CHEM 334 Quantitative Analysis Laboratory

Determination of an Acid by Titration & Potentiometry

Introduction

Titrations can be performed using a wide variety of reagents, typically called titrants, and with a wide range of indicators and methods to determine the end point. In this experiment, the titration is followed by repeated measurement of the pH of the analyte as the titrant is dispensed. The pH profile is then analyzed to provide several key quantities of the analyte. Much more information is available when the entire pH profile is recorded as compared to the single-point measurement of an end point. For example, the true equivalence point is accessible. This method can be generalized and applied to other types of titrations, for example, reduction-oxidation titrations.

Procedures

Preparation of Sodium Hydroxide Titrant: Prepare 500 mL of a 0.1 M sodium hydroxide solution by dilution of a 1 M sodium hydroxide stock reagent or from solid NaOH. This dilution need only be performed to 5% accuracy, that is, using a graduated cylinder and an Erlenmeyer flask. Store the diluted solution in a polyethylene bottle. Standardize the diluted solution against dry, solid KHP (potassium hydrogen phthalate) using phenolphthalein as an indicator and label the bottle with the concentration of sodium hydroxide together with the accuracy (as represented by the 95% confidence limit). (The student should be able to explain why this limited accuracy is sufficient for the dilution and why it is **not** desirable to perform the dilution operation with higher accuracy.)

pH Meter Operation: The modern pH meter used in this experiment is controlled by an internal microprocessor running a widely recognized operating system using a solid-state hard disk. It has several different connectors capable of interfacing to a variety of electrochemical sensors. It also features several other different connectors for connection to computer interfaces. It is capable of operating in a number of different data acquisition modes. For this experiment, it will be placed in the simplest of services: continuous measurement and display of pH value of the solution into which the probe is immersed. A short demonstration will provide the student with the necessary details on the meter's proper operation.

pH Meter Probe Storage: The active tip of the probe must be kept in an aqueous solution at all times with only limited exposure to the atmosphere being permissible. Of course it is necessary to expose the

Figure 1. pH combination probe suspended in electrode arm with storage vial covering the active tip.

active tip to the atmosphere when moving the probe from one solution to another and this exposure is not harmful to the probe so long as it is limited to a few minutes at a time. For longer intervals, the probe must be placed in its customary storage solution (a pH 4.0 buffer not water) contained inside a small vial with a cap equipped with an O-ring clamp (Figure 1).

pH Meter Probe Rinsing and Use: When transferring the probe from one solution to another it is necessary to clean the active tip of the probe to prevent transfer of the former solution to the latter solution. However, the procedure for cleaning the probe is specific and important to the probe's proper operation. The rinsing procedure follows: (1) suspend the probe above a waste beaker. (2) Rinse the probe with distilled deionized water from the middle of the probe's shank (definition: the straight, narrow, shaft like part of various objects connecting two more important or complex parts, as the stem of a pipe) down to the active tip. (3) Wipe the probe's shank using a soft tissue in a single stroke from the middle down to the active tip. (4) Wick away any remaining solution from the active tip by gently patting (*not wiping*) the bottom of the active tip. Do not touch the actual active tip components.

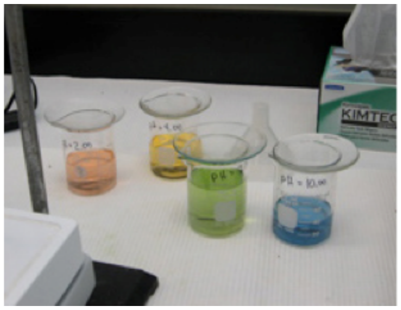

Figure 2. Standard buffer solutions used for calibration of the pH meter. Color-coded acid-base indicators are added in the solutions to provide convenient visual identification of the solutions.

pH Meter Standardization: The pH meter and probe require periodic calibration or standardization to ensure conformance to the manufacturer's published specifications. This operation is performed daily and consists of the sequential immersion of the probe into several different buffer solutions, typically with pH values of 4.0, 7.0 and 10.0 and recording the measured values into the meter. The meter then computes correction data and applies this data into its subsequent measurements. This operation is performed at the beginning of each laboratory session by teaching staff (Figure 2).

Titration Measurement: Set up a stand holding a 25 mL burette and fill it with the standardized sodium hydroxide titrant using standard procedures. Add a magnetic stirrer, a 150 mL beaker, a small magnetic stir bar and a pH meter to the layout as shown in Figure 3. Add the analyte to the beaker and fill with distilled deionized water to the 50 mL mark (the exact amount of water is not critical, why?). Adjust the spinning speed fast enough so that a small vortex is formed but slow enough that no splashing occurs. Insert the probe below the surface of the solution into the edge of the beaker so that it does not interfere with the stir bar and *vice versa*. Record the pH at this time and after repeated addition of 0.5 to 1.0 mL of titrant continuing until a total of 25 mL of titrant has been added. Wait for the pH to stabilize between each addition as indicated by an unchanging measurement value on the meter and the appearance of the word "stable" on the display.

After completing a set of measurements on a particular analyte, remove the probe from the beaker and rinse it off with distilled deionized water (put it in the storage vial if it will

Figure 3. Measurement setup including beaker, pH probe in electrode arm, magnetic stir plate and bar and burette.

not be used for more than five minutes). If another titration is to be performed then refill the burette and clean the beaker.

Analytes: Perform a complete titration on each of several different samples: (1) a sample of approximately 0.35 g of unknown concentration KHP (weigh precisely), (2) 0.5 mL of ~1.0 M phosphoric acid and last (3) a blank using distilled deionized water. It is not necessary to carry out replicate samples. (Why?)

Results

Report the results of the standardization of the sodium hydroxide titrant including the suitable error analysis. It is not necessary (nor appropriate) to describe the entire standardization process as it has been documented previously.

Plot the pH of each of the titrated solutions (the blank, the KHP sample and the phosphate acid sample) as a function of added titrant on the same axes and on the same figure. Compute the first and second derivatives (see Harris, section 11-5, p 210) and determine all equivalence points for all samples. Plot the derivatives for the unknown KHP sample on a second figure. Clearly show how interpolation was used in determining each equivalence point.

Report the concentration of the KHP sample in % (by weight). Include a suitable uncertainty analysis.

Report the exact concentration of ~1 M phosphoric acid solution. Include a suitable uncertainty analysis.

Discussion

In addition to a customary discussion of the results presented in this Report compare and contrast the colorimetric determination of a titration equivalence point using an acid-base indicator versus electrochemical determination of a titration equivalence point using a pH meter. In addition, discuss why it is not necessary and even *not* desirable to perform the preparation of 1 M sodium hydroxide operation with higher accuracy. Also, discuss the considerations in the choice of the total volume of the analyte solution used in the titration.

References

Harris, D.C., "Quantitative Chemical Analysis" (2007) 7th edition, Freeman & Co., NY, Chapter 11, especially sections 11-5, 11-6, 11-7 and 11-8.