Analytical Chemistry

Lecture 5

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BUFFER SOLUTIONS

Buffer solutions

Definition **"Solutions which resist changes in pH when small quantities of acid or alkali are added."**

a solution that contains a weak acid/conjugate base mixture or a weak base/conjugate acid mixture

- **able to neutralize acids and bases without allowing the pH of the solution to change greatly**

Acidic Buffer (pH < 7) made from a weak acid (ethanoic acid) + its sodium or potassium salt (sodium ethanoate)

Alkaline Buffer (pH > 7) made from a weak base (ammonia) + its chloride salt (ammonium chloride)

Uses

- **Standardising pH meters**
- **Buffering biological systems (eg in blood)**
- **Maintaining the pH of shampoos**

Buffers and the Common-ion Effect

A buffer works through the ***common-ion effect***.

Acetic acid in water dissociates slightly to produce some acetate ion:

$$CH_3COOH(aq) + H_2O(l) \rightleftharpoons CH_3COO^-(aq) + H_3O^+(aq)$$

acetic acid — acetate ion

If CH_3COONa is added, it provides a source of CH_3COO^- ion, and the equilibrium shifts to the left. CH_3COO^- is ***common*** to both solutions.

The addition of CH_3COO^- reduces the % dissociation of the acid.

Buffers

- A buffer consisting of a mixture of the weak acid(CH_3COOH) and its salt (CH_3COONa^+), and Will undergo the following changes on the addition of acid or base:

- If the base is added (^-OH) to the solution it will be buffered by the following reaction with acetic acid:

  $CH_3COOH + {}^-OH \rightarrow CH_3COO^- + H_2O$

  So the pH will not change significantly

Buffers

- If acid (H^+) is added, it will be buffered by another reaction, this time using the salt (CH_3COO^-):

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

  The pH will not alter significantly because the CH_3COOH formed is a weak acid
- Addition of more base increases A^- and decreases (HA) and this doesn't alter the pH much until $[A^-]>>>>[HA]$

The buffering power is greatest when pH=pKa , i.e. when the acid and the salt are at the same concentration

How a Buffer Works

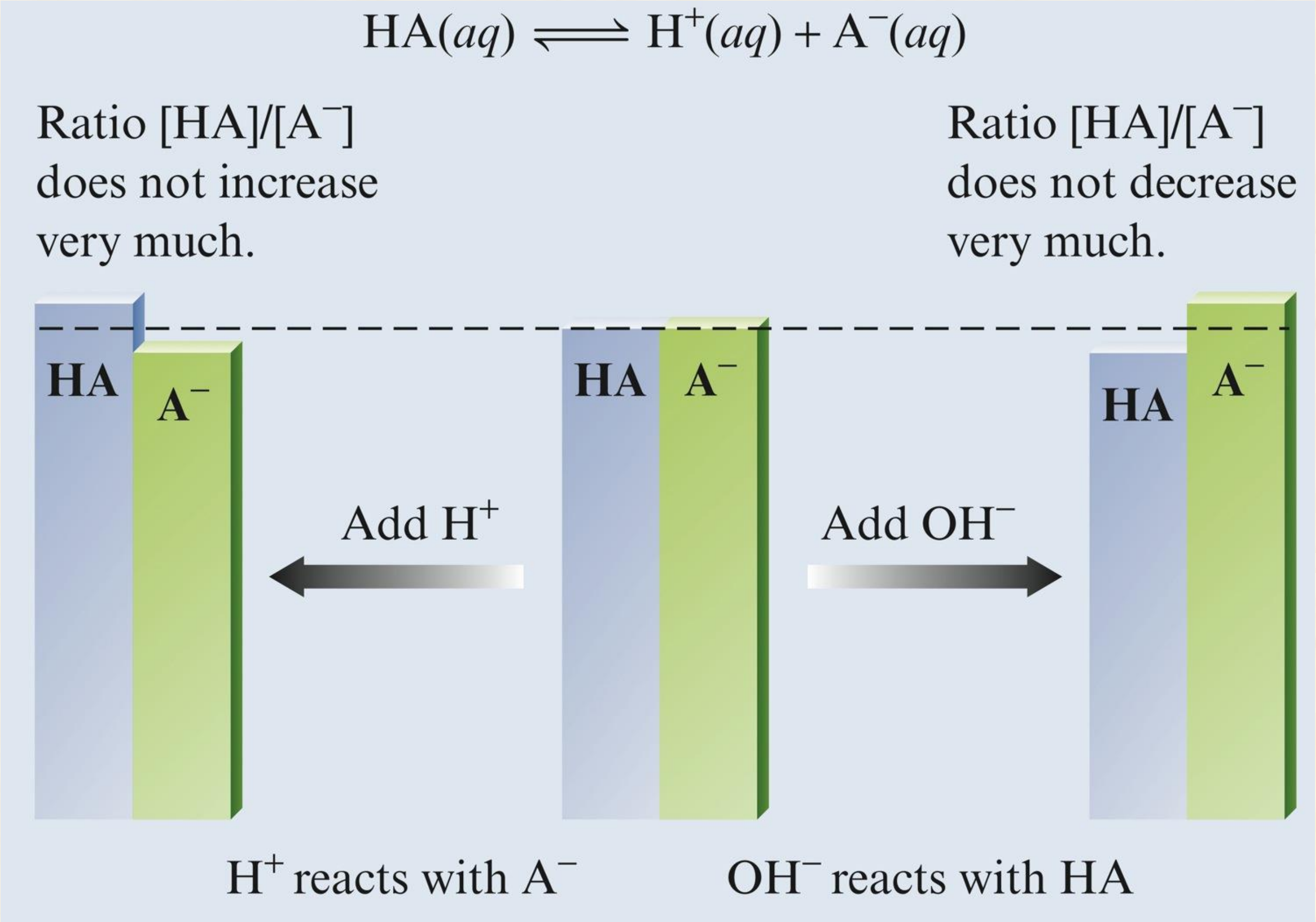
The buffer components (HA and A^-) are able to consume ***small*** amounts of added OH^- or H_3O^+ ***by a shift in equilibrium position***.

$$CH_3COOH(aq) + H_2O(l) \rightleftharpoons CH_3COO^-(aq) + H_3O^+(aq)$$

Added OH^- reacts with CH_3COOH, causing a shift to the right.

Added H_3O^+ reacts with CH_3COO^-, causing a shift to the left.

The shift in equilibrium position absorbs the change in $[H_3O^+]$ or $[OH^-]$, and the pH changes only slightly.



Effect of added H^+ or OH^- on a buffered system.

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

in buffer solution with HA & A^-:

- addition of H^+
  neutralization:
  $H^+ + A^- \rightarrow HA$

- [HA] increases slightly
  $[A^-]$ decreases slightly
  $[HA]/[A^-]$ increases
  $[H^+]$ increases
  pH decreases

- addition of OH^-
  neutralization:
  $OH^- + HA \rightarrow A^- + H_2O$

- [HA] decreases slightly
  $[A^-]$ increases slightly
  $[HA]/[A^-]$ decreases
  $[H^+]$ decreases
  pH increases

Buffer Action

Buffer action occurs as

- the weak acid in a buffer neutralizes base.
- the conjugate base in the buffer neutralizes acid.
- the pH of the solution is maintained.

Alkaline buffer solutions - action

Alkaline buffer

Very similar but is based on the equilibrium surrounding a weak base; AMMONIA

$$NH_3(aq) + H_2O(l) \rightleftharpoons OH^-(aq) + NH_4^+(aq)$$

relative concs. **HIGH** **LOW** **LOW**

but one needs ;

a large conc. of $OH^-(aq)$ to react with any $H^+(aq)$ added

a large conc of $NH_4^+(aq)$ to react with any $OH^-(aq)$ added

There is enough NH_3 to act as a source of OH^- but one needs to increase the concentration of ammonium ions by adding an ammonium salt.

Use AMMONIA (a weak base) + AMMONIUM CHLORIDE (one of its salts)