INCREASE IN STRENGTH OF POTASSIUM HYDROXIDE VOLUMETRIC SOLUTION ON STANDING.

A. H. CLARK, PH. G., CHICAGO, ILL.

During the course of the investigation on the keeping quality of standard volumetric solutions, and reported during the past three years, and also in practice as well, I noted a peculiar thing regarding the keeping of standard potassium hydroxide V. S.

While the facts, as related, may not be new to many of you, I have been unable to find a statement in the literature covering this particular point. On inquiry I have found but one chemist that has noted the same thing as I have regarding this solution. I believe that wider publicity should be given this important matter, and hence this brief note.

Both normal potassium hydroxide V. S. and fiftieth normal *increase* in strength materially on standing, the latter in particular. The data that I have is not complete, as it was some time before I could bring myself to believe that this is true, and some of the records were not preserved. One normal solution which I now have originally had a factor of 1.0235, and now has a factor of 1.0600. This is about two years old. Others have shown about the same increase, but the figures are not available. In the case of N/50 potassium hydroxide solution, the increase is more marked and rapid. I have seen a solution, 10 cc. of which would exactly neutralize two cc. N/10 acid increase in strength, on standing over night, until but 8.5 cc. were required to neutralize 2 cc. N/10 acid.

The explanation offered by the one chemist mentioned above was that the alkalinity of the glass was taken up by the solution. I am unable to offer anything further in the way of explanation than this. The character of glass from which the container is made may have considerable to do with it. The N/50 solutions, on which I noted such an increase, were kept in a 500 cc. volumetric flask, while the normal solutions were kept in a two-gallon amber bottle.

THE SAPONIFICATION OF FIXED OILS WITHOUT HEAT.

G. N. WATSON, LAWRENCE, KANSAS.

While determining the saponification number (Koettstorfer number) of several samples of linseed oil, I found it necessary to leave some of them over night before completing the operation. All of the samples had been treated with N/2 alcoholic KOH. (25 cc.). Some of them had been heated the prescribed half hour, and some had not. While titrating the samples with N/2 HCl the next morning, I titrated a few of the unheated samples before discovering my mistake. Upon redetermining the saponification values of these samples by the usual method, I was surprised to find that the results by both methods checked very closely.

Tests were made on a linseed oil, whose saponification value was known, to

determine whether saponification could be carried to completion within a length of time that would permit of the method being used in the determination of saponification numbers of oils. It was found that saponification began immediately and proceeded very rapidly during the first few minutes; that at the end of one-half hour, 9.8 cc. of N/2 KOH or 70 percent of the amount required for complete saponification (14 cc.) had been consumed; that at the end of two hours, 13.6 cc. or over 97 percent had been consumed in the process of saponification. At the end of five hours, 99.5 percent, and at or before the expiration of sixteen hours, saponification was complete, as was shown by the number of cc. of N/2 KOH used in the process and also by the fact that at the end of twenty, thirty-two and sixty-four hours, respectively, the same number of cc. of N/2 KOH were found to have been consumed.

To illustrate graphically, let the time, expressed in hours represent the ordinates and the number of cc. of N/2 KOH consumed, the abscissas. It will be noted that saponification is very rapid during the first thirty minutes and is nearly completed at the end of five hours, while at the expiration of sixteen hours or less, saponification is complete.*

To test the method still further, other fixed oils were saponified both with and without the application of heat. The results of the investigation are as follows:

Cc. of N/2 KOH Consumed in Saponification of 2 cc. of Oil.

	Hot, ½ Hr.	Cold, 16 Hrs.
Lard Oil	15.64	15.64
Castor Oil	13.22	13.12
Exp. Oil of Almond	13.98	14.04
Oil of Poppy	13.83	13.83
Cocoanut Oil	18.76	18.76
Olive Oil	13.93	13.93
Sesame Oil	13.78	13.73

A period of sixteen hours was allowed for the above saponifications in the cold. It will be noted that practically the same result was obtained by both methods.

A search of the literature on the subject of saponification in the cold developed the fact that Henriques (Annual Report, Connecticut Agr. Exp. Station, 1892, p. 30), worked out a process for the saponification in the cold of fats. His method is based upon the solution of the fat in petroleum ether, in which condition it is easily attacked by the alcoholic alkali. With those fats, which give easily volatile ethers it was found that the results by the cold process were somewhat higher than those by the hot process, due no doubt to the fact that the volatile ethers were driven off during the process of heating.

Where but a few determinations are to be made and the results are wanted at the earliest possible moment, the usual method of saponification by heat must necessarily be employed. However, when a large number of determinations are to be made and especially when the facilitites for heating are limited, much time can be economized by letting the samples, after treating with alcoholic alkali, stand over night. The above results indicate that the operator may rest assured of the proper saponification values.

UNIVERSITY OF KANSAS.

*The drawing furnished with this paper could not be reproduced.—EDITOR.