13. Buffers (IV · 19)

a) Purpose

prevents a significant change in pH when acid or base is added

No Buffer	With Buffer
0.1 mol HCl added to water	0.1 mol HCl added to water
pH changes 6 units! (7 to 1)	containing "buffer system"
	pH changes only 0.08 units!

b) Acidic Buffer Systems

i) 1 mol CH_3COOH in 1 L water: *(buffers against base only)*

$$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$$

0.98 mol   0.01 mol   0.01 mol

① If add OH^-, the H_3O^+ present will "mop up" (neutralize) the OH^- added. Thus, no net increase in pH.
The equilibrium will also shift right to replace the H_3O^+ used to neutralize the OH^-.

② But, if add H_3O^+, the equilibrium will shift left but will quickly stop as soon as CH_3COO^- is used up. Thus, the pH will decrease.

ii) 1 mol CH_3COOH and 1 mol $NaCH_3COO$ in 1 L water: (buffers against acid and base)

$$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$$

1 mol   1 mol
(from $NaCH_3COO$)

① If add OH^-, system prevent pH increase as described above.

② If add H_3O^+, there is now plenty of CH_3COO^- which can react with the H_3O^+, shift the equilibrium to the left, and prevent a decrease in pH.

iii) Why is it called an "acidic" buffer system?

$$Ka = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]}$$

$1.8 \times 10^{-5} = \frac{[1.0M][H_3O^+]}{[1.0M]}$ $\quad 1.8 \times 10^{-5} = [H_3O^+]$ $\quad pH = 4.74$

This is an acidic buffer system because it will maintain pH around 4.74

iv) Example: If we add 0.1 mol HCl to 1L water that contains the above buffer system, what is the change in pH?

$$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$$

1.1 mol 0.9 mol

0.1 mol of CH_3COO^- reacts with the 0.1 mol H_3O^+, shifting equilibrium to the left, thus decreasing CH_3COO^- by 0.1 mol and increasing CH_3COOH by 0.1 mol.

$Ka = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]}$ $\quad 1.8 \times 10^{-5} = \frac{[0.9M][H_3O^+]}{[1.1M]}$

$2.2 \times 10^{-5} = [H_3O^+]$ $\quad pH = 4.66$ $\quad$ pH change = 4.74 – 4.66 = **0.08**

v) An acidic buffer is made of a weak acid (CH_3COOH) and a salt containing its conjugate base ($NaCH_3COO$)

c) Basic Buffer Systems

i) 1 mol NH_3 and 1 mol NH_4Cl in 1 L water:

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

1 mol 1 mol (from NH_4Cl)

① If add OH^-, excess NH_4^+ mops it up

② If add H_3O^+, OH^- mops it up and excess NH_3 shifts right to replace OH^-

ii) Why is it called a "basic" buffer system?

$$Kb = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

$$1.79 \times 10^{-5} = \frac{[1.0M][OH^-]}{[1.0M]} \qquad 1.79 \times 10^{-5} = [OH^-] \qquad pOH = 4.74 \quad pH = 9.25$$

This is a basic buffer system because it will maintain pH around 9.25

iii) A basic buffer system is made of a weak base (NH_3) and a salt containing its conjugate acid (NH_4Cl).

d) Weak Acid/Base Titrations are Buffers

i) titrations of a weak acid with a strong base sets up a buffer equilibrium system

$$CH_3COOH + NaOH \rightleftharpoons NaCH_3COO + H_2O$$

Halfway to the equivalence point (V _) is when we have a buffer because $[CH_3COOH] = [CH_3COO^-]$

ii) titrations of a weak base with a strong acid also sets up a buffer system

$$NH_3 + HCl \rightleftharpoons NH_4Cl$$

Halfway to the equivalence point (V _) is when we have a buffer because $[NH_3] = [NH_4^+]$

e) Application

i) The Haemoglobin enzyme in blood works at an optimum pH of 7.4

pH > 7.4 O_2 not released

pH < 7.4 O_2 not picked up

ii) Blood has a buffer system to prevent drastic pH changes

Two linked Equilibria: $CO_2 + H_2O \rightleftharpoons H_2CO_3$
(excess in blood)

$H_2CO_3 + H_2O \rightleftharpoons H_3O^+ + HCO_3^-$
(excess in blood)

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