ON PHENOLPHTHALEIN AND METHYLORANGE AS INDICATORS.

BY MARY BIDWELL BREED.

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In using phenolphthalein as an indicator in alkalimetry, there are certain precautions necessary that have not been sufficiently insisted upon in the literature of the subject. The following experience, however, will show the necessity for great care in its use.

During the standardization of a hydrochloric acid solution against normal caustic potash, phenolphthalein and methylorange were both used as indicators; and it was observed that, while with methylorange 20 cc. of the acid required only an average of 19.443 cc. of the alkali for neutralization, with phenolphthalein the same amount of acid required an average of 19.765 cc. of alkali, a difference which would introduce a considerable error. The same results were obtained with phenolphthalein, even when the solution was heated to boiling, and so it was believed that carbon dioxide could not be the cause of the discrepancy. That the source of the difficulty lay with the phenolphthalein, and not with the methylorange, seemed probable from the fact that it took more alkali to bring the color of phenolphthalein than to discharge that of methylorange; and also from the fact that, while the amounts of alkali used with the former varied from 19.65 cc. to 19.8 cc., those used with the latter were practically constant, differing only by 0.025 cc. Nothing could be found in the literature of the subject that threw any light on the problem. Fresh solutions, prepared with great care, gave analogous results, and after many fruitless attempts to explain the discrepancy, it was concluded that traces of carbon dioxide, dissolved by the alkali, must after all be the source of error. This would explain matters; for acid potassium carbonate, which would be formed in the solution during titration, is neutral to

phenolphthalein, but alkaline to methylorange; and, therefore, as part of the alkali had been rendered neutral to phenolphthalein, it would take more of the solution to affect that indicator than to affect methylorange. This explanation was proved to be correct by prolonged, hard boiling of the solution, when using phenolphthalein. Alkali was titrated with acid, in this case, and it was found that, by boiling ten minutes or so after the end point had been apparently reached, the color could be made to reappear, and that it continued to reappear after each addition of acid until the amount of acid used was exactly equal to that used with methylorange. As the end point was approached, longer and longer periods of boiling were necessary after each drop added. A single titration never took less than an hour.

In view of this, a word of caution seems necessary. It is never safe to use phenolphthalein unless the solution is known to be absolutely free from carbon dioxide, or unless it is boiled long and thoroughly after the end point is apparently reached. As it is nearly impossible to keep a solution of caustic alkali entirely free from carbon dioxide, a titration with phenolphthalein is often as tedious as a gravimetric determination.

Phenolphthalein is probably used at present more extensively than any other indicator, but these objections make it desirable to adopt something more reliable and convenient. Methylorange is not affected by carbon dioxide, and when a sufficiently dilute solution is used, its end point is sharp. It has been found very satisfactory for sensitiveness and accuracy, and it is therefore strongly recommended wherever it is possible to use it.

CHEMICAL LABORATORY,

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DISCUSSION.

MR. HAINES suggested that the glass beaker may have been attacked by the boiling alkaline solution, resulting in extraction of alkali from the glass, especially if the boiling was continued as long as an hour. Such action has been

observed even with Bohemian glass. The glass is stated to be generally attacked as a whole. As regards phenolphthalein and methylorange he wished to call attention to the statement by R. T. Thomson, in his comprehensive papers on indicators (*Chemical News*, **47**, 123, 184, and **44**, 32, 38, 119), that phenolphthalein has five times greater delicacy or sensitiveness than methylorange. In other words, in 100 cc. of distilled water, the former requires but 0.1 cc. of excess of deci-normal solution, while the latter requires 0.5 cc. of excess to produce the full change of color. In solutions of normal strength the difference is scarcely noticeable. He showed that this difference was not due to carbonic acid, but to the interference of neutral salts of sodium potassium, and ammonium formed during titration, which affect the delicacy of methylorange, but not phenolphthalein, except in the case of salts of ammonia. Neutral salts of calcium, barium and magnesium have the same effect upon methylorange. Mr. Haines said that in recently making some determinations, requiring the use of both of these indicators, he had found the above statement as to this difference to be correct. A fresh standard solution of sodium hydrate, made from metallic sodium and carefully protected, gave practically the same results as an old solution of ordinary sodium hydrate in white sticks. In determining alumina volumetrically in sodium aluminate by the method described by Lunge (*Jour. Soc. Chem. Industry*, 1891, p. 314), in which both indicators are used and the amount of alumina is calculated from the difference of results of titration, Mr. Haines obtained results which agreed very closely with gravimetric estimations in the same solutions if the above correction for difference in delicacy of indicators was applied. Generally, methylorange is used only in a cold solution, but Lunge has shown that in estimating alumina volumetrically with methylorange, the solution should be heated to 30° to 40° C., but not exceeding the latter temperature. The action in the cold solution is too slow and the alumina is apt to be underestimated. Only dilute solutions of alumina should be used.

Phenacetolin also is a more delicate indicator than

methyloange, being similar in this respect to phenolphthalein. In estimating calcium, magnesium and sodium carbonates, as in Hehner's method of determining hardness of waters, Mr. Haines has found, as others have also, that phenacetolin is preferable to methyloange, but in this case the former must be used hot, the latter cold. He finds that the alcoholic solution of phenacetolin keeps very much better if it is not filtered from the insoluble residue found in the article as sold.

Mr. Haines has also experienced some difficulty in obtaining the true methyloange (helianthin). Sutton incorrectly describes it as of a bright orange-red color; Allen states it is orange-yellow. An article of bright orange-red color sold in this country as methyloange gave the *reverse* of the correct colors with acids and alkalies and was so wanting in delicacy as to be practically worthless.

The article recently obtained from Bullock & Crenshaw, which agrees nearly with Allen's description, he had found to be perfectly satisfactory.

MR. HENRY PEMBERTON, Jr., remarked that in titrating with phenolphthalein and with methyloange as indicators, different results would be obtained if the standard alkali contained alumina. This impurity is not infrequently present in sodium or potassium hydrate. Even a small amount of alumina [*about* 0.002 grams] will require when methyloange is used 1 cc. of $\frac{N}{10}$ acid more than when phenolphthalein is used.

In regard to titrations with phenolphthalein in the presence of ammonium salts, J. H. Long has shown* that correct results are obtained when the solution is kept cold, and a sufficient quantity of the indicator is employed.

PROF. E. S. KEISER, in reply to Mr. Haines, said that while according to R. T. Thomson, methyloange was not as sensitive as phenolphthalein, other observers had found it to be more sensitive. For example, J. Wieland (*Berichte d. Deutschen Chem. Gesell.*, **16**, 1989), found that from three to four times as much of a $\frac{1}{100}$ normal solution was required

* *American Chemical Journal*, **11**, 84.

to bring about the change of color with phenolphthalein as with methylorange. That is the phenolphthalein is less sensitive than the methylorange. Experiments made in the speaker's laboratory indicated that methylorange when used in the proper dilution was fully as sensitive as phenolphthalein. The great objection, however, to the use of phenolphthalein in ordinary titrations is its sensitiveness to carbon dioxide, and that it is neutral to acid carbonates. For example, R. B. Warder (*American Chem. Journal*, **3**, 55) has shown that alkaline solutions of this indicator can be decolorized by shaking them with air, and that by simply breathing upon the red liquid the color is discharged. The phenolphthalein is not colored by acid carbonates. Mr. Haines would find in the paper by R. T. Thomson, to which he refers, that that author distinctly states that when alkaline hydroxides containing alkaline carbonates are titrated and phenolphthalein is used as indicator, the color disappears when the hydroxide is neutralized and the carbonate changed to acid carbonate. That if the solution is then boiled the color reappears because the acid carbonate is decomposed, and more acid must be added and the titration continued until the color no longer appears in the boiling solution.

As it is almost impossible to prevent standard alkali solutions from absorbing carbon dioxide from the air, it is evident that the strength of such solutions will constantly change if the determinations are made with phenolphthalein as the indicator. On the other hand, if the titrations are made with methylorange as the indicator the results are in no way influenced by the amount of carbon dioxide that has been absorbed. Hence, in all ordinary work it is advisable to use methylorange.