which is possible in the ordinary comparison of an acid and base by buret readings.

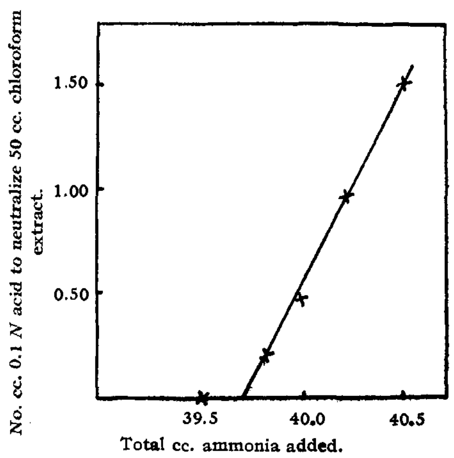

Fig. 1.

II. Temperature Method.—The second method here presented for the preparation of a neutral solution of ammonium citrate, like the conductivity method, is a physical method. It was suggested by the fact that, during the addition of the first 35 cc. of ammonia to the citric acid in the former method, so much heat was developed that the solution had to be cooled at least twice during the mixing. After the neutral point is reached, there is no appreciable heat effect due to further additions of ammonia.

The experiments were carried out in a Dewar flask of about 200 cc. capacity, provided with a platinum stirrer and a thermometer graduated to tenths of degrees. The citric acid and ammonia solutions were the same as those used in the former method. Again, 100 cc. of citric acid solution was partially neutralized with 36 cc. of ammonia solution in an ordinary beaker. The cooled solution was then poured into the Dewar flask. The beaker was washed several times with water and the washings poured into the Dewar flask, so that the final volume of solution was about 150 cc. Just as in the previous method, the ammonia solution was added from a buret provided with a small delivery tube, which extended to the bottom of the flask. Ammonia was now added in portions of 0.5 cc. and the mixture stirred for about $^1/_2$ minute. After $1^1/_2$ minutes no further rise of temperature was noticed. After each addition of 0.5 cc. of ammonia there was a constant rise of temperature of about 0.40° until the buret reading was 39.50 cc. of ammonia. For the next 0.5 cc. of ammonia the rise of temperature was only 0.16°. Beyond 40 cc. practically no change in temperature occurred. The neutral point is therefore between 39.5 cc. and 40 cc. of ammonia. The exact neutral point is found by plotting the curve, using the number of cc. of ammonia as abscissa and the rise of temperature as ordinate. This point is found to be 39.7 cc., the same reading as was found by the extraction method.

TABLE II.

Total ammonia added. Cc.	Temperature.
36.0	21.50°
36.5	21.88
37.0	22.25
37.5	22.62
38.0	23.04
38.5	23.40
39.0	23.70
39.5	24.12
40.0	24.28
40.5	24.30
41.0	24.30
42.0	24.32
45.0	24.32

The "temperature method" was further confirmed by its use with solutions of sulphuric acid and ammonia, both about twice normal. The rise of temperature, taken with the same thermometer as before, was constant until the neutral point was reached. The results obtained are given in Table III and the neutral point agrees exactly with that found by the direct titration of the ammonia against the acid.

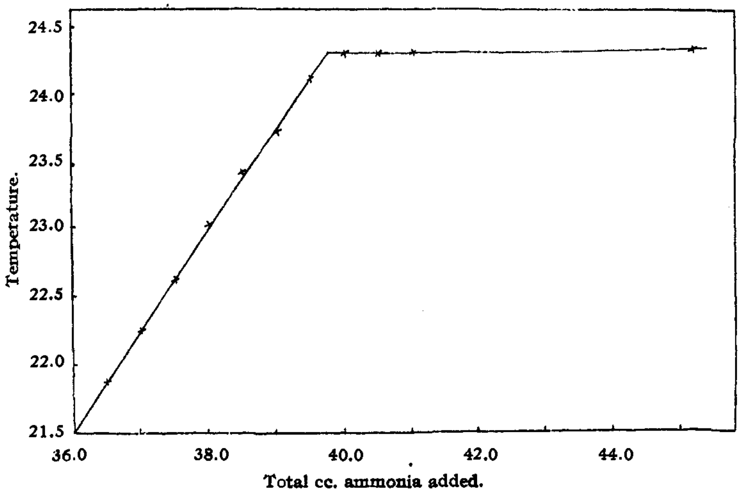

Fig. 2.

TABLE III.

Ammonia added to 40 cc. acid. Cc.	Temperature.
38.5	27.62°
39.0	27.70
39.5	27.79
40.0	27.88
40.5	27.96
40.1	28.05
41.5	28.05
42.0	28.01
42.5	27.98
43.0	27.95

Both methods here presented are for the determination of the proportion in which ammonia and citric acid must be mixed to arrive at a neutral solution. These proportions vary of course with the strength of the separate solutions. From the proportion found large quantities of neutral ammonium citrate may be prepared, after which the solution may be diluted to the required density.

Summary.

In this paper two methods are proposed for the determination of the end point in the titration of a weak acid by a weak base, where the ordinary indicators fail. In the first method an index of the excess of ammonia is obtained by shaking out with chloroform and by titrating the chloroform with a dilute acid. In the second method the rise in temperature due to the heat of neutralization is observed as the titration proceeds, the end point being at the break in the heating curve. Both these methods are simpler than the method formerly proposed where the conductivities of solutions must be determined at constant temperature.

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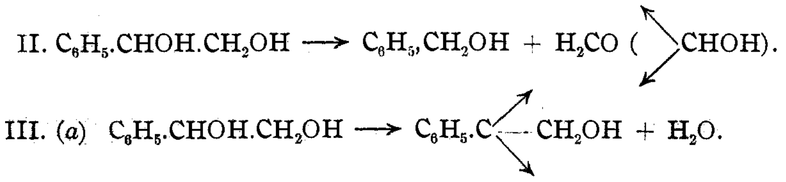
THE PREPARATION AND THE OXIDATION OF STYROLENE ALCOHOL.

BY WM. LLOYD EVANS AND LOU HELEN MORGAN.

Received October 31, 1912.

The work presented in this report was undertaken with two distinct purposes in view. First, to determin the mechanism of the oxidation reaction of styrolene alcohol with any given reagent, *i. e.*, which one of the five theoretical possibilities this reaction follows; and, second, as a result of these studies, to establish, if possible, the experimental conditions whereby mandelic aldehyde might be isolated as an intermediate oxidation product. From the well known experiments of Nef[1] with mandelic aldehyde acetate, it was to be expected that if the free aldehyde was isolated at a temperature approaching 100°, it would immediately rearrange to benzoyl carbinol, the oxidation chemistry of which is understood.[2] The experiments of Wohl and Lange[3] and more recently those of Kranz[4] with lactic aldehyde seem to indicate that this substance is sufficiently stable at ordinary temperatures to be easily identified. In fact, Kranz reports it to be a white crystallin compound melting at 101–102°.

The dissociation of styrolene alcohol in the process of oxidation may be regarded as taking place in any one or all of the following ways:[5]



$$\text{I. } C_6H_5.CHOH.CH_2OH \longrightarrow C_6H_5.CHO + CH_3OH.$$

$$\text{II. } C_6H_5.CHOH.CH_2OH \longrightarrow C_6H_5,CH_2OH + H_2CO\ (\ \rangle CHOH).$$

$$\text{III. } (a)\ C_6H_5.CHOH.CH_2OH \longrightarrow C_6H_5.C\langle\!-\!-CH_2OH + H_2O.$$

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[1] *Ann.*, **335**, 266.

[2] Work is now being carried on in this laboratory by Mr. C. R. Parkinson and myself with a view of synthesizing mandelic aldehyde and studying its properties. W. L. E.

[3] *Ber.*, **41**, 3612.

[4] *Chemicke Listy*, **5**, 323–7; *C. A.*, **6**, 739.

[5] Compare THIS JOURNAL, **34**, 1101.