Buffer Action:-

Resists changes in pH when small amount of acid or alkali are added to it.

Acidic buffer = weak acid + salt of the acid (Acid + strong base)

$$CH_3COONa \longrightarrow CH_3COO^- + Na^+$$
$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$

- if an acid is added, the extra H^+ combines with acetate → undissociated HAc, so $[H^+]$ remains constt.

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

- if an alkali is added, the OH^- ions is removed by reaction with undissociated acid to form water — so $[H^+]$ remains constt

$$CH_3COOH + OH^- \longrightarrow CH_3COO^- + H_2O$$

Prep^n of Buffers:-

$$\underset{\text{limiting reagent}}{NaOH} + CH_3COOH \longrightarrow \underbrace{\underset{\text{salt}}{CH_3COONa} + H_2O + \underset{\text{excess weak acid}}{CH_3COOH}}_{\text{Buffer solution}}$$

Alkali buffer :- pH > 7.0

Weak base + salt of the base (made from base + strong acid)

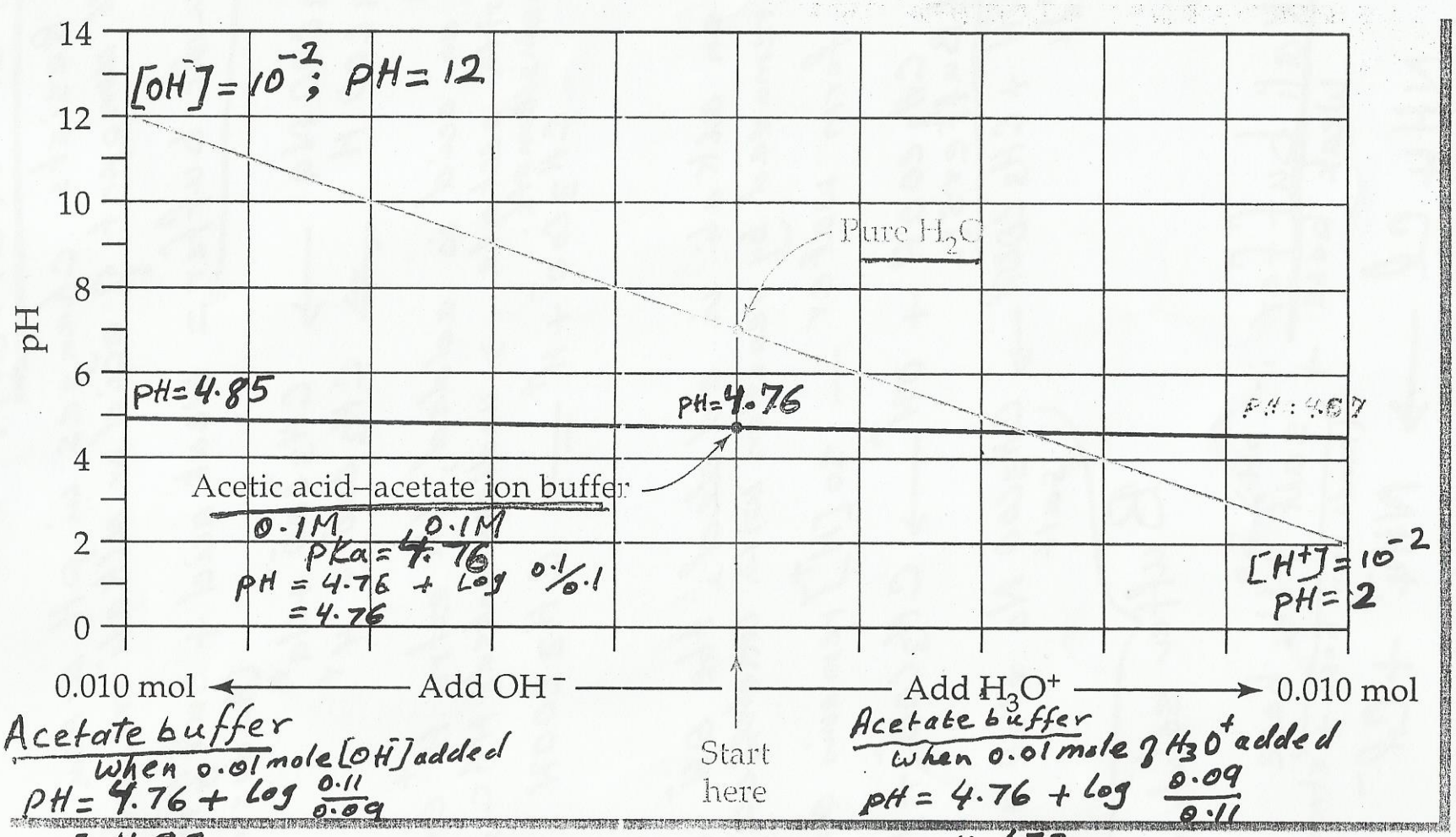
$$NH_4Cl \longrightarrow NH_4^+ + Cl^-$$

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

Excess H^+ combines with OH^- ; excess OH^- combines with $NH_4^+ \rightarrow NH_3$

Figure 10.5 The effect of a buffer solution on pH

$$pH = pKa + \log \frac{[\text{conjugate base}]}{[\text{conjugate acid}]}$$



Acetate buffer when 0.01 mole [OH⁻] added

$pH = 4.76 + \log \frac{0.11}{0.09}$

$= 4.85$

Acetate buffer when 0.01 mole of H_3O^+ added

$pH = 4.76 + \log \frac{0.09}{0.11}$

$= 4.673$

Buffer Calculations:-

1) Buffer consist of 0.2 mole CH_3COONa in 500ml of 0.1M CH_3COOH ($K_a = 1.8 \times 10^{-5}$ M) What is its pH?

$$pH = pK_a + \log \frac{Base}{Acid}$$

$$pH = \underbrace{\log 1.8 \times 10^{-5}}_{pKa} + \log \frac{\overset{2 \times 0.2}{0.4}}{0.1}$$

OR

$$K_a = \frac{[H^+] \times 0.4}{CH_3COOH} = 1.8 \times 10^{-5}$$

$$[H^+] = 4.5 \times 10^{-6} \text{ M}$$

$$pH = -\log 4.5 \times 10^{-6} = 5.4$$

2) Calculate mass of sod. propionate to be dissolved in 1l of 1M propionic acid (M.W.=96) to give buffer of pH = 4.5 (pKa = 4.87)

$pH = 4.5$ $\quad [H^+] = 10^{-4.5}$

$pKa = 4.87$ $\quad K_a = 10^{-4.87}$

$$K_a = \frac{[H^+][\text{propionate}]}{\text{propionic acid}}$$

or use Handerson-Hasselbalch Eq.

$$[\text{Propionate}] = \frac{1 \times 10^{-4.87}}{10^{-4.5}} = 0.427 \text{ M}$$

$$0.427 \times \frac{96.08 \text{ (M.W.)}}{1.0} = 41.0 \text{ gr.}$$

3) Calculate pH of a buffer when 18 ml of 0.1 M HCl is added to 32 ml of 0.1 M NH_3 ($pK_b = 4.75$)

(1) Calculate excess NH_3 and salt formed

$$HCl \text{ moles} = \frac{18}{1000} \times 0.1 = 1.8 \times 10^{-3}$$

$$NH_3 \text{ moles} = \frac{32}{1000} \times 0.1 = 3.2 \times 10^{-3}$$

Ammonium salt $= 1.8 \times 10^{-3}$

excess Ammonia $= 3.2 \times 10^{-3} - 1.8 \times 10^{-3} = 1.4 \times 10^{-3}$

Molar conc. of salt $= \dfrac{1.8 \times 10^{-3}}{50/1000} = 3.6 \times 10^{-2}$ M

" " of NH_3 $= \dfrac{1.4 \times 10^{-3}}{50/1000} = 3.2 \times 10^{-2}$ M

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

$$10^{-4.75} = \frac{3.6 \times 10^{-2}}{3.2 \times 10^{-2}} \times OH^-$$

$$[OH^-] = 0.889 \times 10^{-4.75} = 1.58 \times 10^{-5} \text{ M}$$

$$pOH = -\log 1.58 \times 10^{-5} = 4.8$$

$$pH = 14 - 4.8 = 9.2$$

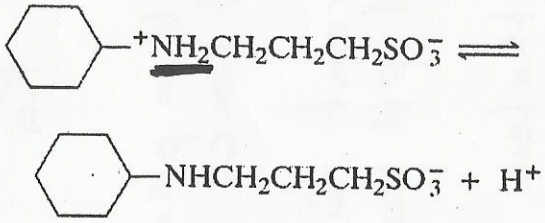
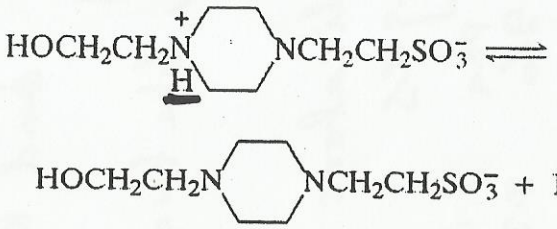
OR

$$pOH = pK_b + \log \frac{[\text{salt}]}{[\text{weak base}]}$$

$$pOH = 4.75 + \log \frac{3.6 \times 10^{-2}}{3.2 \times 10^{-2}}$$

$$= 4.75 + 0.05 = 4.8 \; ; \; pH = 14 - 4.8 = 9.2$$

Table 2.6
Some synthetic buffers

Name (Abbreviation)	pK_a	Useful pH Range	Ionization Reaction[a]
N-(2-Acetamido)-2-aminoethanesulfonic acid (ACES)	6.9	6.4–7.4	$H_2NCOCH_2\overset{+}{N}H_2CH_2CH_2SO_3^- \rightleftharpoons H_2NCOCH_2NHCH_2CH_2SO_3^- + H^+$
3-(Cyclohexylamino)propanesulfonic acid (CHAPS)	10.5	10.0–11.0	
N-(2-Hydroxyethyl)piperazine-*N'*-2-ethanesulfonic acid (HEPES)	7.5	7.0–8.0	
Tris(hydroxymethyl)aminomethane (TRIS)	8.3	7.5–9.0	$(HOCH_2)_3C\overset{+}{N}H_3 \rightleftharpoons (HOCH_2)_3CNH_2 + H^+$

[a] Each reaction shows the two predominant forms (acid and base) present in the useful pH range.

INDICATORS

- often organic dye → different colors in acidic and alkaline sol.

- weak acid / base

$$HIn_{(aq)} \rightleftharpoons H^+ + In^-$$

For Litmus Red Blue

In presence of acid → HIn red

In presence of base → In^- blue.

$$K_a = \frac{[H^+][In^-]}{HIn}$$

$$\frac{[HIn]}{[In^-]} = \frac{[H^+]}{K_a}$$

so, color of indicator depends on pH or $[H^+]$ and K_a.

when pH = pKa, the two colors have equal conc.

So different indicators change color over different pH ranges

e.g.	pKa	pH range	Color in acid	Color in alkali
phenolphthalein	9.6	8.3 – 10.0	Colorless	Pink
Methyl orange	3.7	3.1 – 4.4	Red	Yellow

In order for an indicator to be effective, color change (called the end-point) must occur rapidly at the equivalence point

e.g.

Property	"Phenolphthalein"	Methyl orange
pKa	9.6	3.7
pH range	8.3 – 10.0	3.1 – 4.4
Color in acid	Colorless	Red
" " alkali	Pink	Yellow
Useful for	Titrations involving strong bases	Titrations involving strong Acids