Analytical chemistry

Lecture №15

ACID–BASE TITRATIONS PART I

An acid–base titration involves a **neutralization reaction in which an acid is reacted** with an equivalent amount of base.

Acid–base titrations are also called ***prototropic titrations*** *or* ***acidimetric*** *and* ***alkalimetric*** *titrations. According to the IUPAC, the term acidimetric titration" is reserved* for the titration of a base with a standard *acid* solution. It is the opposite of the term "alkalimetric titration."

$$HCl + NaOH \rightarrow NaCl + H_2O$$

$$H_3O^+ + OH^- \rightarrow 2\,H_2O$$

$$Na_2CO_3 + HCl \rightarrow NaHCO_3 + NaCl$$

$$H_3O^+ + CO_3^{2-} \rightarrow HCO_3^- + H_2O$$

Standard Solutions

The standard reagents used in acid/base titrations are always strong acids or strong bases, most commonly HCl, $HClO_4$, H_2SO_4, NaOH, and KOH. Weak acids and bases are never used as standard reagents because they react incompletely with analytes.

Standard solutions of *acids* are prepared by diluting concentrated hydrochloric, perchloric, or sulfuric acid.

Standard solutions of *bases* are usually prepared from solid sodium, potassium, and barium hydroxides.



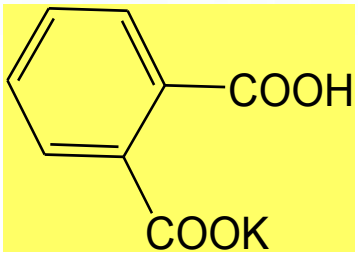

Primary Standard substances for *acids*

$Na_2B_4O_7 \cdot 10\ H_2O$ **Borax**

$NaHCO_3$

$Na_2C_2O_4$

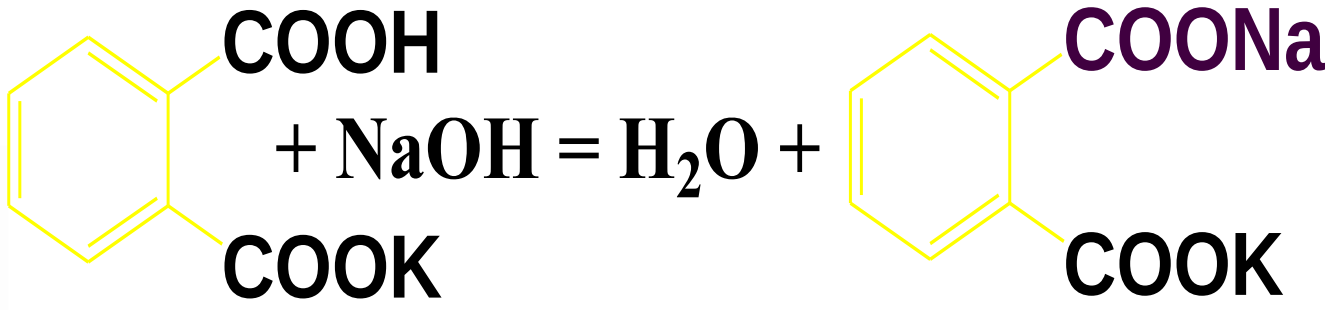
Standard substances for *bases*



$KHC_8H_4O_4$

$H_2C_2O_4 \cdot 2H_2O$

C_6H_5COOH



Sodium tetraborate decahydrate

$$Na_2B_4O_7 + 2HCl + 5\ H_2O = 2NaCl + 4\ H_3BO_3$$

$$Na_2CO_3 + 2HCl = 2NaCl + H_2CO_3$$

$$2NaOH + H_2C_2O_4 = 2H_2O + Na_2C_2O_4$$

$$NaOH + C_6H_5COOH = H_2O + C_6H_5COONa$$

These bases cannot be obtained in primary-standard purity, and so, all must be standardized after they are prepared.

Absorption of carbon dioxide by a standardized solution of sodium or potassium hydroxide leads to a negative systematic error in analyses in which an indicator with a basic range is used;

Solutions of bases should be stored in polyethylene bottles rather than glass because of the reaction between bases and glass.

Selected Primary Standards for the Standardization of Strong Acid and Strong Base Titrants

Standardization of Acidic Titrants

Primary Standard	Titration Reaction	Comment
Na_2CO_3	$Na_2CO_3 + 2H_3O^+ \rightarrow H_2CO_3 + 2Na^+ + 2H_2O$	a
TRIS	$(HOCH_2)_3CNH_2 + H_3O^+ \rightarrow (HOCH_2)_3CNH_3^+ + H_2O$	b
$Na_2B_4O_7$	$Na_2B_4O_7 + 2H_3O^+ + 3H_2O \rightarrow 2Na^+ + 4H_3BO_3$	

Standardization of Basic Titrants

Primary Standard	Titration Reaction	Comment
$KHC_8H_4O_4$	$KHC_8H_4O_4 + OH^- \rightarrow K^+ + C_8H_4O_4^{2-} + H_2O$	c
C_6H_5COOH	$C_6H_5COOH + OH^- \rightarrow C_6H_5COO^- + H_2O$	d
$KH(IO_3)_2$	$KH(IO_3)_2 + OH^- \rightarrow K^+ + 2IO_3^- + H_2O$	

[a]The end point for this titration is improved by titrating to the second equivalence point, boiling the solution to expel CO_2, and retitrating to the second equivalence point. In this case the reaction is

$$Na_2CO_3 + 2H_3O^+ \rightarrow CO_2 + 2Na^+ + 3H_2O$$

[b]TRIS stands for *tris*-(hydroxymethyl)aminomethane.

[c]$KHC_8H_4O_4$ is also known as potassium hydrogen phthalate, or KHP.

[d]Due to its poor solubility in water, benzoic acid is dissolved in a small amount of ethanol before being diluted with water.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Detection of the End Point: Indicators

There are two major types of end points that are widely used in neutralization titrations. The first is a visual end point based on indicators. The second is a *potentiometric end point in which the potential of a* glass/calomel electrode system is determined with a pH meter or another voltagemeasuring device. The measured voltage is directly proportional to pH.

An acid/base indicator is a weak organic acid or a weak organic base whose undissociated form differs in color from its conjugate base or its conjugate acid form.

$$\underset{\text{acid color}}{HIn} + H_2O \rightleftharpoons \underset{\text{base color}}{In^-} + H_3O^+$$

$$\underset{\text{base color}}{In} + H_2O \rightleftharpoons \underset{\text{acid color}}{InH^+} + OH^-$$

The color of the ionized form is markedly different from that of the nonionized form.

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

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

The human eye is not very sensitive to color differences in a solution containing a mixture of HIn and In^-, particularly when the ratio $[HIn]/[In^-]$ is greater than about 10 or smaller than about 0.1.

HIn, exhibits its pure acid color when

$$\frac{[HIn]}{[In^-]} \geq \frac{10}{1}$$

and its base color when

$$\frac{[HIn]}{[In^-]} \leq \frac{1}{10}$$

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

$$[H_3O^+] = 10K_a$$

$$[H_3O^+] = 0.1\,K_a$$

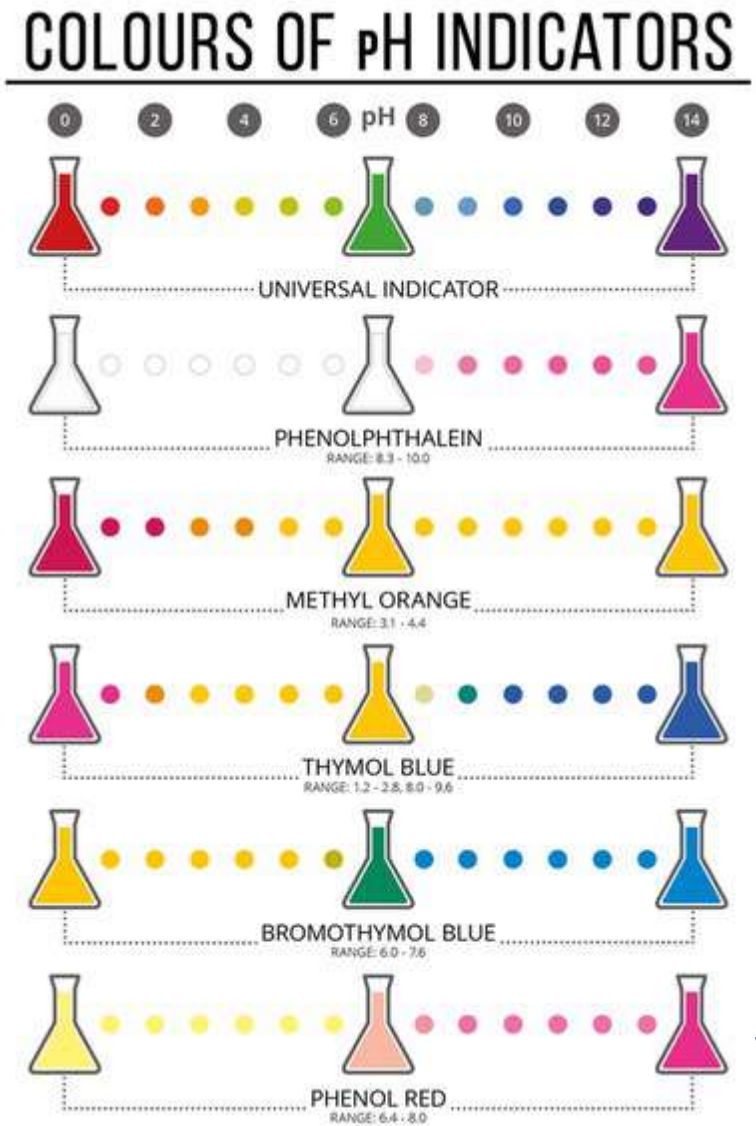
$$\text{pH(acid color)} = -\log(10K_a) = pK_a + 1$$

$$\text{pH(basic color)} = -\log(0.1K_a) = pK_a - 1$$

$$\text{indicator pH range} = pK_a \pm 1$$

Choose an indicator with a pK_a *near the equivalence point pH.*

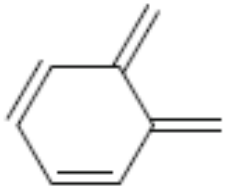
Origin of the Color Change



The appearance of the color or its change is due to structural changes of the indicator after the capture or the loss of a proton. The new structure is endowed with an increase or a decrease in its resonance possibilities with respect to the initial one. This is the origin of the color change.

In most cases, but not necessarily, the coloration change due to the medium's acidity is related to the appearance of a p-quinonic structure a or, more rarely, to that of an o-**quinonic** structure b:

a

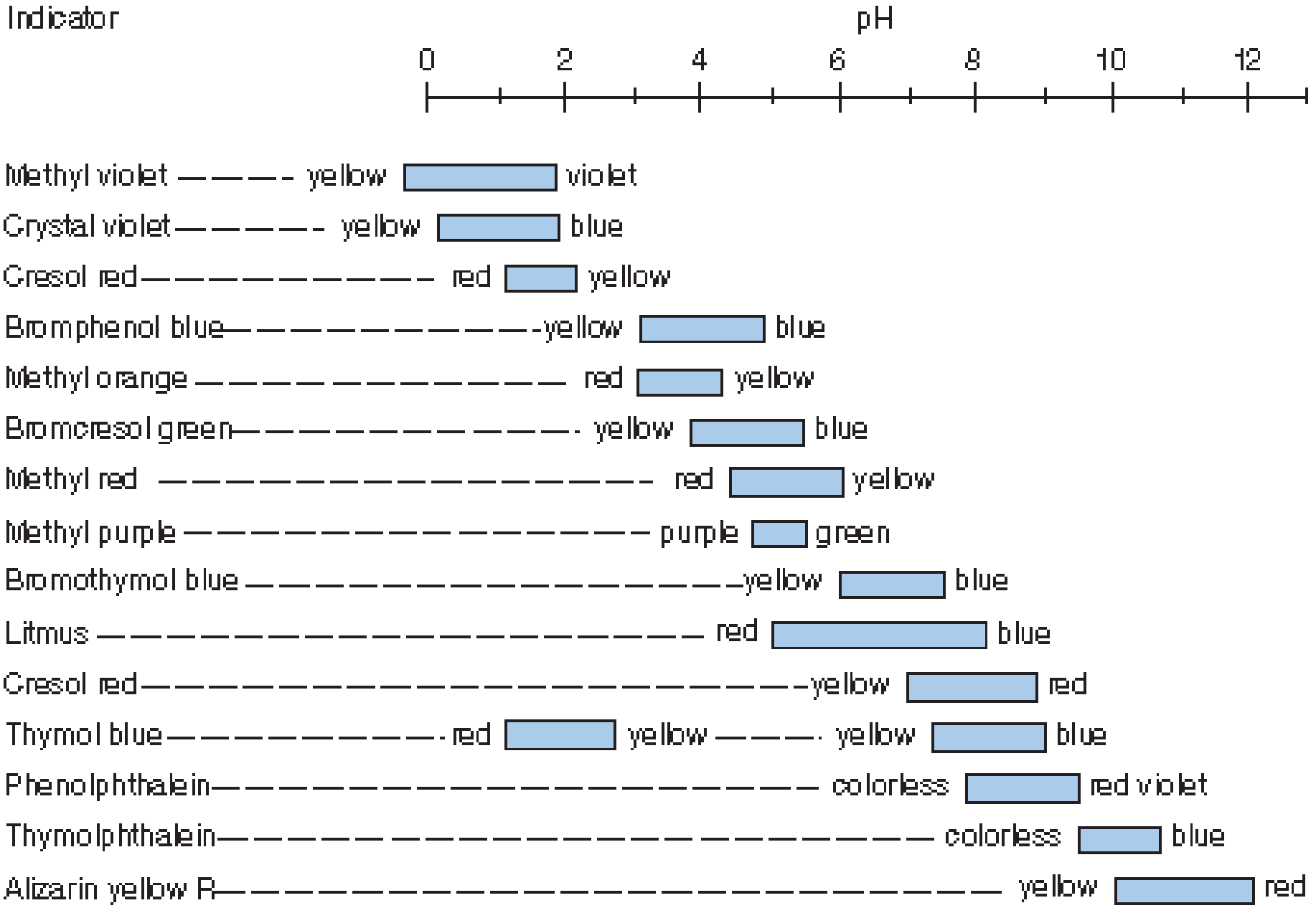


b

methyl orange (helianthin), whose bicolor indicator is the sodium salt of the 4-dimethylaminoazobenzen-4-sulfonic acid

phenolphthalein, which is a unicolor indicator

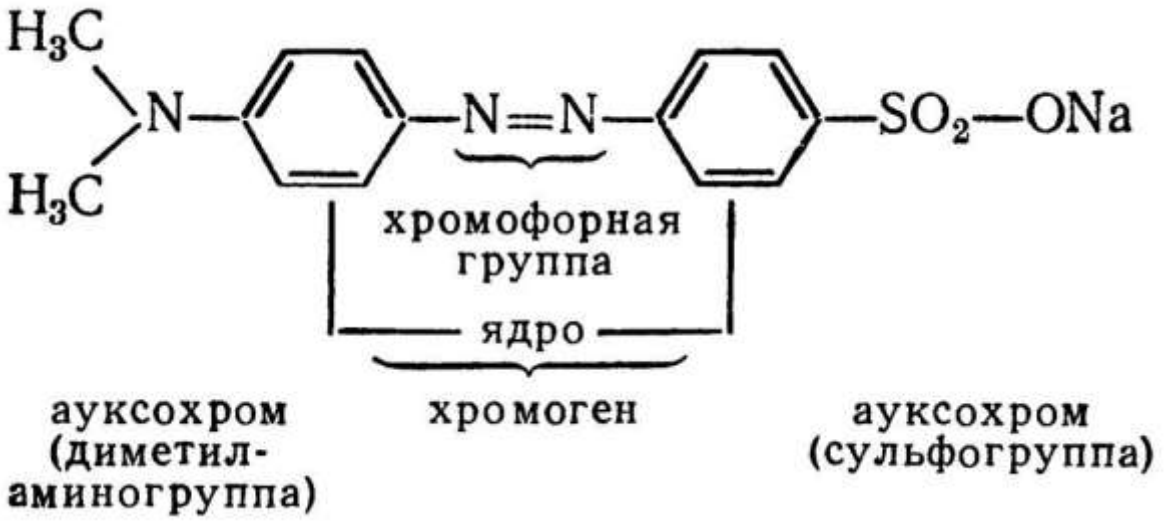
pH transition ranges and colors of some common indicators



From the simple qualitative point of view, we have known for more than a century that colored molecules bring characteristic atom groups called ***chromophores*** *(part* responsible for bringing the color). They are unsaturated groups, such as

–N = N – (azo)	– CH = N – (imino),
–N = O (nitroso)	> C = S (thiocarbonyl),
$-NO_2$ (nitro)	> C = O (carbonyl),
–N(O) = N – (azoxy)	> C = C < (ethenyl).

Sometimes the sole presence of one of these groups is not sufficient to confer a color to the molecule that brings it. In order to develop a color, it must possess a supplementary group called an ***auxochrome*** *(increasing the color).*

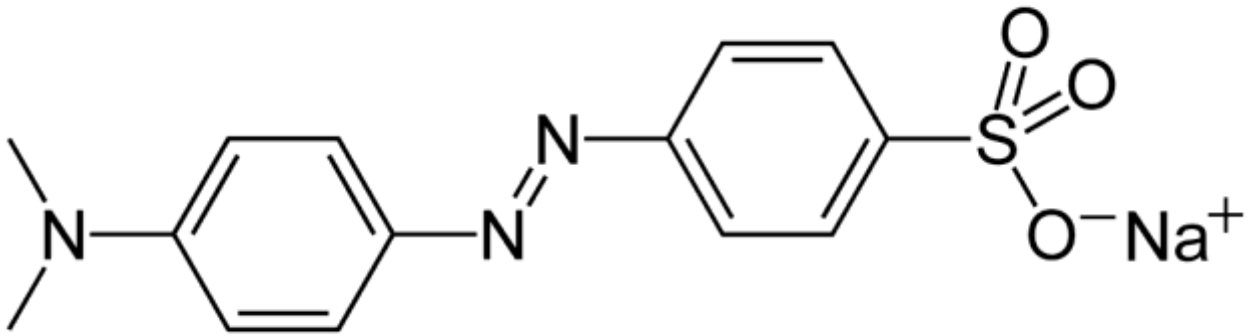


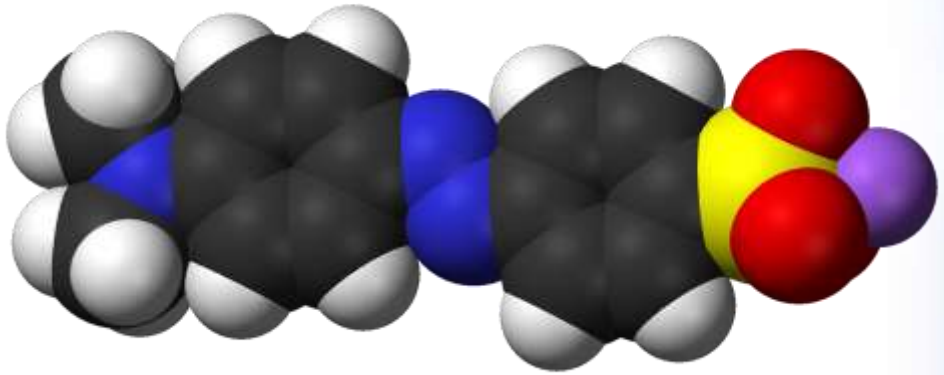
Methyl orange (helianthin), whose bicolor indicator is the sodium salt of the 4-dimethylaminoazobenzen-4-sulfonic acid.

pK_a = 3,36

pT ≈ 4

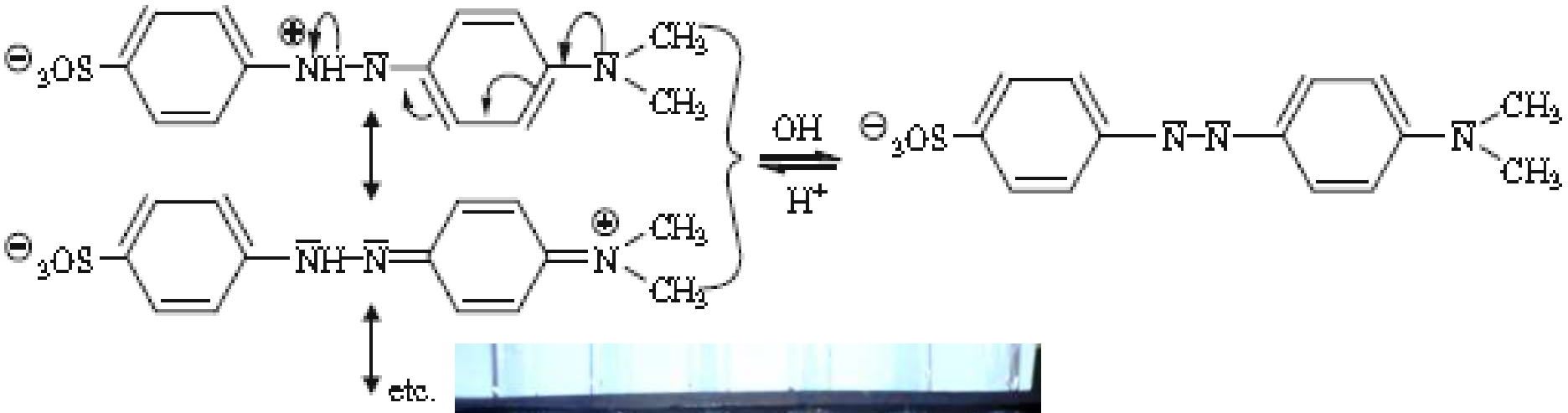
pH range
3,1 – 4,6





pT - titration indicator is the pH value in the range of coloring change at which the most drastic change of the color is observed.

methyl orange



acidic form (red)

basic form (yellow)(azoic).

The acidic form (red) exhibits two principal limit forms, one with an azo rest and the other one with a p-quinonediimine rest. The basic form (yellow) presents a principal limit form with an azo structure.

Phenolphthalein, unicolor indicator. It is a derivative of triphenylmethane. Its acidic form, symbolized by H_2In, is **colorless**.

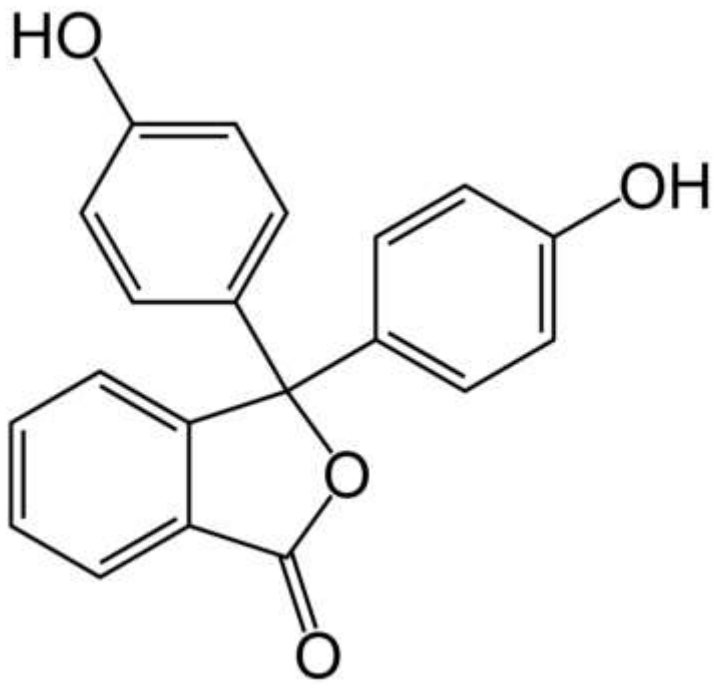
pT ≈ 9

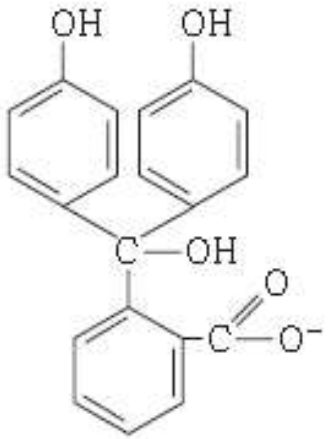
pH range
8,2 – 9,8

pK_{a1} = 8,83

pK_{a2} = 9,32

pK_{a3} = 11,73





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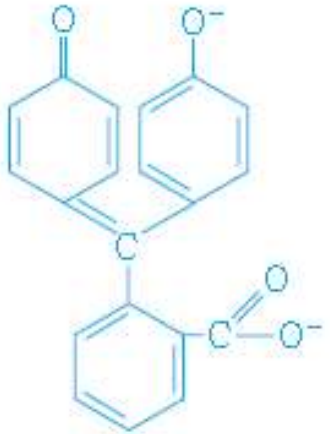
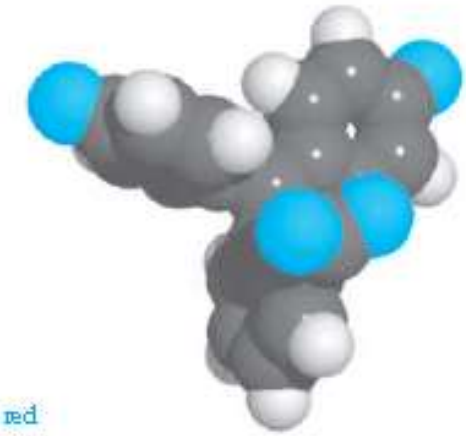
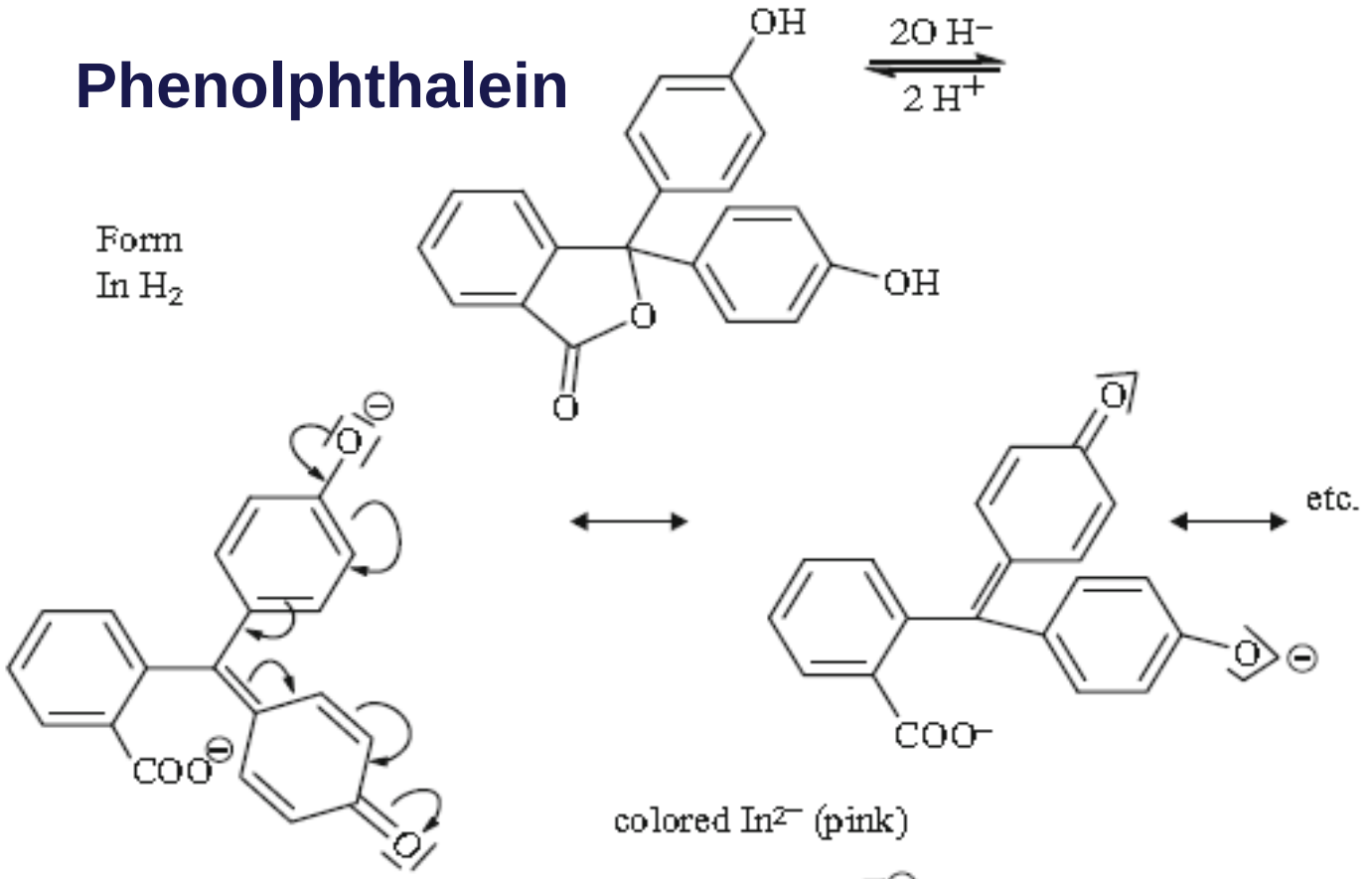


+

H_3O^+

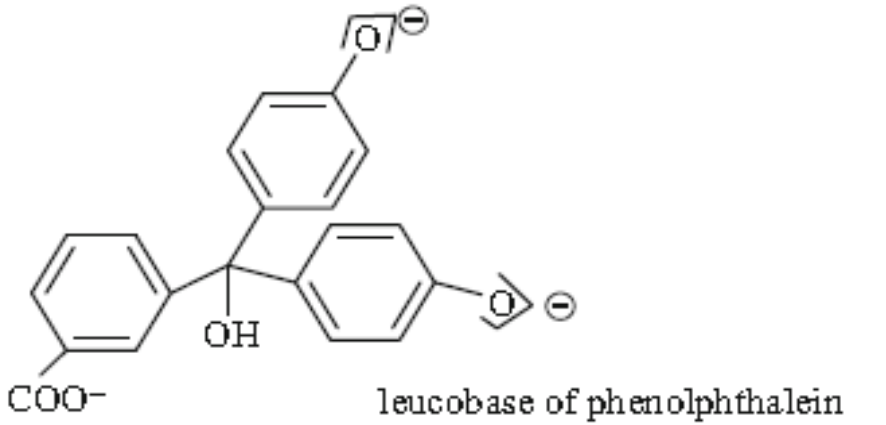


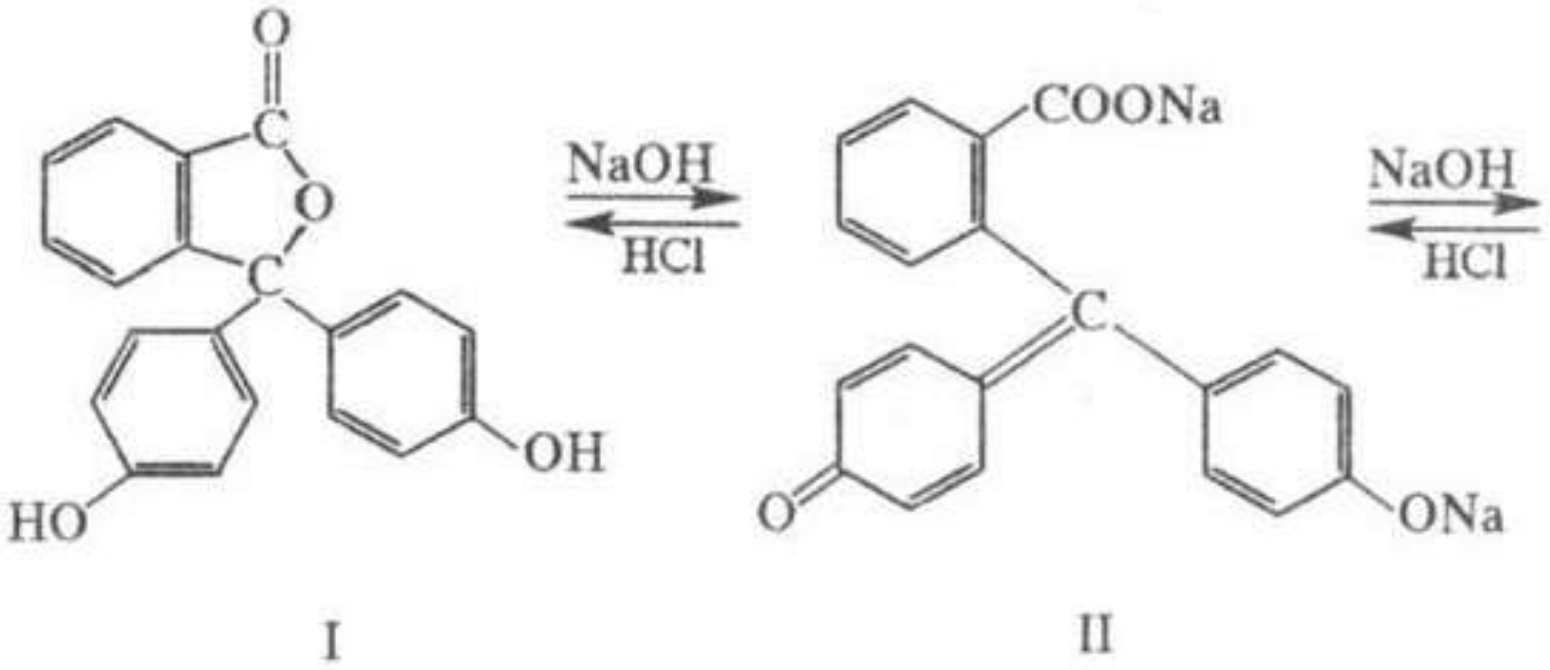
Phenolphthalein



It can lose two protons almost equally easily since the ionization constants of both phenol functions are very close to each other. The pink form In^{2-} is then obtained.

both principal limit forms of In^{2-} are p-quinonic. In sufficiently concentrated alcoholic alkali, the pink form adds a hydroxide ion, yielding another colorless form, InOH.





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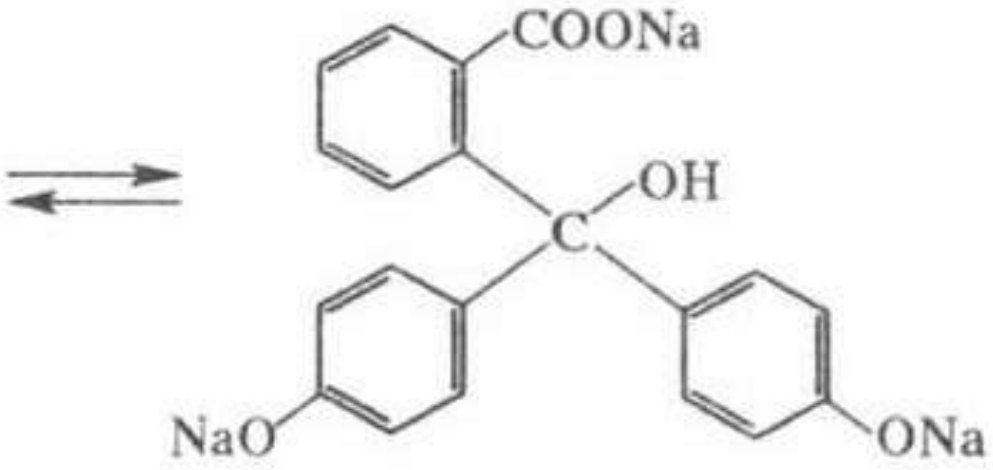


III

We can distinguish among:

• **bicolor indicators** (e.g., methyl orange).

• **unicolor indicators** (e.g., phenolphthalein).

• **mixed indicators**, which are mixtures of two indicators. They can be

– a mixture of two pH-sensitive indicators, for example, the mixture of phenolphthalein and 1-naphtolphtalein in a suitable proportion for the titration of phosphoric acid to the diprotic stage (equivalence point pH=8.7).

– a mixture of one pH-sensitive indicator and another one that is pH-insensitive.

An example is provided by Tashiri's indicator used for the titration of ammonia solutions by sulfuric acid. It is a mixture of methyl red (pH-sensitive) and methyl blue (pH-insensitive). The color change is from violet (red+blue) for pH*<4.2 to green (yellow+blue) for pH>6.2. At pH=5.5, the color is pink.*

The mixed indicators are used when one wants to obtain a sharp color change over a narrow and selected range of pH.

• **universal or multiple-range indicators**, which are mixtures of several indicators. They permit color changes over a considerable portion of the pH range. They are suitable only for qualitative goals such as the approximate determination of a solution's pH.

Structurally, the indicators form three groups: phthaleins (e.g. phenolphthalein);sulphonephthaleins (e.g. phenol red); and azo compounds (e.g. methyl orange).

Some Important Acid/Base Indicators

Common Name	Transition Range, pH	pK_a*	Color Change†	Indicator Type‡
Thymol blue	1.2–2.8	1.65§	R – Y	1
	8.0–9.6	8.96§	Y – B	
Methyl yellow	2.9–4.0		R – Y	2
Methyl orange	3.1–4.4	3.46§	R – O	2
Bromocresol green	3.8–5.4	4.66§	Y – B	1
Methyl red	4.2–6.3	5.00§	R – Y	2
Bromocresol purple	5.2–6.8	6.12§	Y – P	1
Bromothymol blue	6.2–7.6	7.10§	Y – B	1
Phenol red	6.8–8.4	7.81§	Y – R	1
Cresol purple	7.6–9.2		Y – P	1
Phenolphthalein	8.3–10.0		C – R	1
Thymolphthalein	9.3–10.5		C – B	1
Alizarin yellow GG	10–12		C – Y	2

*At ionic strength of 0.1.

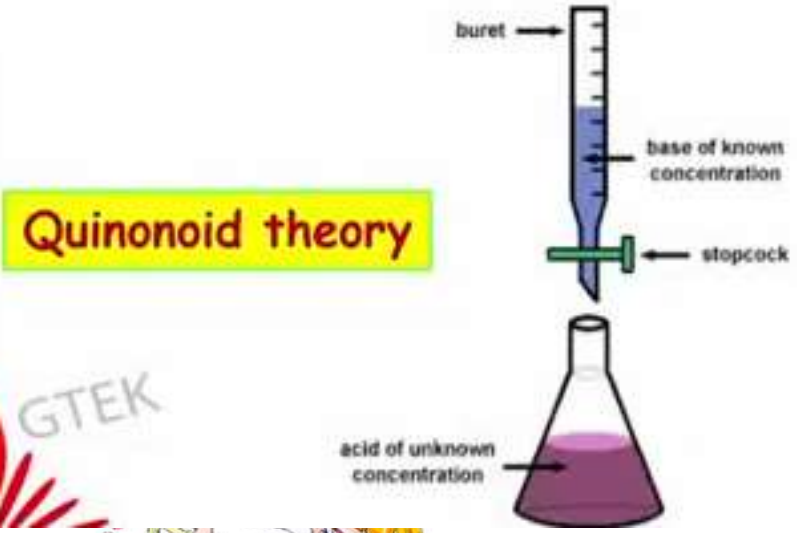
†B = blue; C = colorless; O = orange; P = purple; R = red; Y = yellow.

‡(1) Acid type: $HIn + H_2O \rightleftharpoons H_3O^+ + In^-$; (2) Base type: $In + H_2O \rightleftharpoons InH^+ + OH^-$

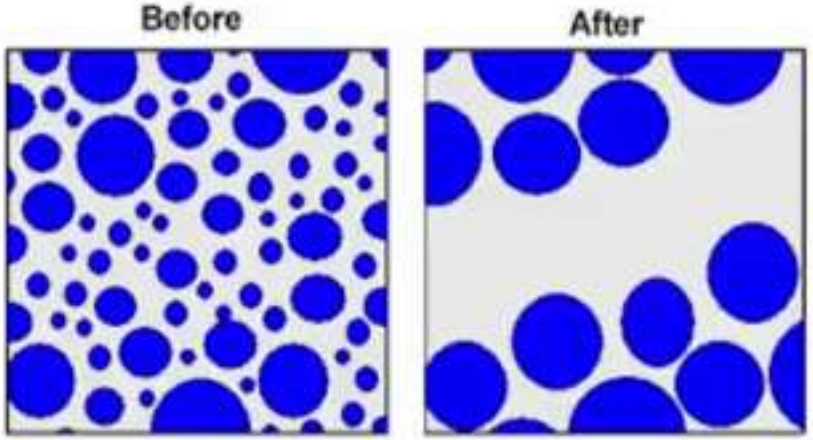
§For the reaction $InH^+ + H_2O \rightleftharpoons H_3O^+ + In$

Theories of indicators

- ✓ There are two theories to explain the function of acid-base indicators
  - ❋ Ostwald's theory
  - ❋ Quinonoid Theory



Quinonoid theory

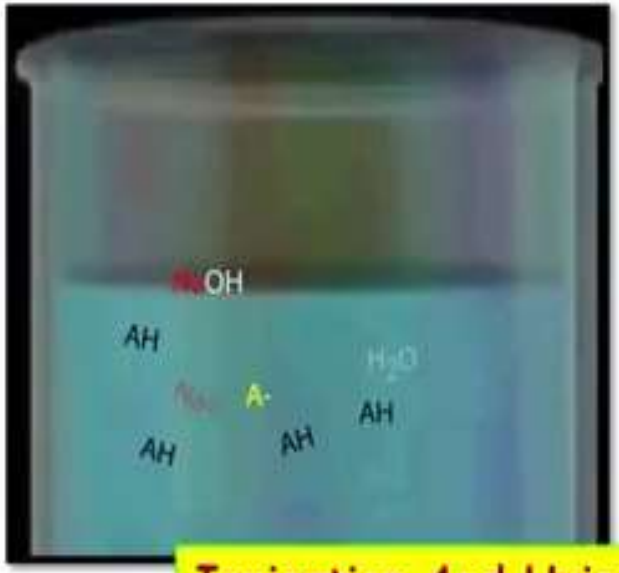


Ostwald Ripening

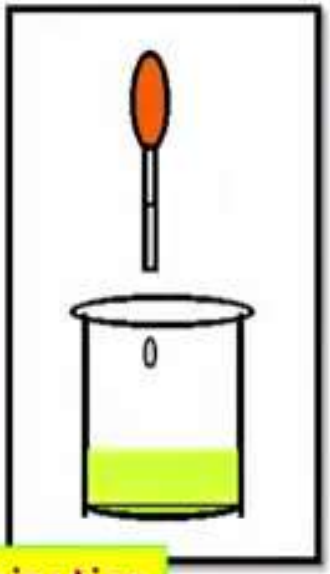
Ostwald's theory

OSTWALD'S THEORY

✓ This theory was proposed by Ostwald's in 1891. It is based on Arrhenius theory.



Ionisation And Unionisation



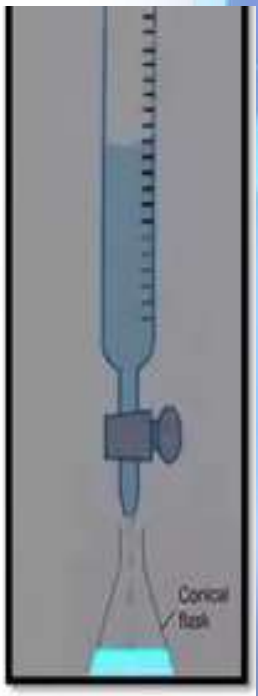
Ostwald's

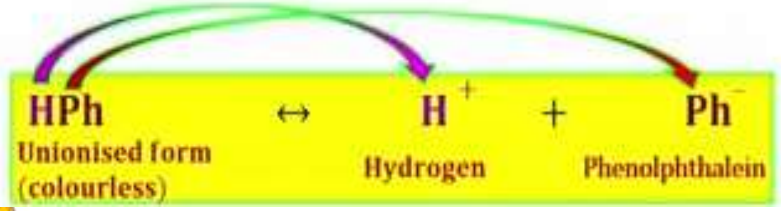
✓ According to this theory, the acid-base indicator is either a weak acid or a weak base.

✓ They are partially ionised in solution. The ionised and unionised forms have different colours.

OSTWALD'S THEORY

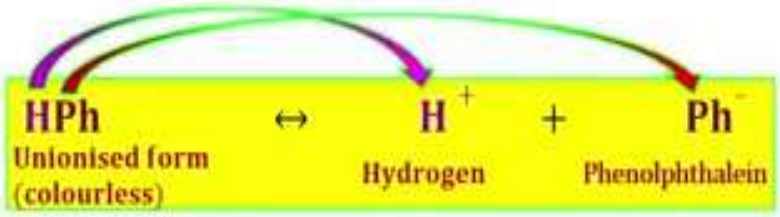
- ✓ The indicator exists predominantly in one of the two forms depending on the nature of the medium and hence there is color change when the nature of the medium changes. Phenolphthalein is a weak acid and it is partially ionised in solutions.





OSTWALD'S THEORY

✓ In acidic medium, excess H^+ ions are present which suppress the dissociation of HpH due to common ion effect.

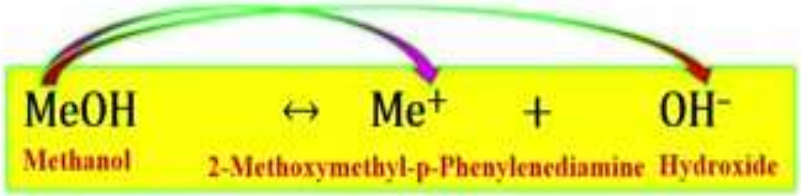


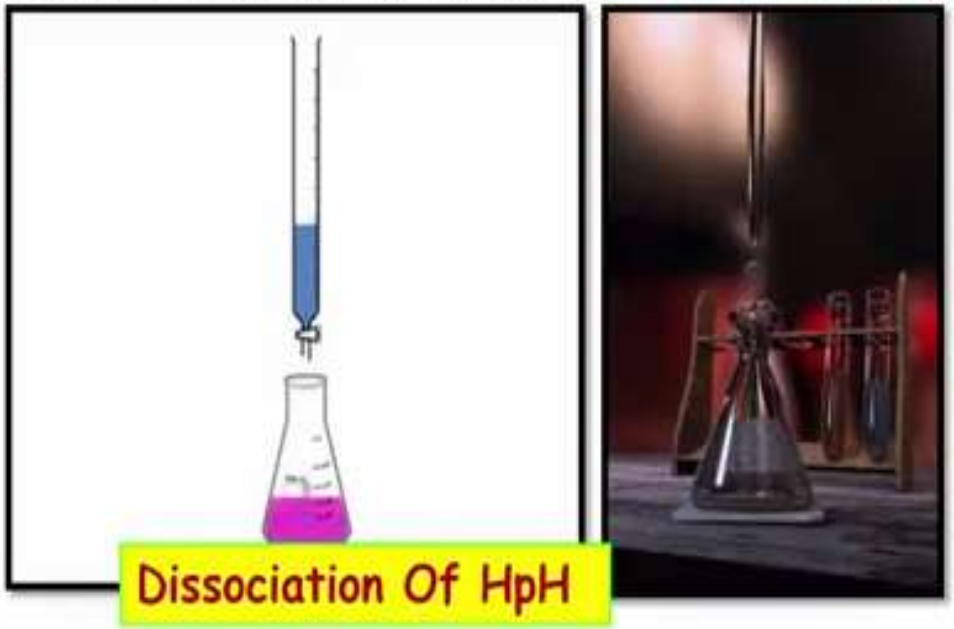
✓ Hence the indicator exists predominantly in unionised form and it is colourless.

✓ In alkaline medium, the OH^- ion neutralises H^+ ion to form water.

OSTWALD'S THEORY

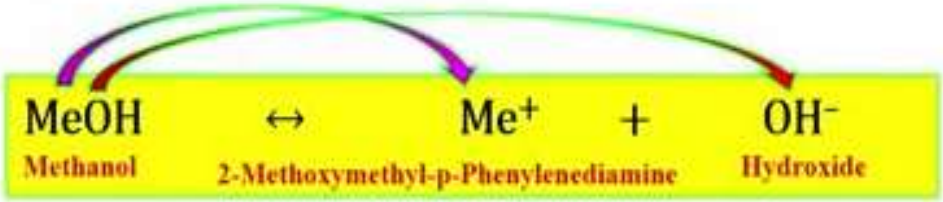
- ✓ Consequently the dissociation of HpH is favoured and the indicator is predominantly in the ionised form and it is pink in colour.
- ✓ Methyl orange is a weak base and its ionisation can be written as



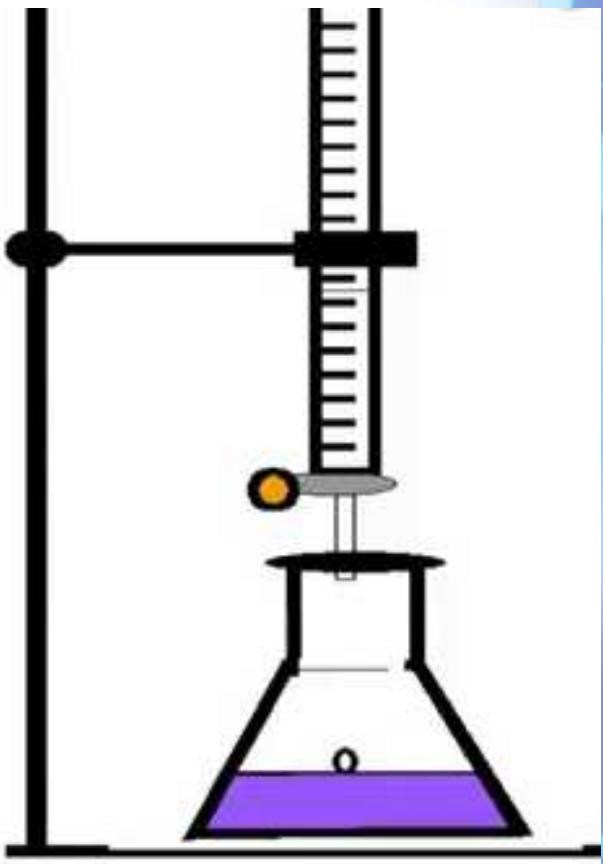


- ✓ In the presence of a base excess OH^- ions suppress the dissociation of MeOH due to common ion effect. Hence in basic medium, the indicator is mostly in unionised form which is yellow.

OSTWALD'S THEORY

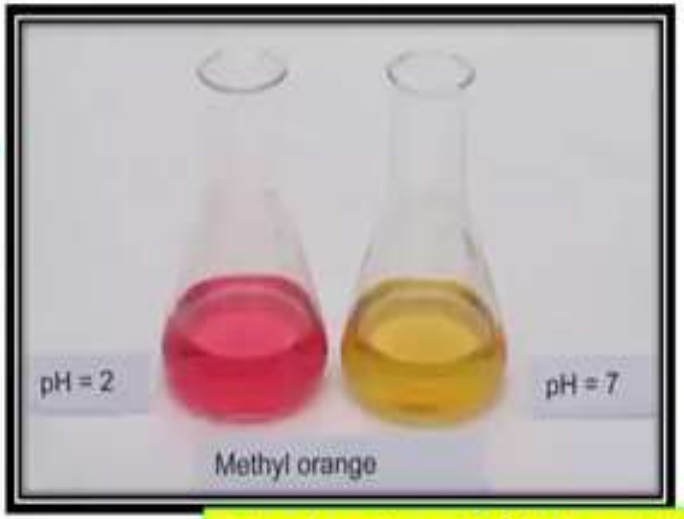


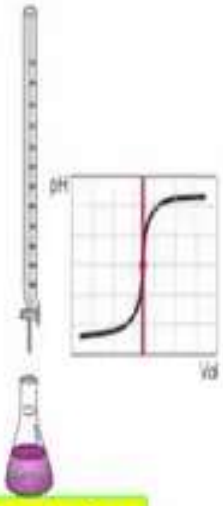
- ✓ In acidic solution the H^+ ions combine with OH^- ions to form unionized water.
- ✓ Hence in acidic solution, the indicator is mostly in ionised form and has pink colour.



OSTWALD'S THEORY

✓ This theory also explains why phenolphthalein is not a suitable indicator in the titration of a strong acid against a weak base.





Ionisation Of Phenolphthalein

✓ The reason is the OH^- ions produced by the weak base at the end point is too low to cause the ionisation of phenolphthalein.

✓ Hence, the pink colour does not appear exactly at the equivalence point.

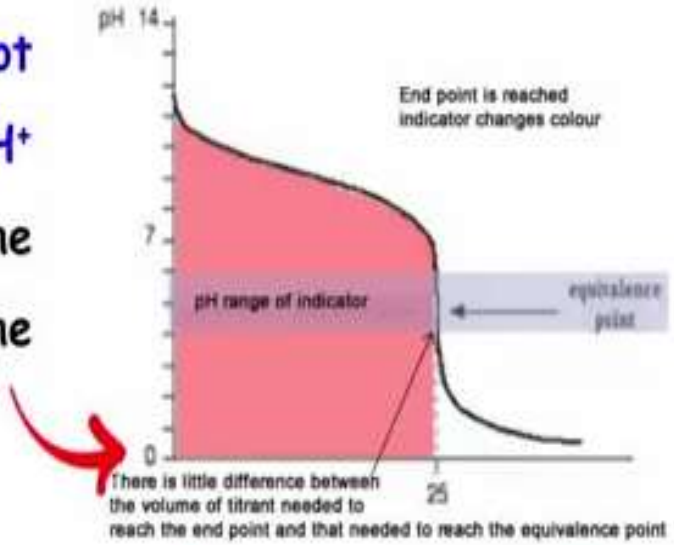
✓ The pink colour appears only after a sufficient excess of the weak base is added.

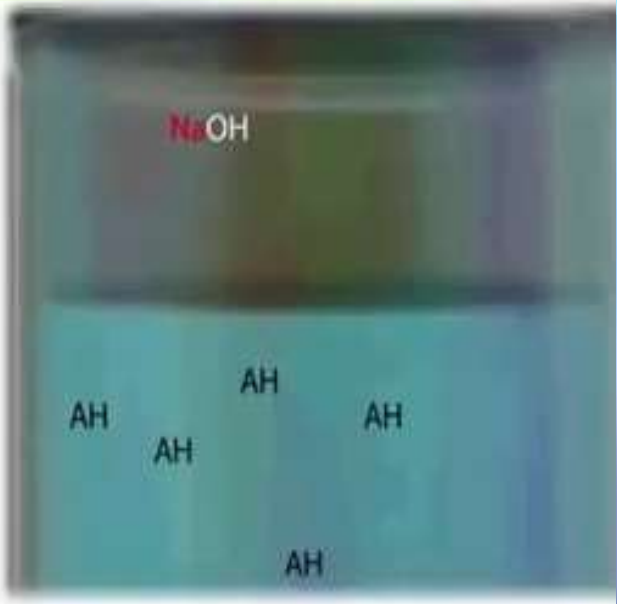
OSTWALD'S THEORY

✓ For a similar reason, methyl orange is not a suitable indicator in the titration of a strong base against a weak acid.

Titration Of A Strong Base And Weak Acid

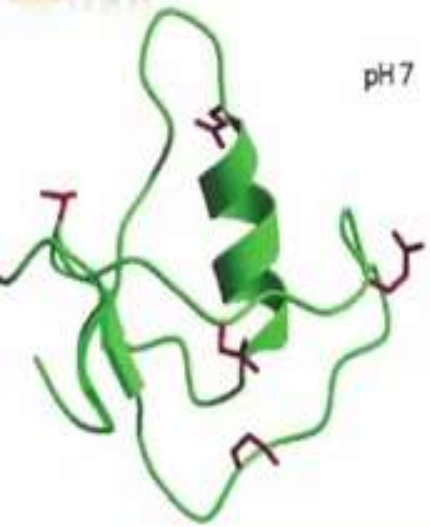
✓ The weak acid does not furnish sufficient H^+ ions to shift the equilibrium towards the right.

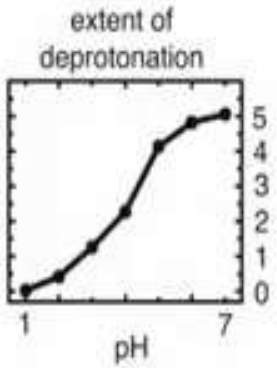




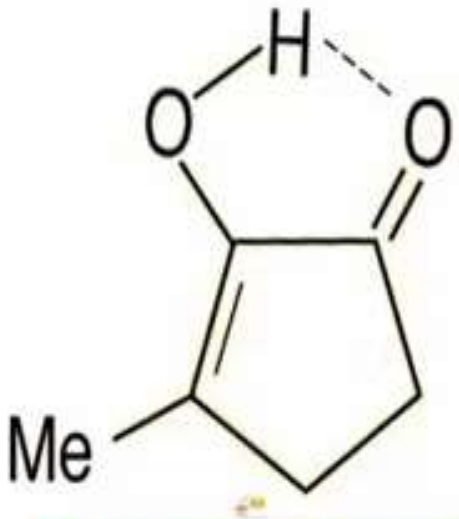
✓ A sufficient excess of the weak acid has to be added to get the colour change.

QUINONOID THEORY





Quinonoid Theory



Tautomeric Forms

✓ According to this theory the colour change of an acid-base indicator arises as a result of structural change.

It is supposed that an indicator exists as an equilibrium mixture of two tautomeric forms namely, benzenoid and quinonoid forms.

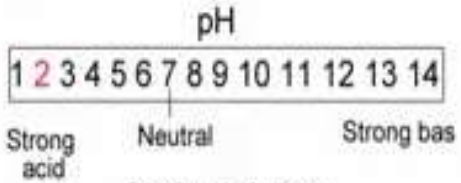
benzenoid form

quinonoid form

QUINONOID THEORY

- ✓ One form exists in acidic solution and the other form in basic solution. At least one of the tautomers is a weak acid or a weak base.

- ✓ The two form possess two different colors and as the pH of the solution containing the indicator is changed, the solution shows a change of color.



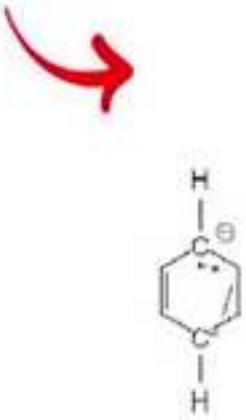
As the solution becomes more acidic the pH gets lower.

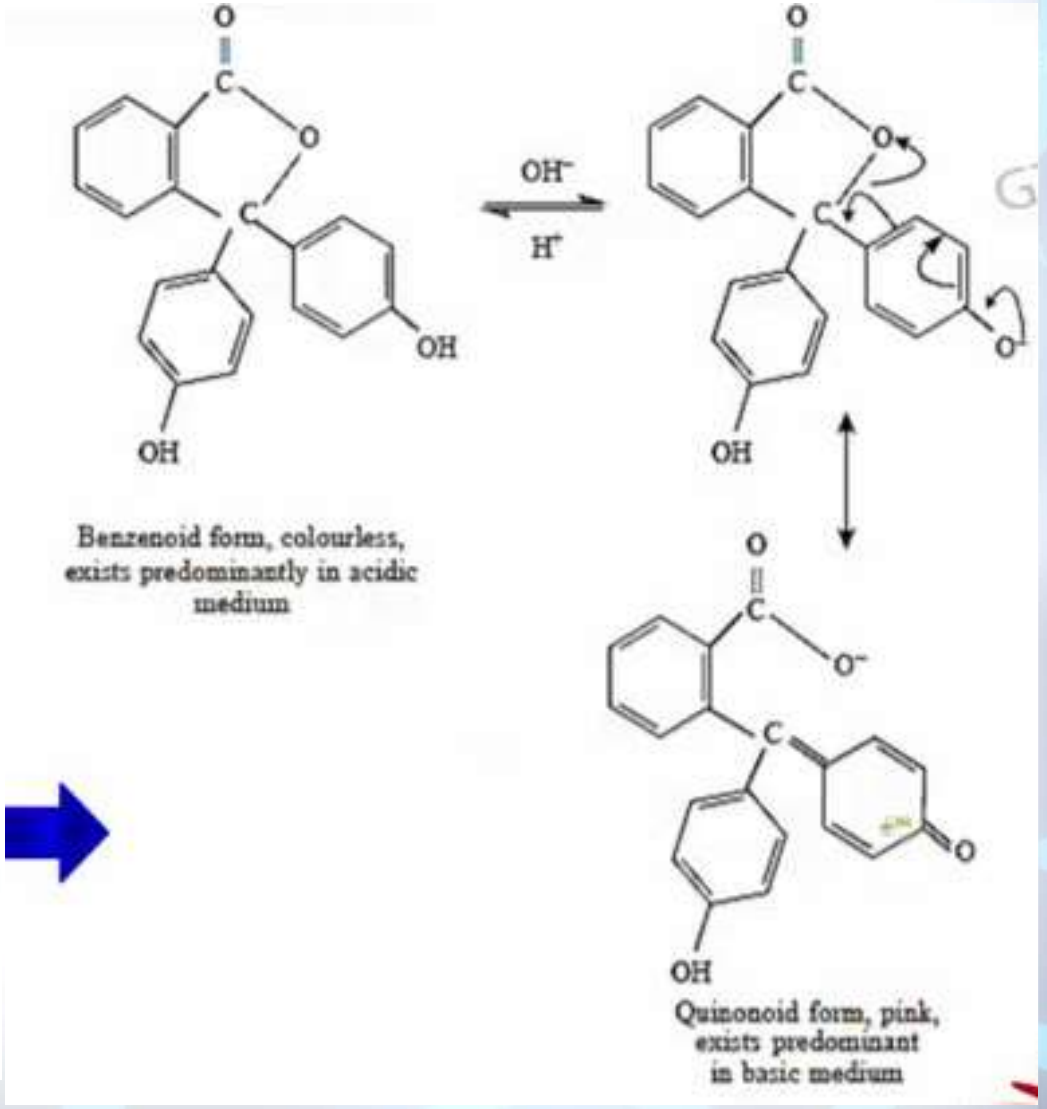
So a pH less than 7 indicates an acidic solution.

- ✓ The color change is due to the fact that one tautomer changes over to the other.

QUINONOID THEORY

- ✓ For example, phenolphthalein is tautomeric mixture of the two forms.





Benzenoid form, colourless, exists predominantly in acidic medium

Quinonoid form, pink, exists predominant in basic medium

Variables that influence the behavior of indicators

1. Influence of the indicator **concentration** on the color-change interval. The color-change interval of a **bicolor** pH indicator is independent of its total concentration. For **Unicolor Indicators** the pH value for which the color is perceptible is a function of the indicator's concentration.

2. Temperature. The color-change interval depends on temperature since its pK_a *value, which is* present in Henderson's relation, depends on it.

3. Ionic strength of the solution. The solution coloration is given by the ratio of concentrations and not by that of activities. The result is that two solutions exhibiting the same coloration may have a pH value that differs significantly from that of the other solution according to the ionic strengths of the solutions.

$$\mathrm{pH} = pK_a + \log\left([\mathrm{In}^-]/[\mathrm{HIn}]\right) + \log\left(\gamma_{\mathrm{In}^-}/\gamma_{\mathrm{HIn}}\right)$$

4. Nature of the other substances present in solution. Indicators may participate in other chemical equilibria than those involving proton exchanges. When this is the case, their indicator property may be modified and even suppressed. For example, they can enter into complexation equilibria with proteins in biological media. This is the case with albumin.

Titration Errors with Acid/Base Indicators

1. Determinate error that occurs when the pH at which the indicator changes color differs from the pH at the equivalence point. This type of error can usually be minimized by choosing the indicator carefully or by making a blank correction.

2. indeterminate error that originates from the limited ability of the human eye to distinguish reproducibly the intermediate color of the indicator. The magnitude of this error depends on the change in pH per milliliter of reagent at the equivalence point, on the concentration of the indicator, and on the sensitivity of the eye to the two indicator colors. On average, the visual uncertainty with an acid/base indicator is in the range of ±0.5 to ± 1 pH unit. This uncertainty can often be decreased to as little as ± 0.1 pH unit by matching the color of the solution being titrated with that of a reference standard containing a similar amount of indicator at the appropriate pH.

Titration Curves

The acid–base titration curve or neutralization curve is the diagram given by the pH of the solution as a function of the volume *V.*

Equivalently, neutralization curves are also the diagrams of pH/ϕ, where ϕ is the **fraction titrated**. It is the ratio of the number of moles of added titrant and the initial number of moles of the titrand:

$$\varphi = CV/C_0V_0.$$ for the equivalence point $\varphi_{ep} = 1$

Stage in the titration:

(1) preequivalence,
(2) equivalence, and
(3) postequivalence.

Titrating a Strong Acid with a Strong Base

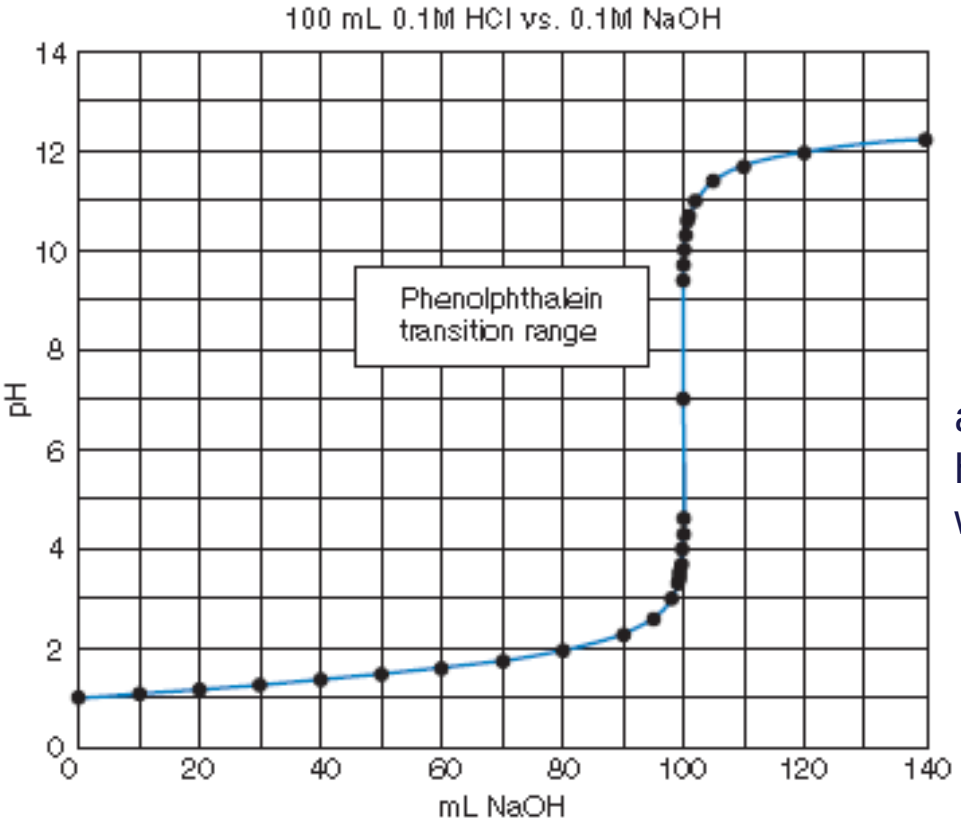
$$H^+ + Cl^- + Na^+ + OH^- \rightarrow H_2O + Na^+ + Cl^-$$

$$H_3O^+ + OH^- \rightarrow 2H_2O.$$

• by definition, before the equivalence point occurs, the H_3O^+ ions remain in excess in the titration vessel. Their concentration is calculated by taking into account the fact that for *CV moles of added hydroxide ions, CV moles of hydroxonium ions* disappear (since the reaction is considered to be complete).We find that

$$[H_3O^+] = (C_0V_0 - CV)/(V_0 + V_0).$$

$$pH = -\log[(C_0V_0 - CV)/(V_0 + V)] \quad \text{(before the endpoint)}.$$



• at the equivalence point (*V = 100 ml, ϕ = 1), the pH value is exactly 7.0;*

$$[Na^+] = [Cl^-], \text{ and}$$

$$[H_3O^+] = [OH^-]$$

$$[H_3O^+] = \sqrt{K_w}$$

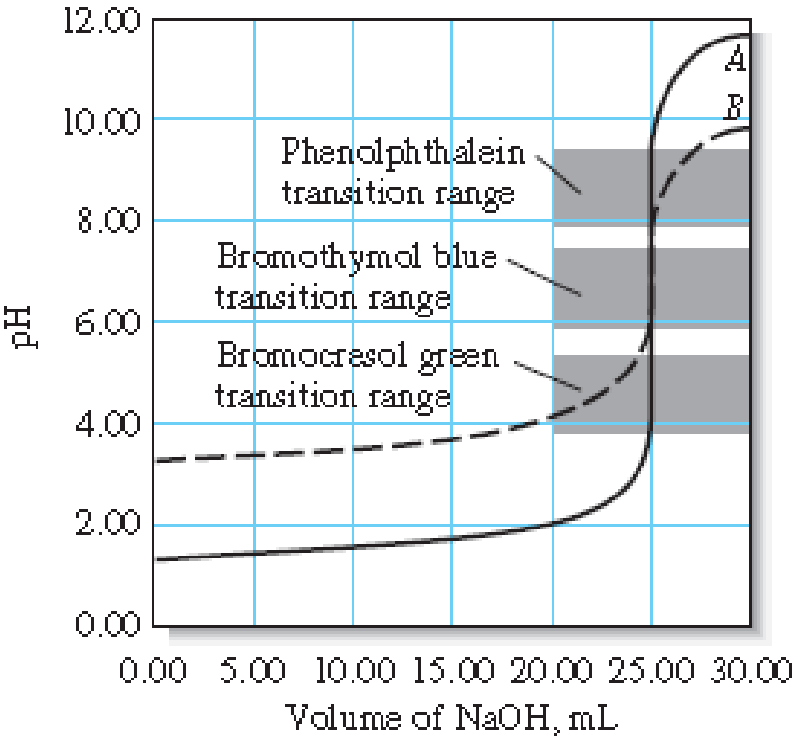
after the equivalence point, there is an excess of hydroxide ions (the strongest base in water), whose concentration is

$$[OH^-] = (CV - C_0V_0)/(V_0 + V).$$

$$pH = pK_w + \log[(CV - C_0V_0)/(V_0 + V)]$$

Changes in pH during the Titration of a Strong Acid with a Strong Base

Volume of NaOH, mL	pH: 50.00 mL of 0.0500 M HCl with 0.100 M NaOH	pH: 50.00 mL of 0.000500 M HCl with 0.00100 M NaOH
0.00	1.30	3.30
10.00	1.60	3.60
20.00	2.15	4.15
24.00	2.87	4.87
24.90	3.87	5.87
25.00	7.00	7.00
25.10	10.12	8.12
26.00	11.12	9.12
30.00	11.80	9.80



$$c_{HCl} = \frac{\text{no. mmol HCl remaining after addition of NaOH}}{\text{total volume soln}}$$

$$= \frac{\text{original no. mmol HCl} - \text{no. mmol NaOH added}}{\text{total volume soln}}$$

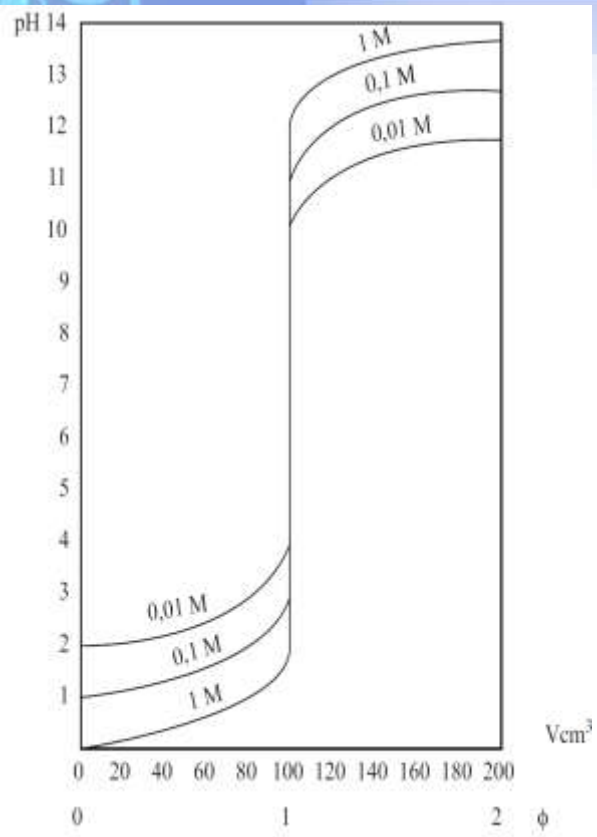
$$[H_3O^+] = [OH^-] = \sqrt{K_w} = \sqrt{1.00 \times 10^{-14}} = 1.00 \times 10^{-7}\,M$$

$$pH = -\log[H_3O^+] = -\log(1.00 \times 10^{-7}) = 7.00$$

$$c_{NaOH} = \frac{\text{no. mmol NaOH added} - \text{original no. of mmoles HCl}}{\text{total volume soln}}$$

Titration curves for HCl with NaOH. Curve ***A****: 50.00 mL of* 0.0500 M HCl with 0.1000 M NaOH. Curve ***B****: 50.00 mL of 0.000500 M HCl* with 0.00100 M NaOH.

The selection of an indicator is not critical when the reagent concentration is approximately 0.1 M. However, that bromocresol green is unsuited for a titration involving the 0.001 M reagent because the color change occurs over a 5-mL range well before the equivalence point. The use of phenolphthalein is subject to similar objections. Of the three indicators, then, only bromothymol blue provides a satisfactory end point with a minimal systematic error in the titration of 0.001 M NaOH.



Some important points emerge from the study of the curve. They must be emphasized:

• at the equivalence point (*V = 100 ml, ϕ = 1), the pH value is exactly 7.0;*

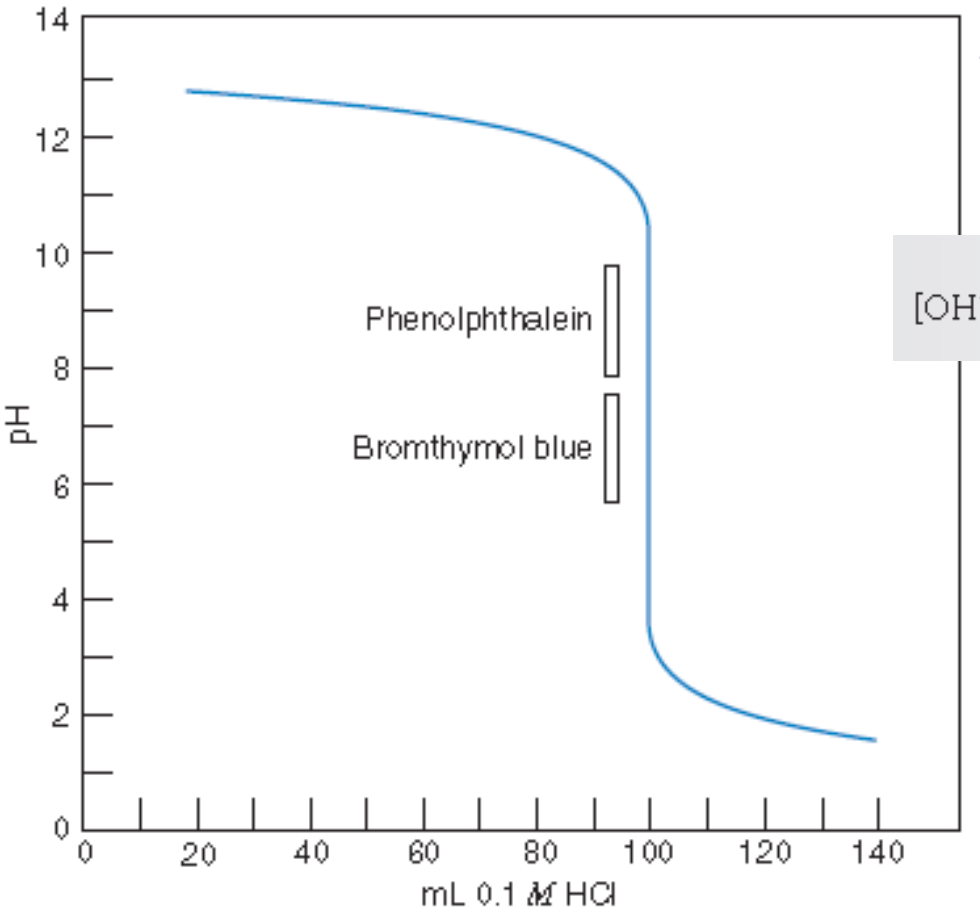
• for the fractions titrated $0 < \phi < 0.9$ and $1.1 < \phi < 2.0$, the curves exhibit weak pH changes. Their weak changes are due to the buffering action of the couples ofwater H_3O^+/H_2O and H_2O/OH^-, which are effective in the zones under consideration;

• in the same zones, the curves do not exhibit an inflection point. This result is emphasized by a comparison with titration curves given by weak acids or bases;

• the curves exhibit an extremely large change in pH occurring in the vicinity of the equivalence point. In the case of 1M solutions, the pH value changes from 3.3 to 10.7 when ϕ changes from 0.999 to 1.001. The strong pH change is due to the buffer capacities of the couples H_3O^+/H_2O and H_2O/OH^-, which are null at pH = 7. This explains the fact that it is impossible to stop such a titration for exactly pH = 7;

• The weaker the concentration is, the weaker the change at the equivalence point will be, too.

Titration of a Strong Base with a Strong Acid



Titration curve for 100mL 0.1 *M NaOH versus 0.1 M* HCl.

• before the equivalence point, the solution in the titration vessel is that of a strong base whose concentration is

$$[OH^-] = (C_0V_0 - CV)/(V_0 + V);$$

$$[OH^-] = c_{NaOH} = \frac{\text{original no. mmol NaOH} - \text{no. mmol HCl added}}{\text{total volume of solution}}$$

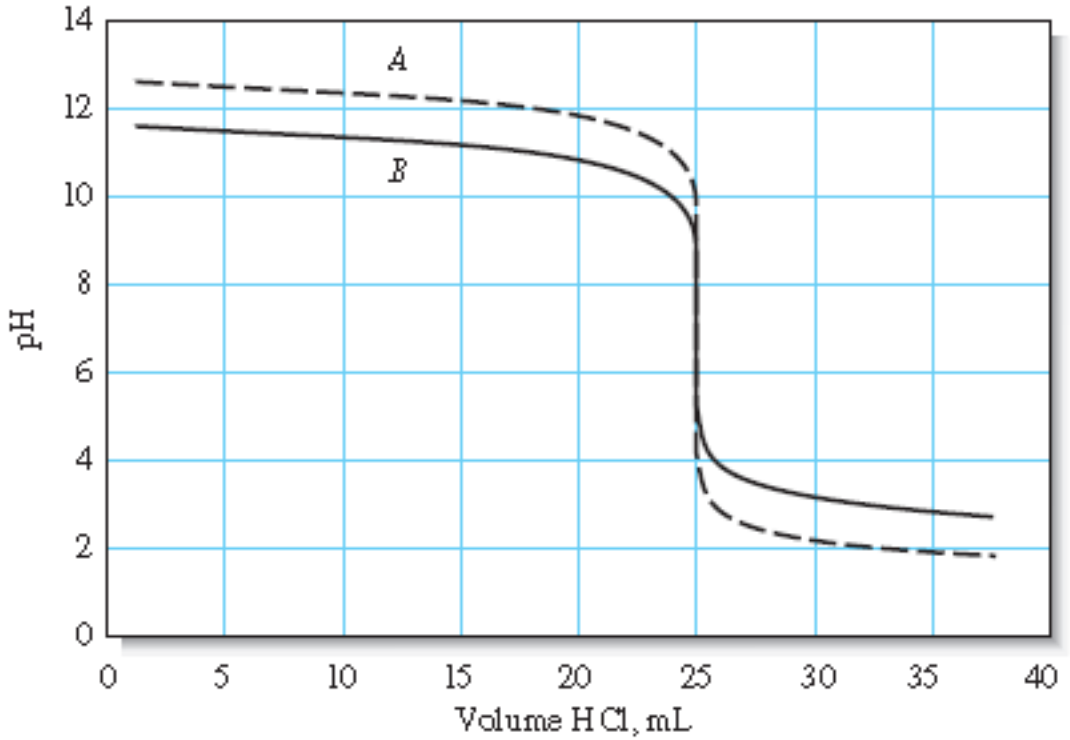
• at the equivalence point, pH = 7;

• after the equivalence point, the solution is that of a strong acid whose concentration is given by

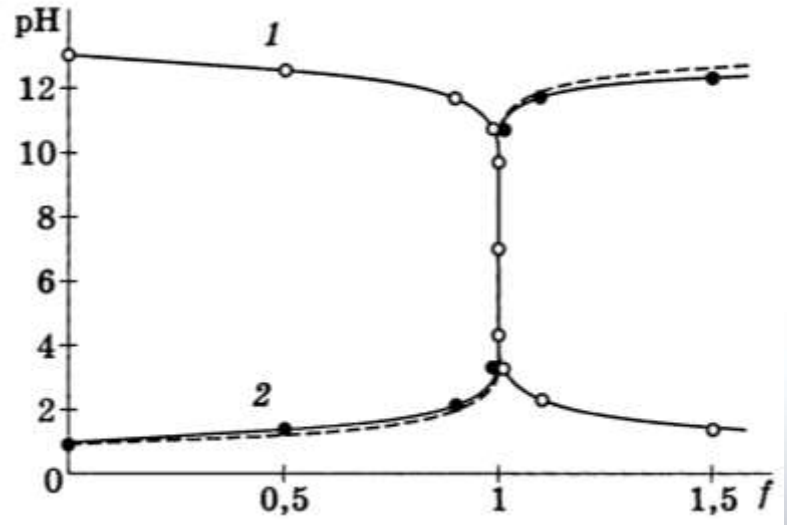
$$[H_3O^+] = (CV - C_0V_0)/(V_0 + V).$$

$$[H_3O^+] = \sqrt{K_w} = \sqrt{1.00 \times 10^{-14}} = 1.00 \times 10^{-7}\,M$$

$$pH = -\log(1.00 \times 10^{-7}) = 7.00$$

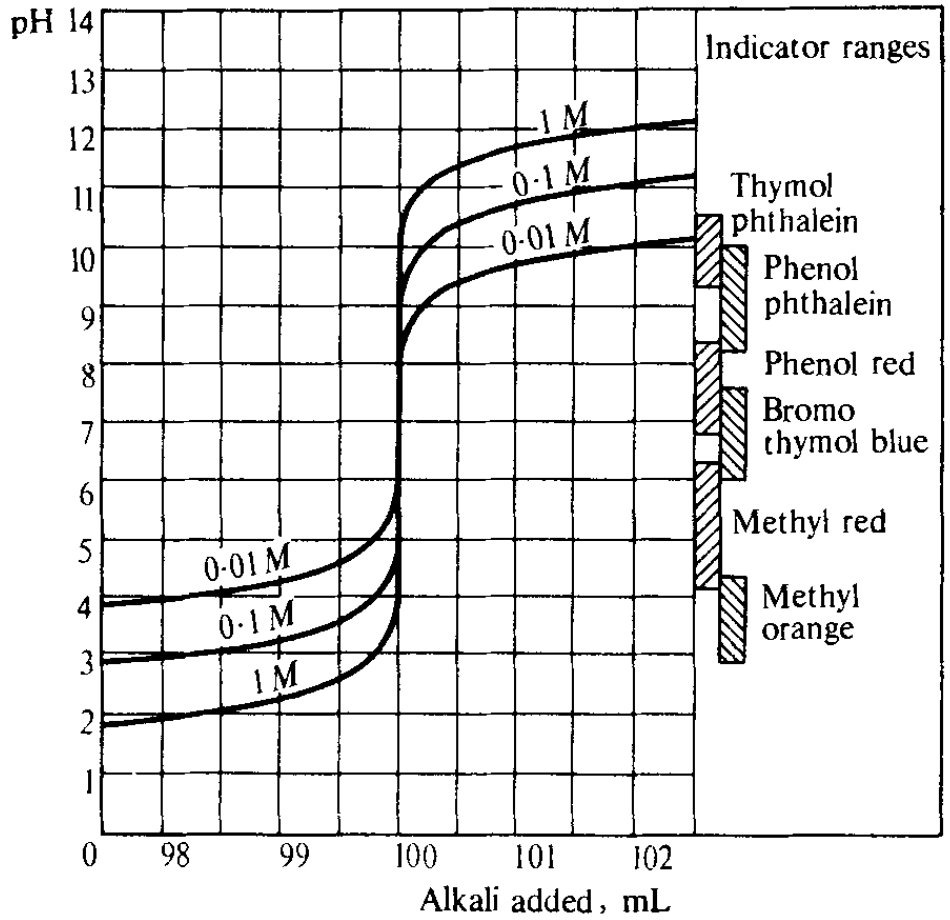


Titration curves for NaOH with HCl. **Curve *A***: *50.00 mL* of 0.0500 M NaOH with 0.1000 M HCl. **Curve *B***: *50.00 mL of 0.00500* M NaOH with 0.0100 M HCl.



The color indicators that can be used are the same as those used for the previous titrations.

Practical Conclusion: Choice of the Indicator



• with the 1 mol/L solutions, any indicator whose color-change interval is located between pH 3.0–10.5 can be suitable. The color change is sharp since a great pH change occurs around the equivalence point. The titration error is negligible. Methyl orange (color-change interval: 3.1–4.4), methyl red (4.2–6.1), bromothymol blue (6.0–7.5), phenol red (6.8–8.4), phenolphthalein (8.4–10.0), and thymolphthalein (9.5–10.5) are suitable;

• with the 0.1 mol/L solutions, any indicator whose color-change interval is located between 4.5–9.5 is suitable. Using methyl orange and phenolphthalein may present some difficulties. It induces a titration error of about 0.2%, which is approximately the same as that due to the graduation of glass flasks;

• with the 10^{-2} mol/L solutions, the color-change interval is located between 5.5–8.5. Methyl red, bromothymol blue, and phenol red are still suitable. Using helianthin induces an error of 1–2%.