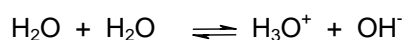## EXPERIMENT 2

pH MEASUREMENT

Objective : To determine the *ionization constant* of various acids.

1   Theory

Water can undergo self-ionization or auto-ionization in which two molecules of water react with each other to form ions in the following manner:

$$H_2O \ + \ H_2O \ \rightleftharpoons \ H_3O^+ \ + \ OH^-$$

This is a very important equilibrium because it is present not only in pure water but also in all aqueous solution. The degree of ionization of water can be characterized by an **equilibrium constant,** K, given by

$$K = \frac{[H_3O^+][OH]}{[H_2O][H_2O]}$$

The molar concentration of water, which appears in the denominator of this expression, is very nearly constant ($\approx$ 55.6 M) in both pure water and dilute aqueous solutions. Therefore, $[H_2O]^2$ can be included with the equilibrium constant K to produce a new combined constant, K_w

$$K_w \ = \ [\,H_3O^+\,] \ [OH^-\,]$$

where K_w is called the **ion product constant** for water, or the **ionization/dissociation constant** of water. This means that the product of the concentration of H_3O^+ and the OH^- ions in any aqueous solutions is a constant. In fact, the value of K_w depends only on temperature. At 25 °C, $K_w = 1.0 \times 10^{-14}$.

A solution is said to be:-

> **neutral** if $[\,H_3O^+\,] = [\,OH^-\,] = 10^{-7}$
> **acidic** if $[\,H_3O^+\,] \ > \ 10^{-7}$
> **basic** if $[\,H_3O^+\,] \ < \ 10^{-7}$

The pH Concept

H_3O^+ and OH^- ions enter into many equilibra in addition to the dissociation of water, so it is frequently necessary to specify their concentrations in aqueous solutions. These concentrations may range from relatively high values to very small ones (for example, from 10 M to 10^{-14} M), and a logarithmic notation has been devised to simplify the expression of these quantities. In general, for some quantity X, the quantity pX is defined as

$$pX \ = \ \log_{10} \frac{1}{X} \ = \ - \ \log_{10} X$$

Thus, the value of the concentration of H_3O^+ ion in a solution can be expressed in terms of its **pH** which is defined as

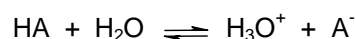$$pH \ = \ \log_{10} \frac{1}{[H_3O^+]} \ = \ - \log_{10} [\,H_3O^+\,]$$

Hence, for a solution with $[\,H_3O^+\,] = 10^{-4}$ M, the pH of the solution is said to be 4. Following the same approach for the hydroxide ion concentration, we can defined the pOH of a solution as

$$pOH \ = \ - \log_{10} [\,OH^-\,]$$

_____

Ionization Constant of Weak Acids

The following is the **ionization** which occurs in an aqueous solution containing a weak acid HA:

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

The equilibrium constant or the **ionization constant**, K_a, for the weak acid HA is

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

In this expression we have again neglected the molar concentration of water which is assumed to be constant. Because the values of K_a cover a wide range, it is more appropriate to substitute K_a with **pK_a** which is defined as

$$pK_a = -\log_{10} K_a$$

Ionization Constant of Weak Bases

The ionization which occurs in an aqueous solution of a weak base B is

$$B + H_2O \rightleftharpoons BH^+ + OH^-$$
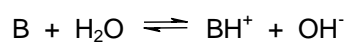
and the ionization constant, K_b given by

$$K_b = \frac{[BH^+][OH^-]}{[B]}$$

and

$$pK_b = -\log_{10} K_b$$

It can be shown that for any acid-base conjugate pair,

$$K_a K_b = K_w$$

pH Meter

A pH meter consists of a pair of electrodes; one sensitive to the H_3O^+ concentration, usually a glass electrode, and the other a reference electrode such as the calomel electrode. The manual for the pH meter gives a full description on its usage and also contains other useful information. Users are required to read this manual carefully before proceeding to use this instrument. The pH meter MUST be **calibrated** using standard buffer solutions before it can be used to measure the pH of any solutions.

2   Materials

Two standard buffer solutions, phenolphthalein indicator, 0.1 M acetic acid solution, propanoic acid, chloroacetic acid, dichloroacetic acid, trichloroacetic acid, and sodium hydroxide.

3   Experimental Procedure

1. Prepare *50% neutralized acid solutions* for each of the given acids in the following manner:

      (i)   Titrate 25 ml of the given acid with 0.1 M sodium hydroxide solution using phenolphthalein as indicator.

      (ii)   Pipette another 25 ml of the same acid into the solution which has been neutralized in (i).

      (Steps (i) and (ii) must be carried our carefully to ensure the success of this experiment.)

2. Calibrate the pH meter using the two standard buffer solutions with pH values of 4.0 and 7.0 (The calibration only needs to be carried out only once.)

3. Measure the pH of the 50% neutralized acid solution prepared in Step 1.

4. Record the temperature of the solution.

5. Repeat Step 1 to Step 4 (except Step 2) for all the acid solutions to be studied in this experiment.

4   References

1. Mattock, George, (1961). *pH measurement and titration.* Heywood.
2. McMillan, Gregory K., (1994). *pH measurement and control.* Instrument Society of America.

nb: Please quote experimental error estimates for all your data presented.

Plagiarism Warning!

Some of these experiments are carried out in groups of usually a pair of students. Therefore expectedly, each member of a group followed an identical procedure in the laboratory and has the same set of raw data. Members of a group are allowed to discuss the analysis of data with one another. However, preparation of the report including data analysis, interpretation and discussion must be prepared by the individual student submitting the report.
The Department does not tolerate plagiarized report!