

THE USE OF METALLIC ELECTRODES AS INDICATORS

SIDNEY J. FRENCH and JOHN M. HAMILTON, Franklin College

The potential difference between a metal and a solution depends not only upon the metal but also upon the solution in which it is immersed. Such potential differences can be readily measured by means of a potentiometer if the metal and its solution is made one element of a cell, the other being any one of a number of stable or non-fluctuating reference electrodes. The electrode commonly used for reference is the calomel cell. If such a combination is used and the concentration of the solution about the metal electrode is gradually changed, a change in the e.m.f. or the combination is noted. Since no change has taken place in the reference electrode, the change measured by means of a potentiometer galvanometer set must be due to a change in the potential difference between the metal and its solution.

If the metal dips in an acid solution and alkali is gradually added, little change is generally noted till the solution is almost neutral. Near the point of neutrality a sharp change is often noted. Metals which do show sharp changes can be used as indicators in determining the end point of an acid-base titration. Conversely, if the metal shows a definite but not too sharp change near the end point it can be used to determine the pH of the solution for the potential difference developed between the metal and its solution is a function of the pH of the solution.

A number of investigators have studied various metals and have shown their suitability for such uses. The so-called hydrogen electrode, the quinhydrone electrode, and others are often used for determining the pH of solutions and may be used as indicator electrodes in titrations. The antimony electrode has been studied by Kolthoff and Hartong¹. It is a suitable indicator electrode.

Recently, a number of studies have been made of other metals which might be used as indicator electrodes. Closs and Kahlenberg² have shown that a number of metals show sufficient change in potential developed at the end point of a titration to warrant their use as indicator electrodes. Tungsten, molybdenum, arsenic, antimony, bismuth, aluminum and tin showed great differences of potential in 0.1 N acids and 0.1 N NaOH. Studies have also been made using two different electrode metals dipping in the same solution in place of the metal-solution reference electrode combination. In such a case both metals may change their potential difference to the solution at the end point of a titration. Holt and Kahlenberg³ have recently made a thorough study of such combinations. By selecting a combination, one member of which shows a considerable change and the other little or no change, a suitable indicator combination can be obtained. They have found that tungsten and graphite give an excellent indication of the end point. The latter shows practically no change of potential at the end point. It therefore behaves as a reference electrode.

Proc. Ind. Acad. Sci. 40: 171-174. (1930) 1931.

¹Kolthoff and Hartung, Rec. Trav. Chim., 44, 113, 1925.

²Closs and Kahlenberg, The Use of Simple Metallic Electrodes in the Potentiometric Titration of Acids and Bases., trans. Am. Electrochem. Soc., 56, 201, 1929.

³Holt and Kahlenberg, Couples in the Titration of Acids and Bases, presented at the 57th meeting of the Am. Electrochem. Soc., May, 1930.

As a general rule, the potential developed by metals is more negative or zinc-like in alkaline solution than in acid. Therefore, the break at the end point is in the direction of a greater negative potential difference. A few of the very active metals such as magnesium and zinc which are acted on by the acid solution show breaks in the reverse direction. Aluminum, however, is not acted upon by dilute acids but is acted on by dilute strong alkalies, hydrogen being evolved. This metal shows a very decided break toward a more negative potential at the end point. Cobalt and nickel show small changes in a more positive direction while lead shows little or no change. Most of the less active metals show changes toward a more negative potential at the end point though the change is small in some cases. Graphite, silver and mercury show but small changes.

Aluminum, because of its decided change at the end point of a titration is a good indicator electrode. This metal electrode was dipped in the acid solution of 0.1 N HCl, 10 cc. of which were diluted with 50 cc. of distilled water. 0.1 N NaOH was added from a burette. The accuracy of the end point was checked by separate titration using phenolphthalein as the indicator. The latter cannot be used as a check in the same solution in which the potentiometric titration is conducted for it was found that the color indicator changed color before the end point was reached while the break in potential was retarded beyond the end point. This effect is probably due to the alcohol present. Aluminum is, of course, acted on by strong alkalies and hydrogen is liberated. However, no visible evolution of hydrogen is seen at the end point. The fact that the metal is attacked by alkali need have no effect on the accuracy of the titration if the metal electrode dips in the acid solution and the latter is neutralized by adding the alkali from a burette.

The chief objection to the use of aluminum as an indicator electrode is that the change of potential at the end point while decided and considerable, is slow. Several minutes are often required for the electrode to come to a constant potential. Furthermore the change is not as sharp as might be desired. 0.2 cc. of alkali at the end point produce a change of from 0.4 to 0.5 volts in the potentiometer reading. Aluminum may, therefore, be considered as not entirely suitable as an indicator electrode. However, it compares favorably with the hydrogen electrode and the quinhydrone electrode for use in titrations and gives a greater change of potential than either of these at the end point.

Among other metals used in an attempt to find a suitable indicator was an alloy of bismuth, lead and tin known as Rose alloy. Peculiarly enough, this alloy when used with a calomel electrode shows a change near the end point of 0.2 to 0.3 volts in a *more positive direction*. This is unusual since each of the metals composing the alloy when measured separately against a calomel electrode show changes in a more negative direction. Lead, however shows little or no change. This alloy can be used as a suitable indicator electrode in conjunction with a calomel or other reference electrode. However, if it could be used with another metal electrode which shows a change in a more negative direction at the end point a very great change in potential should result. It is necessary however, to use a metal which in acid develops a greater negative potential than the alloy electrode, otherwise the changes of potential of each at the end point would tend to offset one another rather than accentuate the total change. Therefore, the non-active metals cannot be used.

Aluminum was tried as the other electrode of the pair with very satisfactory results. This pair gives a total change in e.m.f. at the end point of from 0.7 to 0.8

volts. The pair has several other distinct advantages. A very definite and decided warning of the approaching end point is given. At a point about $\frac{1}{2}$ cc. before the end point is reached when one drop is sufficient to produce a change of 0.6 to 0.7 volts in the reading. The exact end point is unmistakable. The new potential becomes constant much more rapidly than when aluminum is used with a calomel cell. Furthermore, it is not necessary to wait for a constant potential to be established for the sharp and decided change taking place on the addition of the last drop is sufficient indication of the end point.

Since aluminum is attacked by fairly concentrated strong acids some question might be raised as to the accuracy of titrations using this metal as an indicator electrode. The accuracy was therefore tested out.

3 N. solutions of HCl, H_2SO_4 and HNO_3 were used. 10 cc. of each solution was diluted with 50 cc. of distilled water and titrated at once using the aluminum/alloy pair as an indicator of the end point. Three titrations were carried out with each acid and were checked with three titrations using phenolphthalein indicator. No differences could be discovered. However, using HNO_3 a slight cloudiness was noted in the solution just before the end point was reached. Nevertheless, the results obtained were identical with those obtained using the color indicator.

Next, 10 cc. of each of the 3N. acid solutions were diluted with 50 cc. of distilled water and the electrodes were allowed to stand in this solution for 45 minutes before the titration was started. In the case of HCl, bubbles of gas were noted on the aluminum electrode after about seven minutes of standing. The titration in this case showed an error of 0.05 cc.

End point with phenolphthalein—10.45.

End point with Al/alloy indicator—10.40.

With H_2SO_4 no difference could be discovered. The potentiometric and colorimetric methods gave identical results even when the electrodes had been immersed in the acid solution for 45 minutes. With HNO_3 a considerable error was obtained. In this case, the *alloy* was attacked by the acid. The average end point with phenolphthalein was 12.25 and that with the metal electrodes (after standing) was 12.10. However, as was stated before no error was obtained when the titration was carried out at once. When HNO_3 is diluted with sufficient distilled water so that the resulting solution is not more than 0.2 N. no error can be discovered in the titration even after the electrodes have been immersed in the solution for 45 minutes. The only precaution necessary, therefore, in using these electrodes with HNO_3 is to provide for sufficient dilution of the acid with water.

No detailed study has yet been made of the suitability of these electrodes for indicating the end point of ammonia titrations or titrations involving organic bases. The few observations made thus far seem to indicate that they are not good indicators in such cases. The change of potential is gradual and the break at the end point is small. Likewise, no detailed study has yet been made using these metals with weak acids. The few observations noted suggest that the electrodes show the correct end point and a considerable break in potential when weak acids are titrated with strong alkalis. This phase of the problem will be studied further.

The electrodes used were easily prepared. The aluminum was cut from a sheet of commercial aluminum, and was shaped in the form of a paddle. The stem

was tightly united to a copper wire. A glass tube sleeve was slipped down over the joint and was completely filled with a mixture of beeswax and rosin. The Rose alloy can be melted in hot water and shaped in a mold. A copper wire can be sealed into the upper portion of the cooling alloy. All electrodes were carefully sanded and washed in distilled water just before using. In all titrations the solution was stirred using a motor driven glass stirring rod.