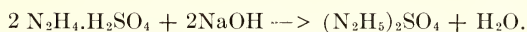


POTENTIOMETRIC TITRATIONS WITH HYDRAZINE SULFATE.

M. G. MELLON AND V. N. MORRIS*, Purdue University.

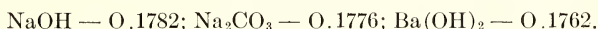
Hydrazine sulfate is readily recrystallized from water, and serves, after drying at 140°, as a primary standard¹ for checking solutions to be used in titrations involving neutralization reactions. With the use of sodium hydroxide, the reaction involved may be represented by the equation—



To show the completion of this reaction one may use either methyl red¹ or methyl orange² as the indicator.

Attention has been called previously³ to the fact that potentiometric titration curves furnish valuable information regarding the course of such reactions, and aid one in selecting a suitable indicator for titrations. The object of the present work was to determine such curves for the titration of hydrazine sulfate with certain basic solutions.

Materials and Apparatus—Commercial hydrazine sulfate recrystallized three times from conductivity water gave a snow-white appearing material, which, when dried, was used in making a fifth normal solution. Using fifth normal hydrochloric acid as a standard, the basic solutions showed the following normalities with methyl orange as the indicator:



The apparatus employed for following the change in hydrogen ion concentration during the course of the reactions was the usual potentiometric arrangement of Poggendorff. Although the compressed hydrogen used was passed through a washing train including the ammoniacal copper solution recommended by Badger,⁴ difficulties were encountered, due, presumably, to a slow poisoning of the electrode. Accordingly, its surface was replantized before each determination. The temperature was approximately 24°.

Experimental Data and Conclusions—*Titration Curves.* 25 ml. portions of the solution of hydrazine sulfate, diluted with a small amount of water, were titrated with the three bases, sodium and barium hydroxides, and sodium carbonate. The results obtained are shown in figure 1 in the form of the usual type of curves for such work, plotting pH values as ordinates and volume of titrating solution as abscissas.

It should be kept in mind that the three basic solutions were not exactly of the same concentration, although appearing so from the curves.

* Experimental work performed by V. N. Morris at University of Minnesota.

¹ Kolthoff—J. Am. Chem. Soc. 46, 2009 (1924).

² Stollé—J. prakt. Chem. [2] 66, 332 (1902).

³ Mellon and Morris—Ind. Eng. Chem., 16, 123 (1924).

⁴ Ind. Eng. Chem., 12, 161 (1920).

The calculated amounts for neutralizing 25ml. of N/5 hydrazine sulfate are:

NaOH - 28.06; Na_2CO_3 - 28.15; and $\text{Ba}(\text{OH})_2$ - 28.37.

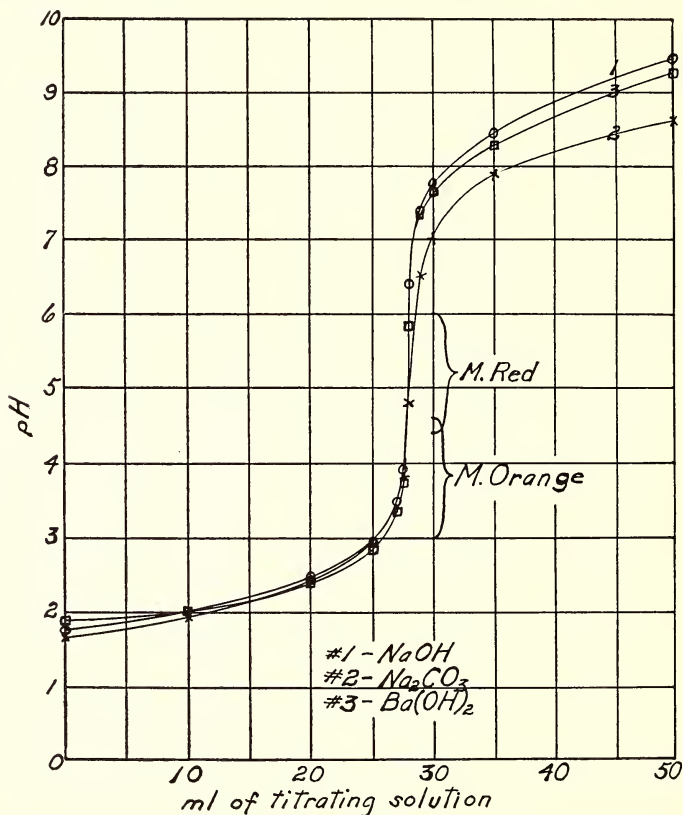


Fig. 1—pH curves showing the course of neutralization in titrating hydrazine sulfate with sodium hydroxide, barium hydroxide, and sodium carbonate.

An inspection of the results obtained indicates, so far as such curves can show, that hydrazine sulfate should be satisfactory for checking either of the two hydroxides titrated, and may be used for the carbonate, providing methyl orange is used as the indicator. This work corroborates the report of Gilbert⁵ for the titration of hydrazine sulfate with sodium hydroxide. With a pH range of 4.4 to 6.0 methyl red should be available for sodium or barium hydroxides, but not for sodium carbonate. In checking this conclusion ordinary titrations were found to be very satisfactory for the two hydroxides, but the end point was not sharp in titrating sodium carbonate in the presence of methyl red.

No particular difficulty was encountered when using the latter indicator during the titration of barium hydroxide, even though barium sulfate was precipitated.

⁵ J. Am. Chem. Soc. 46, 2648 (1924).

Stability of Hydrazine Sulfate. In order to obtain information regarding the stability of a solution of hydrazine sulfate, it was compared with hydrochloric acid after standing about six months. Both of the acidic solutions were titrated with the three basic solutions, using methyl orange as the indicator; closely agreeing results indicated no appreciable change in concentration in the solution of hydrazine sulfate over this period of time.