Session-2018-19

GLA UNIVERSITY
MATHURA
Recognised by UGC Under Section 2(f)
ऋते ज्ञानान्न मुक्तिः
Accredited with A Grade by NAAC

Module-1

Theory of Volumetric and Gravimetric Analysis

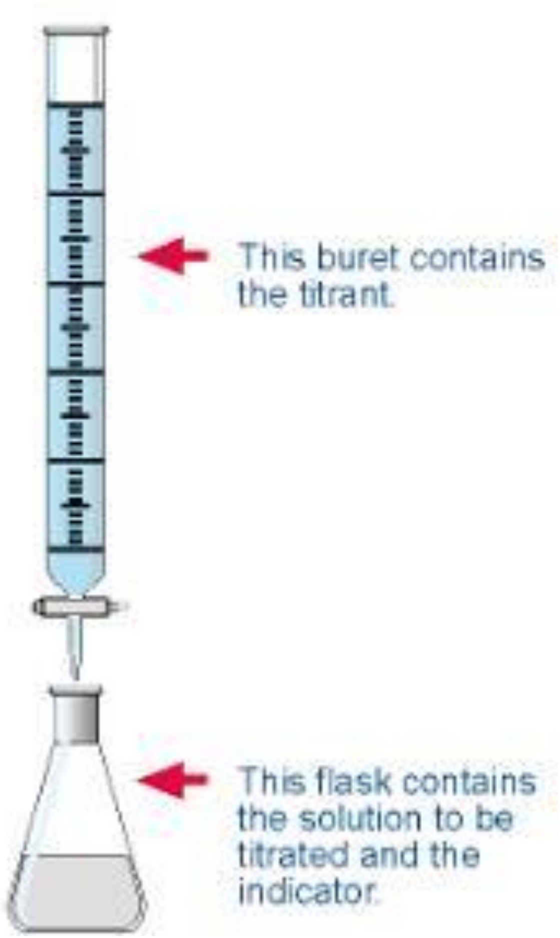
Lecture-6

Presented by:

Dr. Pankaj Kumar Rastogi

Assistant Professor

Objective



- ☐ **Acid base Indicators**
- ☐ **Theory of indicators**

NEUTRALISATION INDICATORS (Acid base indicator)

- A large number of substances, called neutralisation or acid-base indicators, change colour according to the hydrogen-ion concentration of the solution.

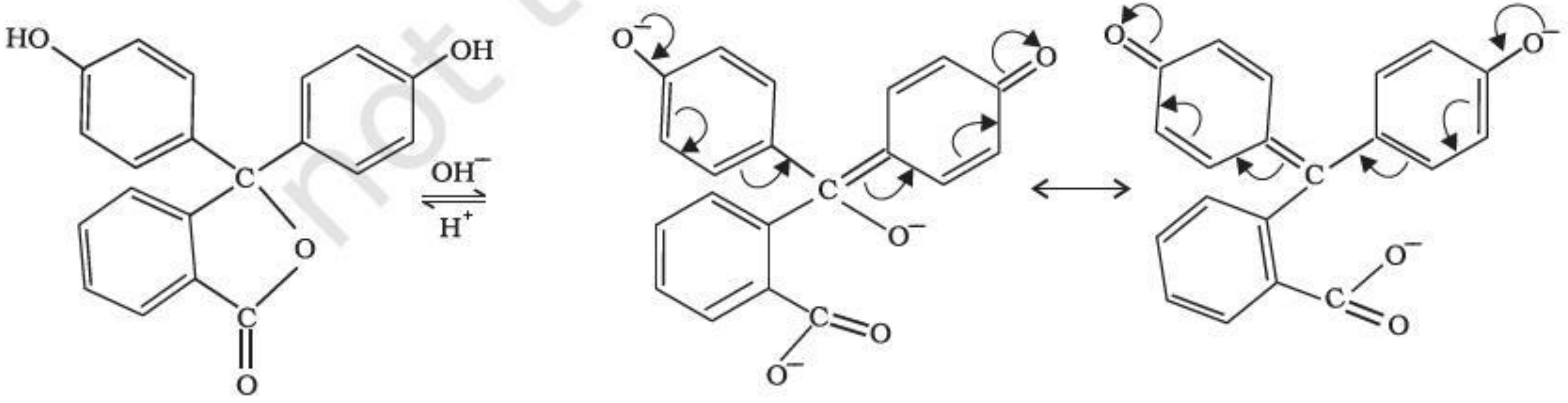
- Acid base indicators are sensitive to pH change. For most acid base titrations, it is possible to select indicators which exhibit colour change at pH close to the equivalence point. We will discuss here about only two indicators – phenolphthalein and methyl orange.

Phenolpthalein

Phenolpthalein is a weak acid, therefore it does not dissociate in the acidic medium and remains in the unionised form, which is colourless.

$HPh \rightleftharpoons$	$H^+ + Ph^-$
Unionised	Ionised
Colourless	Pink

Ionised and unionised forms of phenolphthalein are given below :



(Colourless in acid)

(Pink in alkali)

Fig. 6.1 : Phenolphthalein in acidic and basic medium

colour changes are believed to be due to structural changes, including the

production of quinonoid and resonance forms

$$HPh \rightleftharpoons H^+ + Ph^-$$

$$NaOH \longrightarrow Na^+ + OH^-$$

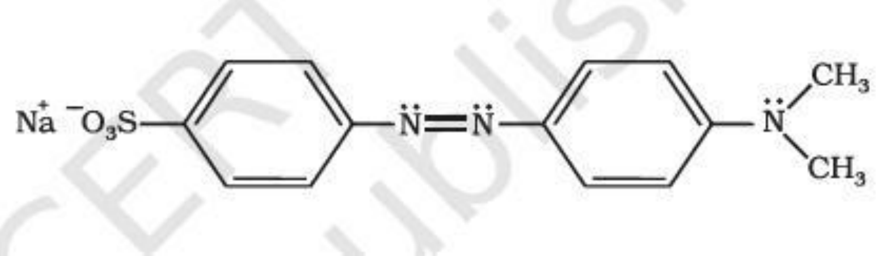
$$H^+ + OH^- \longrightarrow H_2O$$

- In the acidic medium, equilibrium lies to the left.
- In the alkaline medium, the ionisation of phenolphthalein increases considerably due to the constant removal of H_+ ions released from HPh by the OH_- ions from the alkali. So the concentration of Ph_- ion increases in the solution, which imparts pink colour to

the solution.

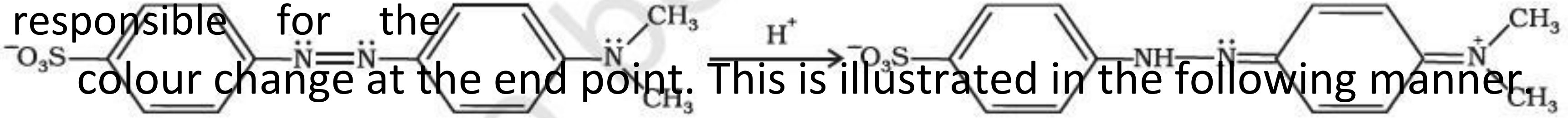
Methyl orange

Methyl orange is a weak base and is yellow in colour in the unionised form. Sodium salt of methyl orange is represented as follows:



- The anion formed from the indicator is an active species, which on accepting a proton (i.e acting as Bronsted Lowry base) changes from the benzenoid form to the quinonoid form.

- The quinonoid form is deeper in colour and thus is responsible for the colour change at the end point. This is illustrated in the following manner.



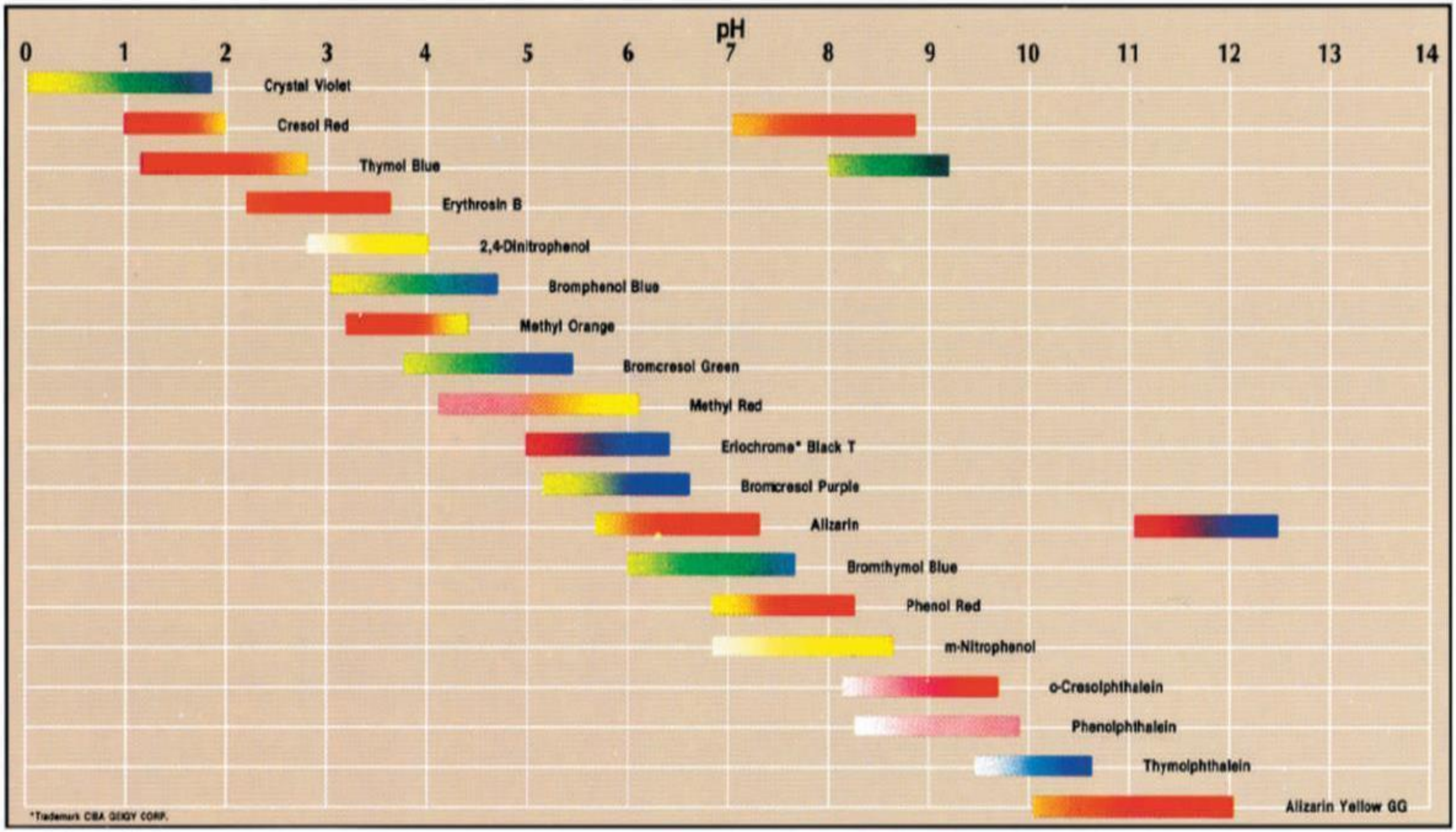
Benzenoid form of the anion
(Yellow in colour)

Quinonoid form of the anion
(Pinkish red in colour)

(Bronsted-Lowry base)

Structures of Methyl orange

Some Acid/Base Indicators and Their Color Changes



Theory of indicator action:

- The first useful theory of indicator action was suggested by W. Ostwald based upon the concept that indicators in general use are very weak organic acids or bases.
- The colour changes are believed to be due to structural changes including the production of quinonoid and resonance forms.

These indicators is that the change from a predominantly 'acid' colour to a predominantly 'alkaline' colour is not sudden and abrupt, but takes place within a small interval of pH (usually about two pH units) termed the colour-change interval of the indicator.

Take an example of $\rightleftharpoons$

Phenolpthalein

The equilibrium between the acidic form In, and the basic form

In, may be expressed as:

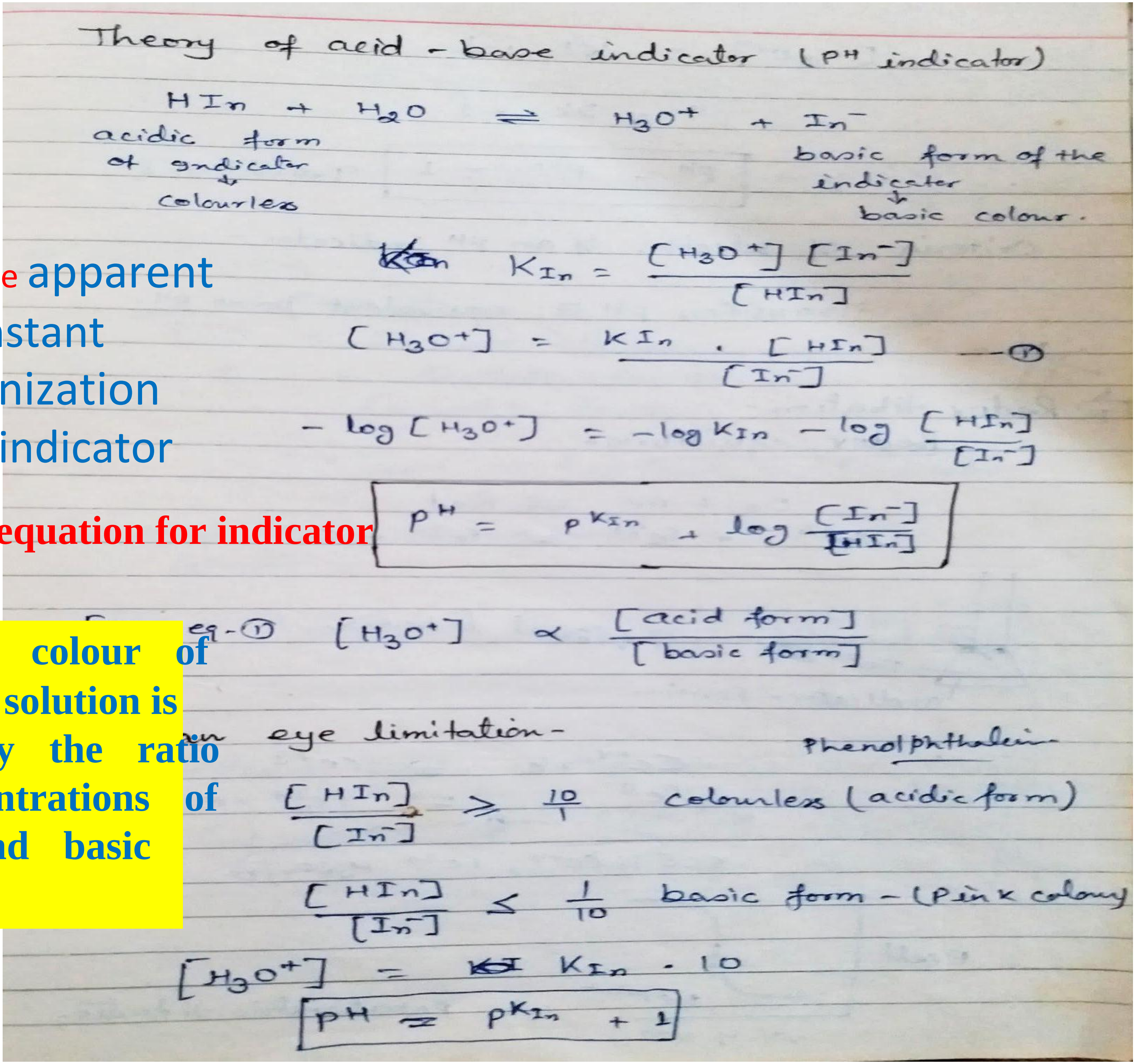
$HIn + H_2O$ $H_3O^+ + In^-$

Acidic form	**Basic form**
Colorless	**Color**

pK$_{In}$, is termed the apparent indicator constant
And Kin is ionization constant for indicator

Handerson equation for indicator

The observed colour of an indicator in solution is determined by the ratio of the concentrations of the acidic and basic forms.



Theory of acid - base indicator (pH indicator)

$$HIn + H_2O \rightleftharpoons H_3O^+ + In^-$$

acidic form of indicator ↓ colourless

basic form of the indicator ↓ basic colour.

$$\cancel{Kin} \quad K_{In} = \frac{[H_3O^+][In^-]}{[HIn]}$$

$$[H_3O^+] = K_{In} \cdot \frac{[HIn]}{[In^-]} \quad — ①$$

$$-\log[H_3O^+] = -\log K_{In} - \log\frac{[HIn]}{[In^-]}$$

$$\boxed{pH = pK_{In} + \log\frac{[In^-]}{[HIn]}}$$

eq-① $[H_3O^+] \propto \frac{[\text{acid form}]}{[\text{basic form}]}$

an eye limitation -

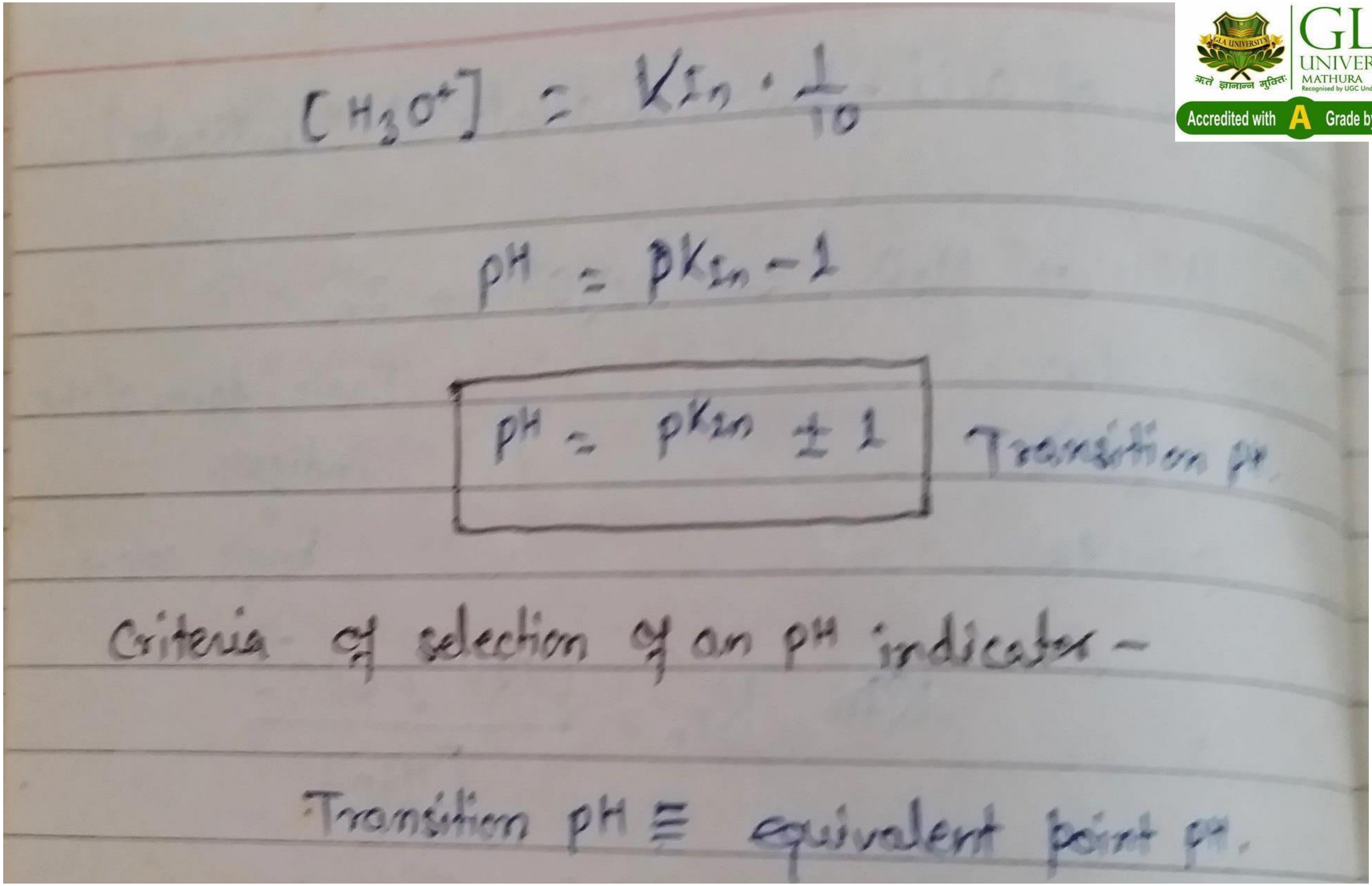
Phenolphthalein

$\frac{[HIn]}{[In^-]} \geq \frac{10}{1}$ colourless (acidic form)

$\frac{[HIn]}{[In^-]} \leq \frac{1}{10}$ basic form - (Pink colour)

$$[H_3O^+] = \cancel{KI} \; K_{In} \cdot 10$$

$$\boxed{pH = pK_{In} + 1}$$



$$[H_3O^+] = K_{In} \cdot \frac{1}{10}$$

$$pH = pK_{In} - 1$$

$$\boxed{pH = pK_{In} \pm 1}$$ Transition pH

Criteria of selection of an pH indicator –

Transition pH ≡ equivalent point pH.

The colour-change interval is accordingly pH = pK;, I 1, i.e. over approximately two pH units. Within this range the indicator will appear to change from one

$$\boxed{pH = pK_{In} + \log \frac{[In^-]}{[HIn]}}$$

dissociated
undissociated

another example,

weak basic indicator (InOH)

$$InOH \rightleftharpoons In^+ + OH^-$$

By applying Law of mass action

$$K_{In_b} = \frac{[In^+][OH^-]}{[InOH]}$$

$$[OH^-] = \frac{K_{In_b} \cdot [InOH]}{[In^+]}$$

$$-\log[OH^-] = -\log\left(K_{In_b} \times \frac{[InOH]}{[In^+]}\right)$$

$$-\log[OH^-] = -\log K_{In_b} + \left(-\log \frac{[InOH]}{[In^+]}\right)$$

$$\boxed{pOH = pK_{In_b} + \log \frac{[In^+]}{[InOH]}}$$

dissociated
undissociated

Colour of the indicator depends upon the ratio of the dissociated ion and undissociated indicator.

For example,

$$\left.\begin{array}{l} HCl \rightarrow H^+ + Cl^- \\ HIn \rightleftharpoons H^+ + In^- \end{array}\right\} \text{Not ionized}$$

Common ion

$$\left.\begin{array}{l} HIn \rightleftharpoons H^+ + In^- \\ NaOH \rightarrow Na^+ OH^- \end{array}\right\} \text{Ionized}$$

Similarly,

Common ion

$$\left.\begin{array}{l} InOH \rightleftharpoons In^+ + OH^- \\ NaOH \rightarrow Na^+ + OH^- \end{array}\right. \text{not ionized}$$

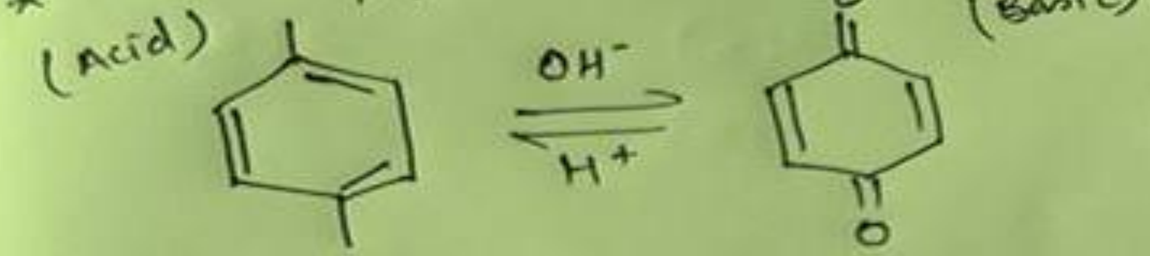
$$\left.\begin{array}{l} InOH \rightleftharpoons In^+ + OH^- \\ HCl \rightarrow H^+ + Cl^- \end{array}\right\} \text{ionized}$$

Resonance theory of Indicators

- Also known as Quinonoid theory
- According to this theory Acid-base indicators are present in two tautomeric forms:—

  One in acidic medium and
  one in basic medium

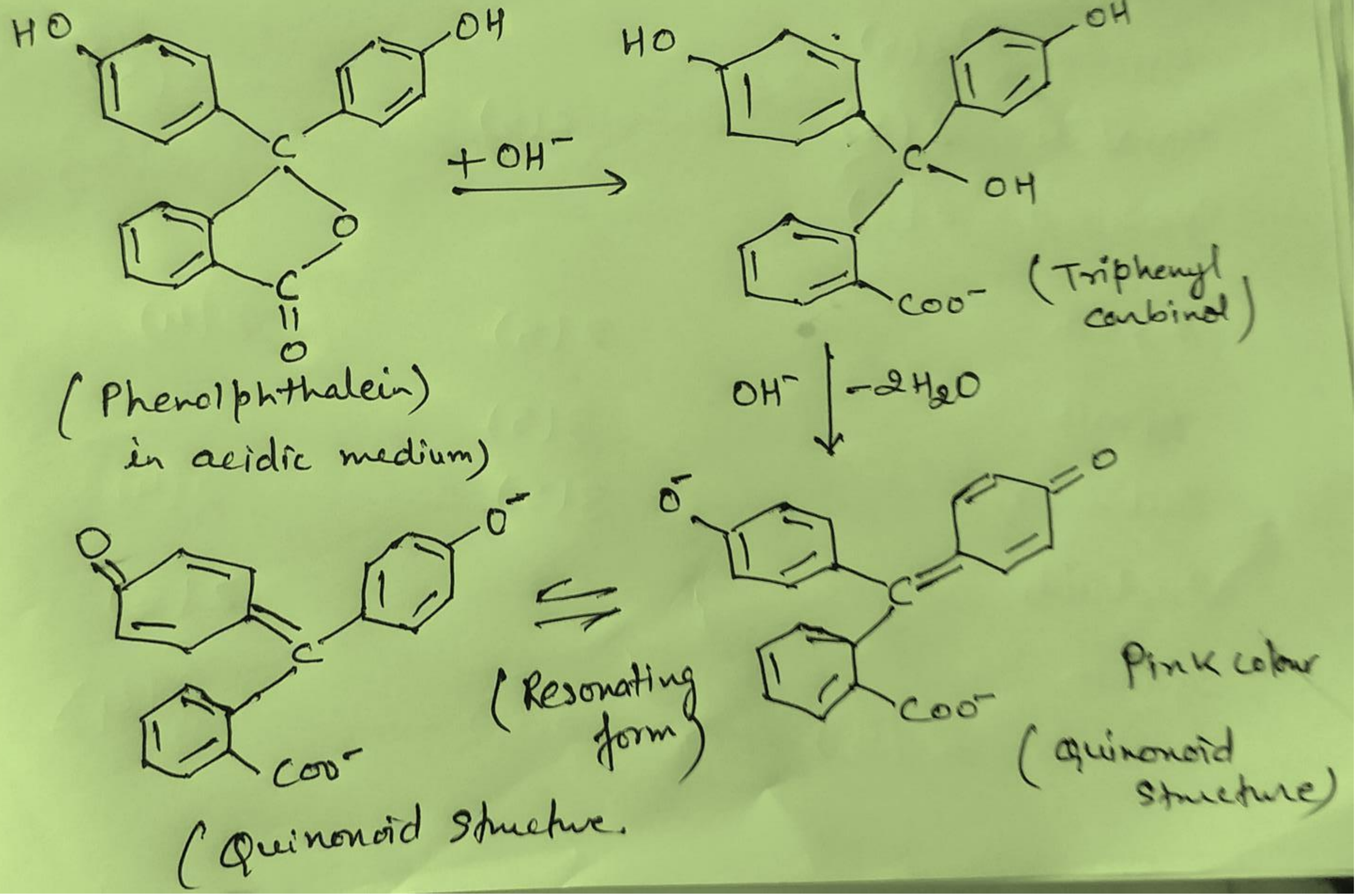
- For example,



(Bengenoid form) (Quinonoid form)

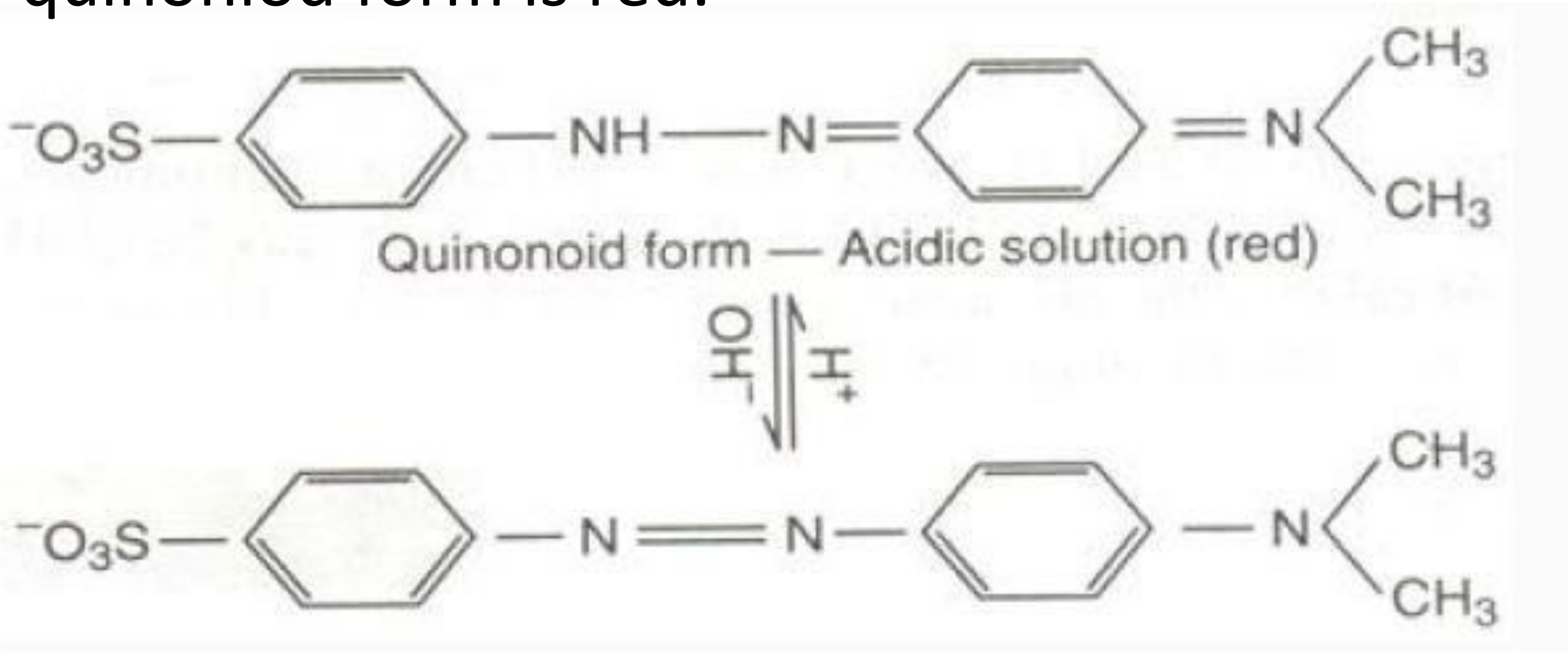
- These two forms are present in the equilibrium
- They will show colour change due to the interconversion of one tautomeric form into other in Acidic and basic medium.

⇒ Take the example of phenolphthalein.



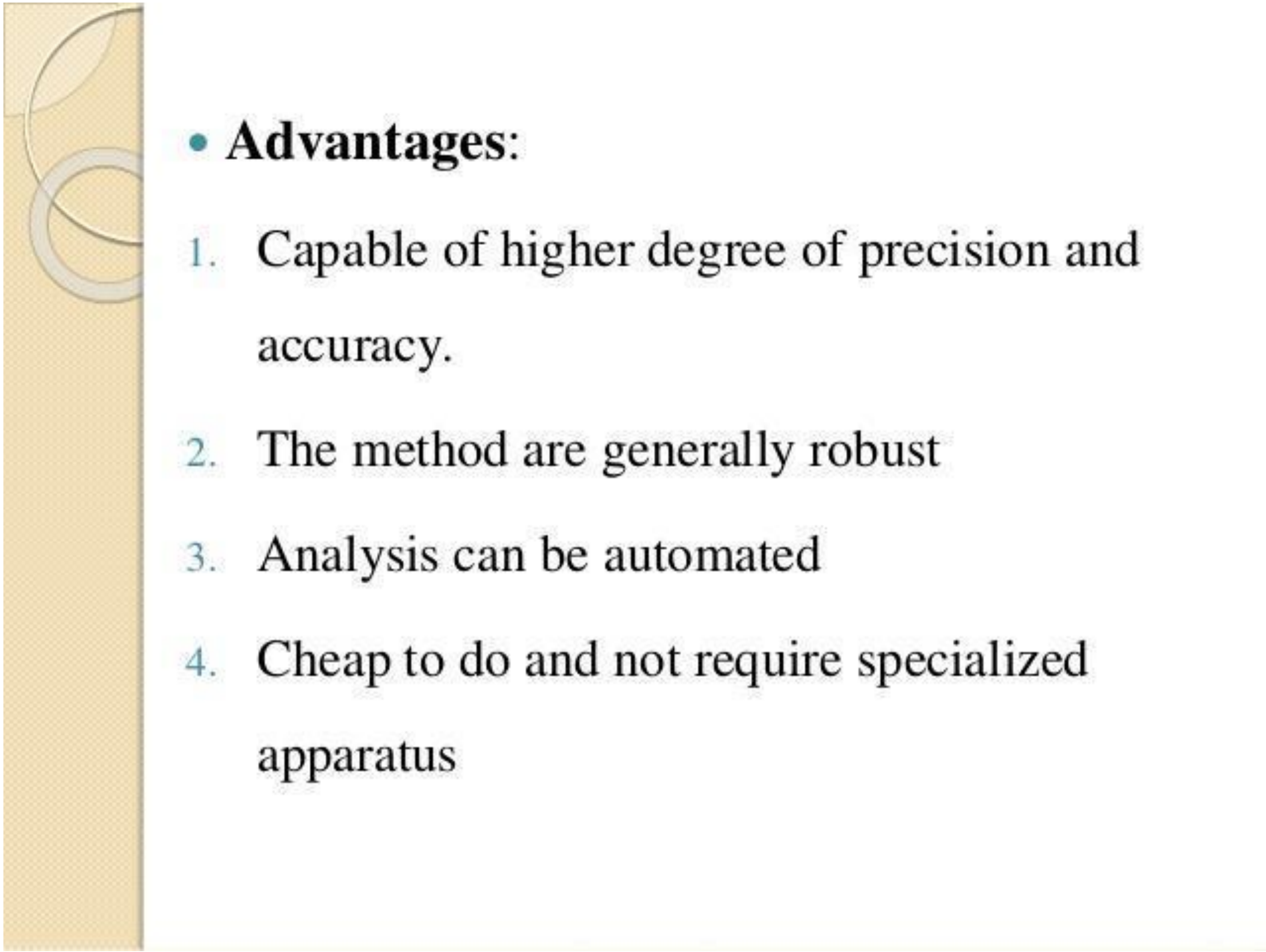
Methyl orange has quinonoid form in acidic solution and benzenoid form in alkaline solution.

The color of benzenoid form is yellow while that of quinoniod form is red.



Indicator	pH Range	Colour of Acidic Solution	Colour of Basic Solution
Methyl Orange	3.2-4.5	Orange	Yellow
Methyl Red	4.4 – 6.5	Red	Yellow
Bromothymol blue	6.0 -7.8	Yellow	Blue
Phenolphthalein	8.3- 10.0	Colourless	Pink
Alizarin Yellow	10.1 – 12.1	Yellow	Red
Litmus	5.5-7.5	Red	Blue
Phenol red	6.8-8.4	Yellow	Red

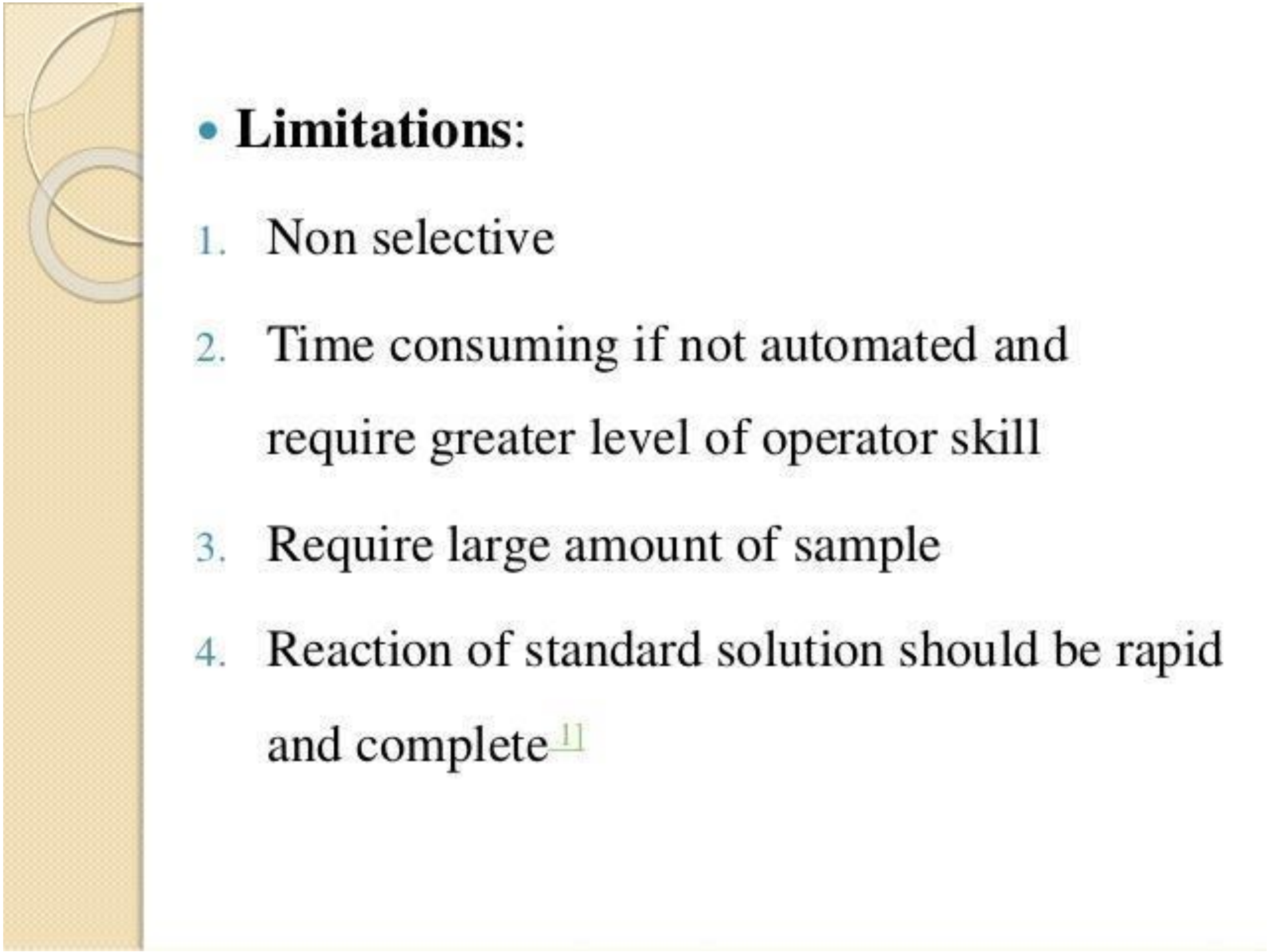
Advantages of titration



- **Advantages**:

1. Capable of higher degree of precision and accuracy.
2. The method are generally robust
3. Analysis can be automated
4. Cheap to do and not require specialized apparatus

Limitations of titration



- **Limitations**:

1. Non selective
2. Time consuming if not automated and require greater level of operator skill
3. Require large amount of sample
4. Reaction of standard solution should be rapid and complete[1]