Chapter Four:

Theory of Neutralization:

Neutralization in acid-base solutions:

Electrolytes: electrolytes are solutes which ionize in a solvent to produce an electrically conducting medium. Or its ionizable substances which are gives positive ion and negative ionic the solvent.

Strong electrolytes: are ionized completely in the solvent.

Weak electrolytes: are only partially ionized in the solvent.

\[ \text{HCl} + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{Cl}^- \]

HCl is a strong electrolyte which is completely ionized.

\[ \text{NH}_3 + \text{H}_2\text{O} \rightarrow \text{NH}_4^+ + \text{OH}^- \]

NH\(_3\) is a weak electrolyte which is partially ionized.

Amphiprotic: is a term refers to substance because it exhibits both acidic and basic properties depending on the solute such as: water, methyl alcohol, ethyl alcohol.

\[ \text{HNO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{NO}_2^- + \text{H}_3\text{O}^+ \]

acid base

\[ \text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ + \text{OH}^- \]

base acid
**Conjugate acids and basis:**

After donating a proton by the acid, the species that remains is capable to accepting a proton to reform the original acid.

\[
\text{acid1} \quad \text{H}^+ + \text{base1} \quad \text{H}_2\text{O} \quad \text{H}^+ + \text{OH}^- \\
\text{acid} \quad \text{conjugate base}
\]

\[
\text{base2} + \text{H}^+ \quad \text{acid2} \quad \text{NH}_3^+ \quad \text{OH}^- + \text{NH}_4^+ \\
\text{base} \quad \text{conjugate acid}
\]

<table>
<thead>
<tr>
<th>Conjugate Acid</th>
<th>Conjugate Base</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCN</td>
<td>CN^-</td>
</tr>
<tr>
<td>HCl</td>
<td>Cl^-</td>
</tr>
<tr>
<td>CH\text{}_3\text{COOH}</td>
<td>CH\text{}_3\text{COO}^-</td>
</tr>
<tr>
<td>NH\text{}_4^+</td>
<td>NH\text{}_3</td>
</tr>
<tr>
<td>H\text{}_2\text{CO}_3</td>
<td>HCO\text{}_3^-</td>
</tr>
</tbody>
</table>

**Hydrogen ion exponent (pH):**

\[
\text{pH} = \text{power of hydrogen} \\
pH = -\log [\text{H}_3\text{O}^+] \quad \text{or} \quad pH = + \log_{10} \frac{1}{[\text{H}_3\text{O}^+]} \\
[\text{H}_3\text{O}^+] = 10^{-\text{pH}}
\]

\[
p\text{OH} = \log [\text{OH}^-] \quad \text{or} \quad p\text{OH} = + \log_{10} \frac{1}{[\text{OH}^-]} \\
[\text{OH}^-] = 10^{-p\text{OH}}
\]
In neutral sol. \([\text{H}_3\text{O}^+] = [\text{OH}^-] \rightarrow \text{pH} = 7\)

In acidic sol. \([\text{H}_3\text{O}^+] > [\text{OH}^-] \rightarrow \text{pH} > \text{pOH}\)

In basic sol. \([\text{H}_3\text{O}^+] < [\text{OH}^-] \rightarrow \text{pH} < \text{pOH}\)

**Ionization constant of water (Kw) :**

\[
\text{H}_2\text{O} \rightarrow \text{H}^+ + \text{OH}^-
\]

\[
\text{H}^+ + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+
\]

\[
\text{H}^+ + 2\text{H}_2\text{O} \rightarrow \text{H}_5\text{O}_2^+
\]

\[
\text{H}^+ + 3\text{H}_2\text{O} \rightarrow \text{H}_7\text{O}_3^+
\]

\[
\text{H}^+ + 4\text{H}_2\text{O} \rightarrow \text{H}_9\text{O}_4^+
\]

\[K = \frac{[\text{H}_3\text{O}^+][\text{OH}^-]}{[\text{H}_2\text{O}]}\]

\[\text{Kw} = [\text{H}_3\text{O}^+][\text{OH}^-]\]

\[10^{-14} = [\text{H}_3\text{O}^+][\text{OH}^-] \quad (x \text{ –log})\]

\[14 = \text{pKw} = \text{pH} + \text{pOH}\]

\[\text{pH} + \text{pOH} = 14\]

**EX.** Calculate pH and pOH for each of :

a) 0.001M HCl

b) 0.001M NaOH

c) 0.001M NaCl

\[
\text{HCl} \rightarrow \text{H}^+ + \text{Cl}^-
\]
\[
\begin{bmatrix}
0.001 & 0 & 0 \\
0 & 0.001 & 0.001 \\
0 & 0.001 & 0.001 \\
\end{bmatrix}
\]

\[ [H^+] = 0.001 \text{M} = 10^{-3} \text{M} \]

\[ \text{pH} = -\log 10^{-3} = 3 \]

\[ \text{pOH} = 14 - 3 = 11 \]

\[ \text{NaOH} \rightarrow \text{Na}^+ + \text{OH}^- \]

\[ [\text{OH}^-] = 0.001 \text{M} = 10^{-3} \text{M} \]

\[ \text{pOH} = -\log 10^{-3} = 3 \]

\[ \text{pH} = 14 - 3 = 11 \]

\[ \text{NaCl} \rightarrow \text{Na}^+ + \text{Cl}^- \]

\[ [\text{H}_3\text{O}^+] = [\text{OH}^-] = 10^{-7} \]

\[ \text{pH} = \text{pOH} = 7 \]

**Calculation of pH:**

1) **weak acid and base**:

a) for weak acid:

\[ \text{HA} \rightleftharpoons \text{H}_3\text{O}^+ + \text{A}^- \]

\[ \text{Ka} = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} \]

\[ [\text{HA}] = \text{Ca} \]
\[ [\text{H}_3\text{O}^+] = [\text{A}^-] \]

\[ \text{Ka} = \frac{[\text{H}_3\text{O}^+]^2}{[\text{Ca}^+]}. \]

\[ [\text{H}_3\text{O}^+] = \sqrt{\text{Ka} \cdot \text{Ca}} \]

\[ \text{pH} = -\log [\text{H}_3\text{O}^+] \]

b) for weak base:

\[ \text{B} + \text{H}_2\text{O} \rightleftharpoons \text{BH}^+ + \text{OH}^- \]

\[ \text{Kb} = \frac{[\text{BH}^+][\text{OH}^-]}{[\text{B}]} \]

\[ [\text{B}^-] = \text{Cb} \]

\[ [\text{OH}^-] = [\text{BH}^+] \]

\[ \text{Kb} = \frac{[\text{OH}^-]^2}{\text{Cb}} \]

\[ [\text{OH}^-] = \sqrt{\text{Kb} \cdot \text{Cb}} \]

\[ \text{pOH} = -\log [\text{OH}^-] \]

\[ \text{pH} = 14 - \text{pOH} \]

**EX.** Calculate pH for benzoic acid sol., Ka = 6.3 \times 10^{-5}, Ca = 6.1 \text{gm/L}, M.wt. = 122 \text{gm/mole}?

\[ \text{pH} = -\log [\text{H}_3\text{O}^+] \]

\[ [\text{H}_3\text{O}^+] = \sqrt{\text{Ka} \cdot \text{Ca}} \]

\[ \text{Ca} = \frac{6.1 \text{ gm/L}}{122 \text{ gm/mole}} = 0.05 \text{ mole/L} \]
\[ [\text{H}_3\text{O}^+] = \sqrt{6.3 \times 10^{-10} - 5 \times 0.05} = \]
\[ \text{pH} = - \log = \]

2) **salts solutions**:

Salts can be classified into:

a) salt derived from strong acid and strong base, NaCl:

\[ \text{NaCl} \rightarrow \text{Na}^+ + \text{Cl}^- \]

\[ [\text{H}_3\text{O}^+] = [\text{OH}^-] = 10^{-7} \]

\[ \text{pH} = \text{pOH} = 7 \]

b) salt derived from strong acid and weak base, NH\(_4\)Cl:

\[ \text{NH}_4\text{Cl} \rightleftharpoons \text{NH}_4^+ + \text{Cl}^- \]

\[ \text{NH}_4^+ + \text{H}_2\text{O} \rightleftharpoons \text{NH}_3 + \text{H}_3\text{O}^+ \]

\[ Ka = \frac{[\text{H}_3\text{O}][\text{NH}_3]}{[\text{NH}_4]} \]

\[ [\text{NH}_4] = \text{Cs} \]

\[ [\text{H}_3\text{O}^+] = [\text{NH}_3] \]

\[ Ka = \frac{[\text{H}_3\text{O}]^2}{\text{Cs}} \]

\[ [\text{H}_3\text{O}^+] = \sqrt{Ka\text{Cs}} \]

\[ \text{Kw} = Ka\text{Kb} \]
\[
[H_3O^+] = \sqrt{\frac{K_a C_s}{K_b}} \quad (x - \log)
\]

\[
pH = \frac{1}{2} \left( pK_w - pK_b - \log C_s \right)
\]

**EX.** Calculate pH for 0.2M of \( \text{NH}_4\text{Cl} \) sol., \( pK_b = 4.72 \)?

\[
pH = \frac{1}{2} \left( 14 - 4.72 - \log 0.2 \right)
\]

\[\text{pH} = \]

c) salt derived from weak acid and strong base, \( \text{NaCN} \):

\[
\text{NaCN} \quad \xrightarrow{\text{Na}^+ + \text{CN}^-} \quad \text{Na}^+ + \text{CN}^- + \text{H}_2\text{O} \quad \rightarrow \quad \text{no ionized}
\]

\[
\text{CN}^- + \text{H}_2\text{O} \quad \xleftrightarrow{\text{HCN} + \text{OH}^-}
\]

\[
K_b = \frac{[\text{HCN}][\text{OH}^-]}{[\text{CN}^-]}
\]

\[\text{[CN]} = C_s \]

\[\text{[HCN]} = [\text{OH}^-] \]

\[
K_b = \frac{[\text{OH}^-]^2}{[\text{CN}^-]}
\]

\[[\text{OH}^-]^2 = K_b C_s \]

\[
\left(\frac{K_w}{[H_3O^+]}\right)^2 = \frac{K_w}{K_a} C_s
\]

\[
[H_3O^+] = \frac{K_w K_a}{C_s} \quad (x - \log)
\]
\[
[H_3O^+] = \sqrt{\frac{K_{w}K_{a}}{C_s}}
\]

\[\text{pH} = \frac{1}{2} (pK_w + pK_b + \log C_s)\]

d) salt derived from weak acid and weak base, \(\text{NH}_4\text{F}\):

\[
\text{NH}_4\text{F} \rightleftharpoons \text{NH}_4^+ + \text{F}^-
\]

\[
\text{NH}_4^+ + \text{H}_2\text{O} \rightleftharpoons \text{NH}_3 + \text{H}_3\text{O}^+ 
\]

\[
\text{F}^- + \text{H}_2\text{O} \rightleftharpoons \text{HF}^+ + \text{OH}^- 
\]

\[
[H_3O^+] = \sqrt{\frac{K_{w}K_{a}}{K_{b}}}
\]

\[\text{pH} = \frac{1}{2} (pK_w + pK_a - pK_b)\]

**Buffer solution:**

Buffer solution is defined as a solution that resist change in pH as a result of either dilution or addition of acid or base.

Buffer solution is a mixture of:

a) weak acid and its salt, \(\text{CH}_3\text{COOH} + \text{CH}_3\text{COONa}\)

b) weak base and its salt, \(\text{NH}_3 + \text{NH}_4\text{Cl}\)

**Q:** why buffer sol. resist the change in pH value in case of dilution or adding acid or base to sol.?

1) When adding a strong acid, like \(\text{HCl}\):

\[
\text{HCl} \rightarrow \text{H}_3\text{O}^+ + \text{Cl}^-
\]

\[
\text{CH}_3\text{COOH} \rightleftharpoons \text{H}_3\text{O}^+ + \text{CH}_3\text{COO}^-
\]
\[
\text{CH}_3\text{COONa} \quad \rightleftharpoons \quad \text{Na}^+ + \text{CH}_3\text{COO}^- \\
\text{H}_3\text{O}^+ + \text{CH}_3\text{COO}^- \quad \rightleftharpoons \quad \text{CH}_3\text{COOH}
\]
From the equation, pH value is not change or it change very little because the hydronium ion from HCl react with CH₃COO⁻ to produce CH₃COOH that is ionized very little, therefor, pH not decrease.

2) When adding a strong base, like NaOH:

\[
\begin{align*}
\text{CH}_3\text{COOH} & \quad \rightleftharpoons \quad \text{H}_3\text{O}^+ + \text{CH}_3\text{COO}^- \\
\text{CH}_3\text{COONa} & \quad \rightleftharpoons \quad \text{Na}^+ + \text{CH}_3\text{COO}^- \\
\text{NaOH} & \quad \rightarrow \quad \text{Na}^+ + \text{OH}^- \\
\text{H}_3\text{O}^+ + \text{OH}^- & \quad \rightleftharpoons \quad \text{H}_2\text{O}
\end{align*}
\]
OH⁻ from the base (NaOH) react with H₃O⁺ from the acid to produce H₂O, and that lead to more dissociation of CH₃COONa to substitute the losses in H₃O⁺ that mean, the sol. will resist the change in pH value when adding a strong base while the sol. still acidic (contain CH₃COOH molecules) nonionized.

**EX.** Calculate the pH change that takes place when 100ml of (a) 0.05M NaOH and (b) 0.05M HCl are added to 400ml of a buffer solution that is 0.2M in NH₃ and 0.3M in NH₄Cl?

The initial pH of the solution is obtained assuming that:

\[
\begin{align*}
[\text{NH}_3] & = M_{\text{NH}_3} = 0.2 \\
[\text{NH}_4^+] & = M_{\text{NH}_4\text{Cl}} = 0.3
\end{align*}
\]
And substituting into the dissociation constant expression for NH₃
\[
\frac{0.3 \, [\text{OH}^-]}{0.2} = 1.76 \times 10^{-5}
\]

\[ [\text{OH}^-] = 1.17 \times 10^{-5} \]

\[ \text{pH} = 14 - (- \log 1.17 \times 10^{-5}) = 9.07 \]

a) addition of NaOH converts part of the NH\(_4^+\) in the buffer to NH\(_3\):

\[ \text{NH}_4^+ + \text{OH}^- \rightarrow \text{NH}_3 + \text{H}_2\text{O} \]

The analytical concentrations of NH\(_3\) and NH\(_4\)Cl then become :

\[ M_{\text{NH}_3} = \frac{400 \times 0.2 + 100 \times 0.05}{500} = \frac{85}{500} = 0.170 \]

\[ M_{\text{NH}_4\text{Cl}} = \frac{400 \times 0.3 - 100 \times 0.05}{500} = \frac{115}{500} = 0.230 \]

When substituted into the dissociation constant expression, these values yield :

\[ [\text{OH}^-] = \frac{1.67 \times 10^{-5} \times 0.170}{0.230} = 1.30 \times 10^{-5} \]

\[ \text{pH} = 14 - (- \log 1.30 \times 10^{-5}) = 9.11 \]

and :

\[ \Delta \text{pH} = 9.11 - 9.07 = 0.04 \]

b) addition of HCl converts parts of the NH\(_3\) to NH\(_4^+\); thus :

\[ \text{NH}_3 + \text{H}_3\text{O}^+ \rightarrow \text{NH}_4^+ + \text{H}_2\text{O} \]

\[ M_{\text{NH}_3} = \frac{400 \times 0.2 - 100 \times 0.05}{500} = \frac{75}{500} = 0.150 \]
\[ M_{\text{NH}_4\text{Cl}} = \frac{400 \times 0.3 + 100 \times 0.05}{500} = \frac{125}{500} = 0.250 \]

\[ [\text{OH}^-] = 1.76 \times 10^{-5} \times \frac{0.150}{0.250} = 1.06 \times 10^{-5} \]

\[ \text{pH} = 14 - (-\log 1.06 \times 10^{-5}) = 9.02 \]

\[ \Delta \text{pH} = 9.02 - 9.07 = -0.05 \]

It is of interest to contrast the behavior of an unbuffered solution with a pH 9.07 to the buffered ones just considered. It is readily shown that the additions of the same quantity of base would increase the pH to 12 – a pH change of 2.93 units. The addition of acid, on the other hand, would decrease the pH by slightly over 7 units.

**Buffering capacity**:

Buffering capacity depends on:

a) The ratio between concentration of both acid and base.

b) The total concentration of each acid and salt.

Maximum buffering capacity can be observed when pH = pKa (ratio of salt to acid is equal to 1.0)

**Calculation of pH for buffer solution**:

1) weak acid and its salt, (CH₃COOH + CH₃COONa)

\[ \text{CH}_3\text{COOH} \rightleftharpoons \text{H}^+ + \text{CH}_3\text{COO}^- \quad \text{.........(1)} \]

\[ \text{Ka} = \frac{[\text{H}][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} \quad \text{.........................(2)} \]

\[ [\text{H}^+] = \text{Ka} \frac{[\text{H}][\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COO}^-]} \quad \text{.........................(3)} \]

\[ \text{CH}_3\text{COONa} \rightleftharpoons \text{Na}^+ + \text{CH}_3\text{COO}^- \quad \text{.........(4)} \]
From equation (1):

\[ [\text{CH}_3\text{COOH}] = [\text{CH}_3\text{COOH}] - [H^+] \]

\[ [\text{CH}_3\text{COO}^-] = [H^+] \]

From equation (4):

\[ [\text{CH}_3\text{COO}^-] = [\text{Na}^+] \]

\[ [\text{CH}_3\text{COO}^-] = [\text{CH}_3\text{COOH}] + [H^+] \]

\[ [\text{CH}_3\text{COO}^-] = [H^+] \]

Substitution in equation (3):

\[ [H^+] = \text{Ka} \frac{[\text{CH}_3\text{COOH}]-[H]}{[\text{CH}_3\text{COONa}]+[H]} \]

Because of the value of \([H^+]\) is very small, then it can be negligible.

\[ [H^+] = \text{Ka} \frac{[\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COONa}]} \]

\[ [H^+] = \text{Ka} \frac{\text{Ca}}{\text{Cs}} \quad (x - \log) \]

\[ \text{pH} = \text{pKa} + \log \frac{\text{Cs}}{\text{Ca}} \quad \text{....... Henderson- Hasselbach} \]

2) weak base and its salt, (NH₃ + NH₄Cl)

\[ \text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ + \text{OH}^- \quad \text{(1)} \]

\[ \text{Kb} = \frac{[\text{OH}^+][\text{NH}_4^+]}{[\text{NH}_3]} \quad \text{.................(2)} \]
\[
[OH^-] = Kb \frac{[NH_3]}{[NH_4^+]} \quad \text{..........................(3)}
\]

\[\text{NH}_4\text{Cl} \underset{\text{NH}_4^+}{\rightleftharpoons} \text{Cl}^- \quad \text{...............(4)}\]

From equation (1):
\[\quad [\text{NH}_3] = [\text{NH}_3] - [\text{OH}^-]\]
\[\quad [\text{OH}^-] = [\text{NH}_4^+]\]

From equation (4):
\[\quad [\text{NH}_4\text{Cl}] = [\text{NH}_4^+]\]
\[\quad [\text{NH}_4^+] = [\text{NH}_4\text{Cl}] + [\text{OH}^-]\]

Substitution in equation (3):
\[\quad [\text{OH}^-] = Kb \frac{[\text{NH}_3] - [\text{OH}^-]}{[\text{NH}_4^+] + [\text{OH}^-]}\]

\[\quad [\text{OH}^-] = Kb \frac{\text{C}_b}{\text{C}_s} \quad \text{(x} - \log)\]

\[\quad \text{pH} = \text{pK}_b + \log \frac{\text{C}_s}{\text{C}_b}\]

**EX.** Calculate pH for a solution prepared by adding 10ml of 0.1M acetic acid to 20ml of 0.1M sodium acetate, \( Ka = 1.75 \times 10^{-5} \)?

we should calculate the conc. of acid and salt, final vol. = 30ml

for \( \text{CH}_3\text{COOH} \):

\[\text{M}_1\text{V}_1 = \text{M}_2\text{V}_2\]

\[0.1\text{m.mole} \times 10\text{ml} = M_2 \times 30\text{ml}\]

\[M_2(\text{HOAc}) = 0.033\text{ m.mole} / \text{ml}\]
For CH₃COONa (OAc-) :

\[ M_1V_1 = M_2V_2 \]

\[ 0.1 \text{ m.mole} \times 20\text{ml} = M(\text{OAc-}) \times 30\text{ml} \]

\[ M(\text{OAc-}) = 0.067 \text{ m.mole/ml} \]

\[ \text{pH} = \text{pKa} + \log \frac{C_a}{C_a} \]

\[ \text{pH} = 4.67 + \log \frac{0.067}{0.033} \]

\[ \text{pH} = 4.67 + \log 2 \]

\[ \text{pH} = 5.06 \]

**EX.** Calculate the vol. of concentrated ammonia and weight of ammonia chloride (NH₄Cl) that is needing to prepare 100ml of buffer sol. with pH = 10 salt conc. = 0.2M, pkb = 4.67 ?

we need to prepare 100ml of 0.02M of NH₄Cl :

m.moles NH₄Cl = 0.2m.mole/ml \times 100ml = 20 m.moles

mg(NH₄Cl) = 20m.moles \times 53.5 \text{ mg/mole} = 107 \times 10^{-3} \text{ mg}

thus , we need 107 mg of NH₄Cl

we can calculate the conc. of NH₃ from :

\[ \text{pOH} = \text{pKw} - \text{pH} \]

\[ \text{pOH} = 14 - 10 = 4 \]

\[ \text{pOH} = \text{pKb} + \log \frac{C_a}{C_b} \]
\[ 4 = 4.67 + \log \frac{0.2 \text{ m.mole/ml}}{[\text{NH}_3]} \]

\[ \log \frac{0.2 \text{ m.mole/ml}}{[\text{NH}_3]} = -0.67 \quad (x - \log) \]

\[ \log \frac{0.2 \text{ m.mole/ml}}{[\text{NH}_3]} = 10^{-0.67} \rightarrow 10^{-1} \times 10^{0.24} = 1.7 \times 10^{-1} = 0.17 \]

\[ [\text{NH}_3] = \frac{0.2}{0.17} = 1.2 \text{ m.mole/ml} \]

**Acid – Base indicators:**

Acid-base indicators are weak organic acids or bases, most of indicators have two colors, one is appear in acidic medium and the other is appear in basic medium (that means, the indicator will change its color when acid or base were adding to sol.).

We can symbolize to the typical reaction of an acid-base indicator as follows:

\[ \text{H}_2\text{O} + \text{HIn} \rightleftharpoons \text{H}_3\text{O}^+ + \text{In}^- \]

acid color                  base color

\[ \text{In}^- + \text{H}_2\text{O} \rightleftharpoons \text{InH}^+ + \text{OH}^- \]

base color                  acid color

Where: \(\text{HIn} = \) acidic indicator

\(\text{In} = \) basic indicator

\[ K_a = \frac{[\text{H}_3\text{O}^+][\text{In}^-]}{[\text{In}]} \quad ...........(1) \]

\[ [\text{H}_3\text{O}^+] = \frac{K_a \times [\text{HIn}]}{[\text{In}^-]} \]
The best indicator is the indicator whose change its color in equivalent point.

The change in color of indicator can be observed in the region where the ratio varies from a tenfold excess of one form to other, therefore, acidic color can be observed when:

\[
\frac{[\text{In}]}{[\text{HIn}]} \leq \frac{1}{10}
\]

And the basic color when:

\[
\frac{[\text{In}]}{[\text{HIn}]} \geq \frac{10}{1}
\]

Some indicators require smaller ratio changes and others longer.

If equation (1) is multiplying by (-log), then:

\[
[H_3O^+] = \frac{K_a \cdot [\text{HIn}]}{[\text{In}^-]} \quad \text{(x-log)}
\]

\[
\text{pH} = pK_a - \log \left( \frac{[\text{In}^-]}{[\text{HIn}]} \right)
\]

when \( \frac{[\text{In}^-]}{[\text{HIn}]} = \frac{1}{10} \) or \( \frac{10}{1} \)

\[
\text{pH} = pK_a - \log \frac{1}{10}
\]

\[
\text{pH} = pK_a - 1
\]

and,
\[ pH = pKa + \log \frac{10}{1} \]

\[ pH = pKa + 1 \]

\[ \Delta pH = pH \text{ basic} - pH \text{ acidic} = (pKa+1) - (pKa - 1) = 2 \]

That means, when we assume that \( pKa = 5 \), the change in color of indicator occur when the pH value variant from (5-1) to (5+1) e.g. (4-6).

Some important Acid-Base indicators

<table>
<thead>
<tr>
<th>Common name</th>
<th>transition range,pH</th>
<th>acid color</th>
<th>base color</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyl yellow</td>
<td>2.9 – 4.0</td>
<td>red</td>
<td>yellow</td>
</tr>
<tr>
<td>Methyl orange</td>
<td>3.1 – 4.4</td>
<td>red</td>
<td>orange</td>
</tr>
<tr>
<td>Bromocresol green</td>
<td>3.8 – 5.4</td>
<td>yellow</td>
<td>blue</td>
</tr>
<tr>
<td>Methyl red</td>
<td>4.2 – 6.3</td>
<td>red</td>
<td>yellow</td>
</tr>
<tr>
<td>Bromothymol blue</td>
<td>6.2 – 7.6</td>
<td>yellow</td>
<td>blue</td>
</tr>
<tr>
<td>Phenol red</td>
<td>6.8 – 8.4</td>
<td>yellow</td>
<td>red</td>
</tr>
<tr>
<td>Phenolphthalein</td>
<td>8.3 – 10.0</td>
<td>colorless</td>
<td>purple</td>
</tr>
<tr>
<td>Thymolphthalein</td>
<td>9.3 – 10.5</td>
<td>colorless</td>
<td>blue</td>
</tr>
</tbody>
</table>

**Types of acid-base indicators:**

The table above shows many acid-base indicators that are used in analytical routine work. Two common indicators are described in the following paragraphs:
1) **Phthaline Indicators**: The best known phthaline indicator is *phenolphthalein*, it is organic weak acid, colorless in acidic sol. and exhibit a variety of colors in alkaline media.

Significant concentrations for color ion is appear in the pH range between 8.0 and 9.8.

2) **Azo Indicators**: Most azo indicators exhibit a color range from red to yellow with increasing basicity. The best known azo indicators is *methyl orange*, it is a weak base has sulphonic group $\text{SO}_3\text{H}$ and dimethylamin.

**Choice of indicators for titration of acid and base**:

End point detection in a neutralization titration based upon the change in color of indicator in equivalent point.

The selection of an appropriate indicator require knowledge the pH changes which occurs throughout titration. Thus, we need to know how neutralization titration curves are derived.

For any sol. to know the pH change throughout titration, it must be plotte titration curve that show the pH change according to the amount of acid or base that will be adding to the sol.

There are two methods to detect titration curves:

1) Calculated method: in this method, pH values are calculated from amount of acid or base that was added to the sol.

2) Practical method: in this method, pH values can be calculate by using an instrumental called "pH-meter".

**The advantages of titration curve are**:

1) Detect the end point of titration.
2) Choice the suitable indicator for titration.

1) **Titration of strong acid with strong base:**

This type can be expressed by titration of 50ml of 0.1N HCl with 50ml of 0.1N NaOH:

a) before adding the base:

\[
\text{HCl} \rightarrow \text{H}^+ + \text{Cl}^- \\
0.1 \quad 0.1 \quad 0.1
\]

\[
\text{pH} = - \log [\text{H}^+] = - \log 0.1 \\
\text{pH} = 1
\]

b) after adding 10ml of NaOH:

\[
\text{HCl} + \text{NaOH} \rightarrow \text{NaCl} + \text{H}_2\text{O} \\
(50 \times 0.1) \quad (10 \times 0.1) \quad 0 \\
5 \quad 1 \quad 0 \\
4 \quad 0 \quad 1
\]

\[
[\text{H}_3\text{O}^+] = \frac{4}{60} = 0.066 \\
\text{pH} = - \log 0.066 = 1.18
\]

c) when adding 50ml of NaOH:
HCl + NaOH → NaCl + H₂O

(50x0.1) (50x0.1) 0
5 5 0
0 0 5

\([\text{H}_3\text{O}^+] = [\text{OH}^-] = 10^{-14}\)

\([\text{H}_3\text{O}^+]^2 = 10^{-14}\)

\([\text{H}_3\text{O}^+] = 10^{-7}\)

\(\text{pH} = -\log 10^{-7} = 7\)

\(d)\) after adding excess of NaOH (60ml):

HCl + NaOH → NaCl + H₂O

(50x0.1) (60x0.1) 0
5 6 0
0 1 5

\([\text{OH}^-] = \frac{1}{(50+60)\text{ml}} = 0.009\)

\(\text{pOH} = -\log 0.009 = 5\)

\(\text{pH} = 14 - 5 = 9\)

The figure shows that the range of \(\text{pH}\) change at equivalent point
is 4 -10, therefore, both of ph.ph and M.O can be use successfully.

2) \textit{Titration of strong base with a strong acid}:
3) **Titration of weak acid with a strong base:**

100ml of 0.1N CH₃COOH with 100ml of 0.1N NaOH, $K_a = 1 \times 10^{-5}$.

a) before adding NaOH:

$$\text{CH}_3\text{COOH} \rightleftharpoons \text{CH}_3\text{COO}^- + H^+$$

$$[H_3O^+] = \sqrt{K_a C_a} = \sqrt{10^{-5} \times 10^{-1}} = 10^{-3}$$

$$\text{pH} = -\log 10^{-3} = 3$$

b) after adding 10ml NaOH:

$$\text{CH}_3\text{COOH} + \text{NaOH} \rightleftharpoons \text{CH}_3\text{COONa} + \text{H}_2\text{O}$$

$$\begin{array}{ccc}
(100\times0.1) & (10\times0.1) & 0 \\
10 & 1 & 0 \\
9 & 0 & 1 \\
\end{array}$$

**Note:** the product from this reaction is weak acid and it’s salt, therefore, it is buffer sol.:

$$\text{pH} = pK_a + \log \frac{C_s}{C_a}$$

$$\text{pH} = 5 + \log \frac{1}{9}$$

$$\text{pH} = 4.05$$

c) when adding 50ml of NaOH:

$$\text{CH}_3\text{COOH} + \text{NaOH} \rightleftharpoons \text{CH}_3\text{COONa} + \text{H}_2\text{O}$$
\[
\begin{array}{ccc}
(100\times0.1) & (50\times0.1) & 0 \\
10 & 5 & 0 \\
5 & 0 & 5 \\
\end{array}
\]

\[ \text{pH} = \text{pKa} + \log \frac{C_S}{C_a} \]

\[ \text{pH} = 5 + \log \frac{5}{5} \]

\[ \text{pH} = 5 \]

d) when adding 80ml of NaOH:

\[ \text{CH}_3\text{COOH} + \text{NaOH} \rightleftharpoons \text{CH}_3\text{COONa} + \text{H}_2\text{O} \]

\[
\begin{array}{ccc}
(100\times0.1) & (80\times0.1) & 0 \\
10 & 8 & 0 \\
2 & 0 & 8 \\
\end{array}
\]

\[ \text{pH} = \text{pKa} + \log \frac{C_S}{C_a} \]

\[ \text{pH} = 5 + \log \frac{8}{2} \]

\[ \text{pH} = 5.6 \]

e) at end point, when adding 100ml of NaOH:

at end point \( \text{m.mole of NaOH} = \text{m.mole of CH}_3\text{COOH} \)
Cs = \frac{10}{100+100} = \frac{10}{200} = 0.05N

Because of the salt is derived from weak acid and strong base, therefore,

\[ \text{pH} = \frac{1}{2} (pK_w + pK_a + \log Cs) \]

\[ \text{pH} = \frac{1}{2} (14 + 5 + \log 0.05 ) \]

\[ \text{pH} = 8.85 \]

f) when adding 120ml of NaOH:

\[ \text{CH}_3\text{COOH} + \text{NaOH} \rightleftharpoons \text{CH}_3\text{COONa} + \text{H}_2\text{O} \]

\[
\begin{array}{c|c|c}
100 \times 0.1 & 120 \times 0.1 & 0 \\
10 & 12 & 0 \\
0 & 2 & 8 \\
\end{array}
\]

\[ [\text{OH}^-] = \frac{2}{100+120} = \frac{2}{220} = 9.1 \times 10^{-3} \]

\[ \text{pOH} = - \log [\text{OH}^-] = - \log 9.1 \times 10^{-3} = 2.04 \]

\[ \text{pH} = 14 - 2.04 = 11.96 \]

**Note 1: Effect of concentration:**

The concentration of analyte and reagent are affects on neutralization titration curves. For example:

The titration of acid or base with 0.1M (curve A) shows that pH change at equivalence point region is large, while the titration with 0.001M shows that the pH change is less but still pronounced (curve B).
**Note 2: Effect of acid:**

Figure below shows the effect of acid conc. measured in $Ka$ value on neutralization curves. at equivalence point region, when $Ka$ is decreased the range of pH change is decrease too. and the titration can be done if $Ka = 10^{-6}$ or more. while when $Ka < 10^{-6}$ the titration cannot be done, because it cannot using any types of indicators.