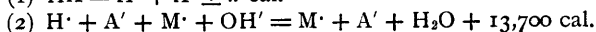
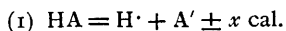


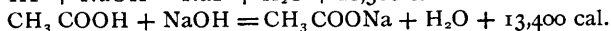
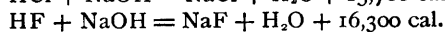
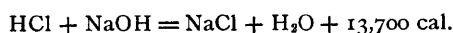
## DISCUSSION.

**Dr. G. Senter** asked if Dr. Veley was of opinion that there is a direct connection between heats of neutralisation and degree of hydrolysis of such a nature that the smaller the heat of neutralisation the greater the hydrolysis. Although not expressly stated, it appeared from the context (*e.g.*, methyl and dimethyl anilines, p. 5) that this was the general idea underlying Dr. Veley's paper.

It is very doubtful, however, if there is any such relationship as that assumed. The neutralisation of a strong base MOH by a weak acid HA may be represented as taking place in the following two stages—



The heat evolved depends, therefore, on the heat of dissociation of the acid, and, as Arrhenius has shown, there is no direct connection between the strength of an acid and its heat of dissociation—the latter may be positive or negative. The following numbers for the heats of neutralisation of hydrochloric acid (very strong), hydrofluoric acid (moderately strong), and acetic acid (very weak), by sodium hydroxide, show this conclusively—



Dr. Veley appears to suggest that the smaller heat of neutralisation in the case of a weak base (or acid) depends partly on incomplete neutralisation. This effect, however, is, in general, small even for very weak bases and acids. It can readily be calculated that when aniline ( $k_b = 4.9 \times 10^{-10}$  at  $25^\circ$ ) is neutralised by hydrochloric acid in molar solution, neutralisation is complete within about  $\frac{1}{2}$  per cent.

The heat of neutralisation is a complicated phenomenon and appears to be influenced by the following factors among others: (1) differences of hydration before and after neutralisation; (2) change in molecular complexity, *e.g.*, hydrofluoric acid; (3) heats of dissociation of the acids and bases concerned; (4) incomplete neutralisation, when the acids or base is *very* weak, or when the reaction takes place in very dilute solution.

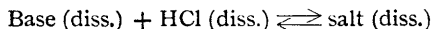
**Mr. F. E. Pollard**, with reference to Dr. Veley's statement that measurements of variations in electrical resistances could not be relied on when the degree of dilution exceeded one part in 20,000, mentioned that he had recently been engaged in experimental work with a new apparatus with which conductivities were determined definitely, in the cases of certain haloid salts and some others, in solutions containing only one part in half a million. It was possible that at no distant date this apparatus might be exhibited at a meeting of the Society.

**Dr. A. C. Cumming** asked the author how he was able to get his water sufficiently pure when working at very extreme dilutions. The practical difficulties on this account must have been considerable.

**Dr. V. H. Veley**, in reply, admitted that the heat values obtained by addition of acids to bases were made up of numerous factors, some of which were, as yet, imperfectly understood. The correction to be applied for hydrolysis to the heat of neutralisation of aniline and hydrochloric acid for the determinations of Luginin and Vignon amounted to 1 per cent. But, however all this might be, it appeared from the very large number of cases examined that the higher the value for heat of

## 28 HYDROLYSIS AND HEATS OF NEUTRALISATION

neutralisation composed of all its factors, the less the hydrolysis value, and conversely. It was true that there were certain exceptions not readily explained by formation of stable hydroxides, &c., such, for example, as pyridine (p. 7), and the speaker had observed that aqueous solutions of its hydrochloride required a long time before final equilibrium set in of the system—



As regards the effect of impurities in the solutions used the method adopted by the author eliminated that of dissolved carbonic acid, which is the main source of error in conductivity determinations, but substances extracted from glass surfaces remained a difficulty, and it was found necessary to accustom or train the glass to the solution to be contained therein. The effect of greasy matters was quite disastrous, and the author reiterated his views expressed elsewhere, that these were mainly due to the slime of certain water bacteria, which distils over with the steam even though the bacteria themselves have been presumably destroyed by the process of boiling.