Quadrant II – Transcript and Related Materials

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Unit: Unit 3 Electrochemistry II

Module Name: Buffer action and mechanism of buffer action

Module No: 3

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Notes

- **Introduction:**

For many purposes in chemistry, it is necessary to have solutions whose pH does not change much even on the addition of appreciable amounts of strong acids or strong alkalis. Such solutions are called **buffer solutions**.

A buffer solution is one which maintains its pH fairly constant even upon the addition of small amount of acid or base.

Two common types of buffer solutions are:

1. a weak acid together with a salt of the same acid with a strong base. These are called **Acid buffers**. For example, CH_3COOH/CH_3COONa, where the salt is formed from acetic acid and a strong base, i.e., sodium hydroxide (NaOH).
2. a weak base and its salt with a strong acid. These are called **Basic buffers**. For example, NH_4OH/NH_4Cl, where the salt is formed from ammonium hydroxide and a strong acid, i.e., hydrochloric acid (HCl).

- **Buffer Action:**

✓ Buffer action can be illustrated by taking example of a common buffer system consisting of solution of acetic acid and sodium acetate (CH_3COOH/CH_3COONa).

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+ \qquad (1)$$

$$CH_3COONa \longrightarrow CH_3COO^- + Na^+ \qquad (2)$$

✓ The ionization of acetic acid and sodium acetate takes place according the equations 1 and 2 respectively. Since the salt, i.e., sodium acetate is completely ionized, it provides the common ions CH_3COO^- in excess. The common ion effect supresses the ionization of acetic acid. This reduces the concentration of H^+ ions which means that the pH of the solution is raised.

✓ Thus, a 0.1 M acetic acid solution has a pH of 2.87 but a solution of 0.1 M acetic acid and 0.1 M sodium acetate has a pH of 4.74. Thus, 4.74 is the pH of the buffer.

✓ On addition of 0.01 mole NaOH, the pH changes from 4.74 to 4.83, while on the addition of 0.01 mole HCl, the pH changes from 4.74 to 4.66. Obviously, the buffer solution maintains fairly constant pH.

- **Mechanism of buffer action of an acidic buffer:**

The pH of the acidic buffer containing acetic acid and sodium acetate is governed by the following equilibrium.

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$

The buffer solution has a large excess of CH_3COO^- ions produced by the complete ionization of sodium acetate.

$$CH_3COONa \longrightarrow CH_3COO^- + Na^+$$

1) Addition of HCl:

Upon the addition of HCl, the increase of H^+ ions is counteracted by association with the excess of acetate ions to form unionized acetic acid. Thus, the added H^+ ions are neutralized and the pH of the buffer solution remains virtually unchanged.

$$CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$$

$$CH_3COONa \longrightarrow CH_3COO^- + Na^+$$

$$CH_3COO^- + H^+ \longrightarrow CH_3COOH$$

However, owing to the increased concentration of CH_3COOH, the equilibrium shifts slightly to the right to increase H^+ ions. This explains the marginal increase of pH of the buffer solution on addition of HCl.

2) Addition of NaOH:

When NaOH is added to the buffer solution, the additional OH^- ions combine with H^+ ions of the buffer to form water molecules. As a result, the equilibrium shifts to the right to produce more and more H+ ions till practically all the excess OH^- ions are neutralized and the original buffer pH is restored.

$$OH^- \longrightarrow H_2O$$

$$CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$$

$$CH_3COONa \longrightarrow CH_3COO^- + Na^+$$

However, a new equilibrium system is set up in which, acetic acid concentration is lower than it was in the original buffer. Consequently H^+ concentration is also slightly less and pH is slightly higher than the buffer pH value.

- **<u>Mechanism of buffer action of a basic buffer:</u>**

Operation of a basic buffer such as NH_4OH/NH_4Cl can also be explained on the same lines as of an acid buffer.

Upon addition of HCl, the H^+ ions combine with OH^- ions of the buffer to form water molecules. The equilibrium,

$$NH_4OH \rightleftharpoons NH_4^+ + OH^-$$

is shifted to the right till all the additional H^+ ions are neutralized and the original buffer pH restored.

When NaOH is added to the buffer solution, OH^- ions associate with excess of NH_4^+ ions to form unassociated NH_4OH. Thus, the pH of the buffer is maintained approximately constant.