Objectives

At the end of this unit the student should be able to :

1- Understand what are the acid – base indicators .

2- know How the acid – base indicators work in order to identify the pH of the solution .

3- Calculate the pH range during which the indicator changes it’s color .

4- select the suitable indicator for a certain acid – base titration .

5- Calculate the relative precision of a certain acid – base titration .

6-Understand why we sometimes have to do titrations in non aqueous solutions .

Introduction

Acid-base titrations depend on the neutralization between an acid and a base when mixed in solution. In addition to the sample, an appropriate indicator is added to the titration chamber, reflecting the pH range of the equivalence point. The acid-base indicator indicates the endpoint of the titration by changing color. The endpoint and the equivalence point are not exactly the same because the equivalence point is determined by the stoichiometry of the reaction while the endpoint is just the color change from the indicator. Thus, a careful selection of the indicator will reduce the indicator error. When more precise results are required, or when the reagents are a weak acid and a weak base, a pH - meter or a conductance meter are used.

This unit describes how simple acid-base indicators work, and how to choose the right one for a particular titration

What Is An Acid – Base Indicator ?

Acid - Base indicators (also known as pH indicators) are substances which change color with pH. They are usually weak acids or bases, which when dissolved in water dissociate slightly and form ions. Consider an indicator which is a weak acid, with the formula HIn. At equilibrium, the following equilibrium equation is established with its conjugate base:

$$HIn + H_2O \;\leftarrow H^+\text{-----} HO^- \rightarrow\; H_3O^+ + In^-$$

acidic color | basic color

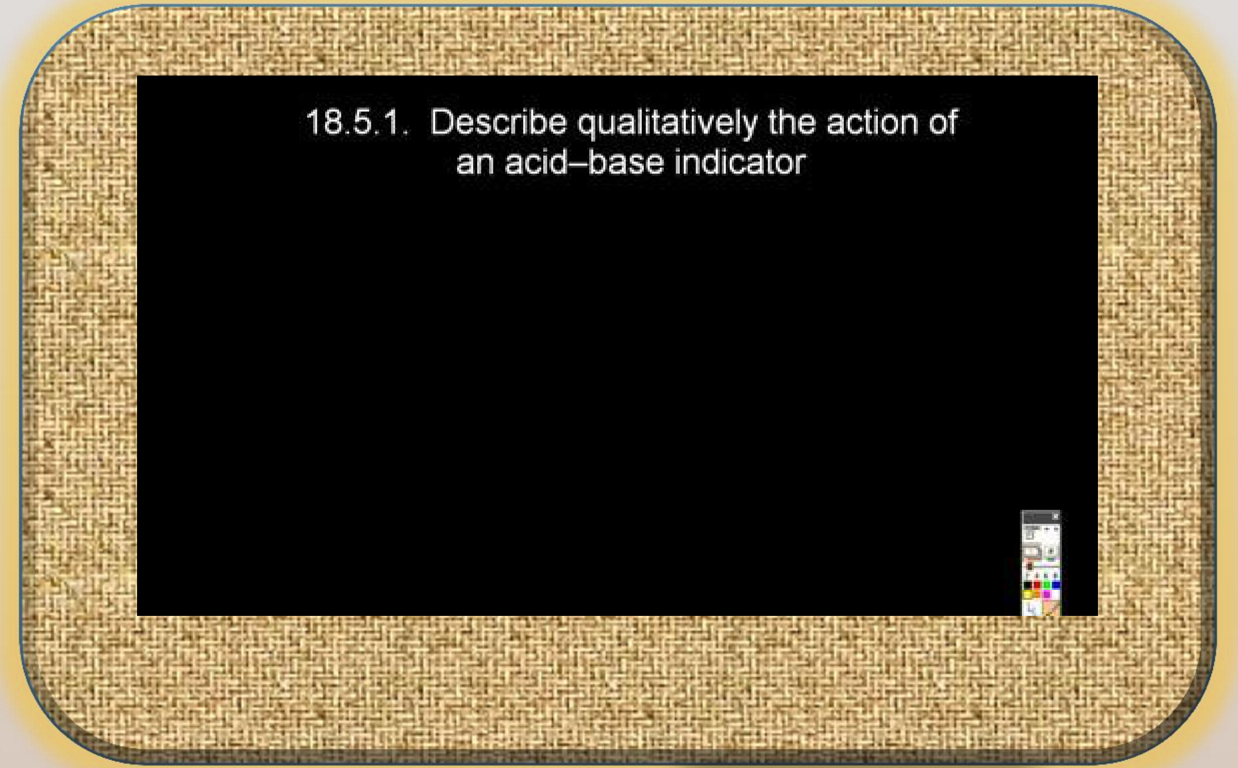
The acid and its conjugate base have different colors. At low pH values the concentration of H_3O^+ is high and so the equilibrium position lies to the left. The equilibrium solution has the color A. At high pH values, the concentration of H_3O^+ is low - the equilibrium position thus lies to the right and the equilibrium solution has color B.

What Is An Acid – Base Indicator ?

We can apply equilibrium law to indicator equilibria - in general for a weak acid indicator:

$$K_{In} = \left(\frac{[H_3O^+][In^-]}{[HIn]} \right)_{eq}$$

K_{In} is known as the **indicator dissociation constant**. The color of the indicator turns from color A to color B or vice versa at its turning point. At this point:



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What Is An Acid – Base Indicator

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

$$K_{In} = [H^+]$$

$$pK_{In} = pH$$

The pH of the solution at its turning point is called the pK_{In} and is the pH at which half of the indicator is in its acid form and the other half in the form of its conjugate base.

How Indicators Work (Litmus)

Indicators as weak acids

Litmus

Litmus is a weak acid. It has a seriously complicated molecule which we will simplify to Hlit. The "H" is the proton which can be given away to something else. The "Lit" is the rest of the weak acid molecule.

There will be an equilibrium established when this acid dissolves in water. Taking the simplified version of this equilibrium:

$$HLit_{(aq)} \rightleftharpoons H^+_{(aq)} + Lit^-_{(aq)}$$

The un-ionised litmus is red, whereas the ion is blue.Now use Le Chatelier's Principle to work out what would happen if you added hydroxide ions or some more hydrogen ions to this equilibrium.

How Indicators Work (Litmus)

Adding hydroxide ions:

Hydroxide ions react with and remove these hydrogen ions.

$$HLit_{(aq)} \rightleftharpoons H^+_{(aq)} + Lit^-_{(aq)}$$

The equilibrium position moves to replace the lost hydrogen ions.

Litmus turns blue.

Adding hydrogen ions:

Add extra hydrogen ions.

$$HLit_{(aq)} \rightleftharpoons H^+_{(aq)} + Lit^-_{(aq)}$$

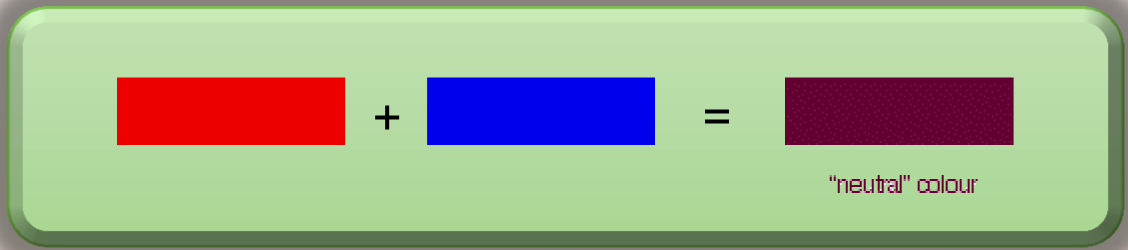
The equilibrium position moves to remove the extra hydrogen ions.

Litmus turns red.

How Indicators Work (Litmus)

If the concentrations of HLit and Lit^- are equal :

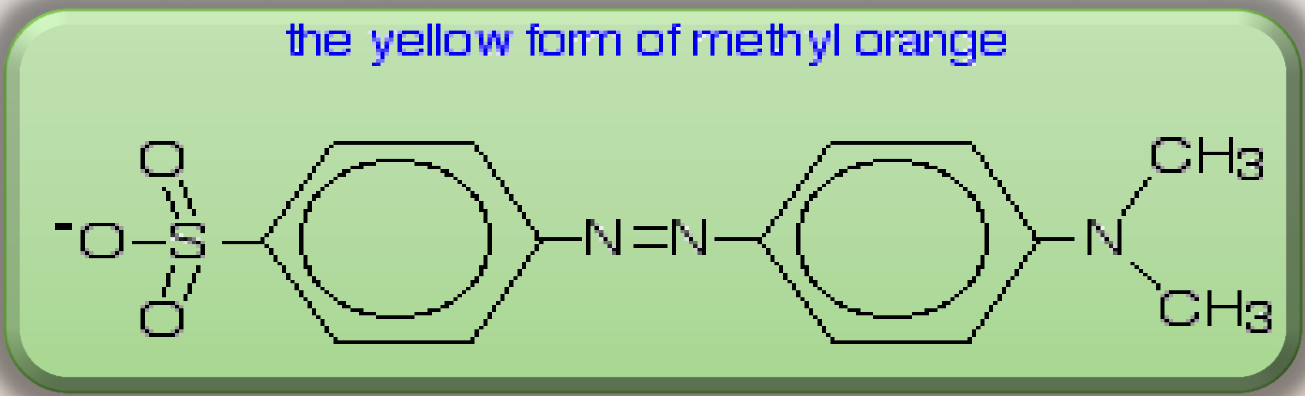
At some point during the movement of the position of equilibrium, the concentrations of the two colors will become equal. The color you see will be a mixture of the two.



The reason for the inverted commas around "neutral" is that there is no reason why the two concentrations should become equal at pH 7. For litmus, it so happens that the 50 / 50 color does occur at close to pH 7 that's why litmus is commonly used to test for acids and alkalis. As you will see below, that isn't true for other indicators.

How Indicators Work (Methyl Orange)

Methyl orange is one of the indicators commonly used in titrations. In an alkaline solution, methyl orange is yellow and the structure is:



You have the same sort of equilibrium between the two forms of methyl orange as in the litmus case -–but the colours are different

$$H\text{-}Meor_{(aq)} \underset{H^+}{\overset{OH^-}{\rightleftharpoons}} H^+_{(aq)} + Meor^-_{(aq)}$$

How Indicators Work (Phenolphthalein)

You should be able to work out for yourself why the color changes when you add an acid or an alkali. The explanation is identical to the litmus case -–all that differs are the colors. In the methyl orange case, the half-way stage where the mixture of red and yellow produces an orange colour happens at pH 3.7 – no where near neutral. This will be explored further in the next slides .

Phenolphthalein

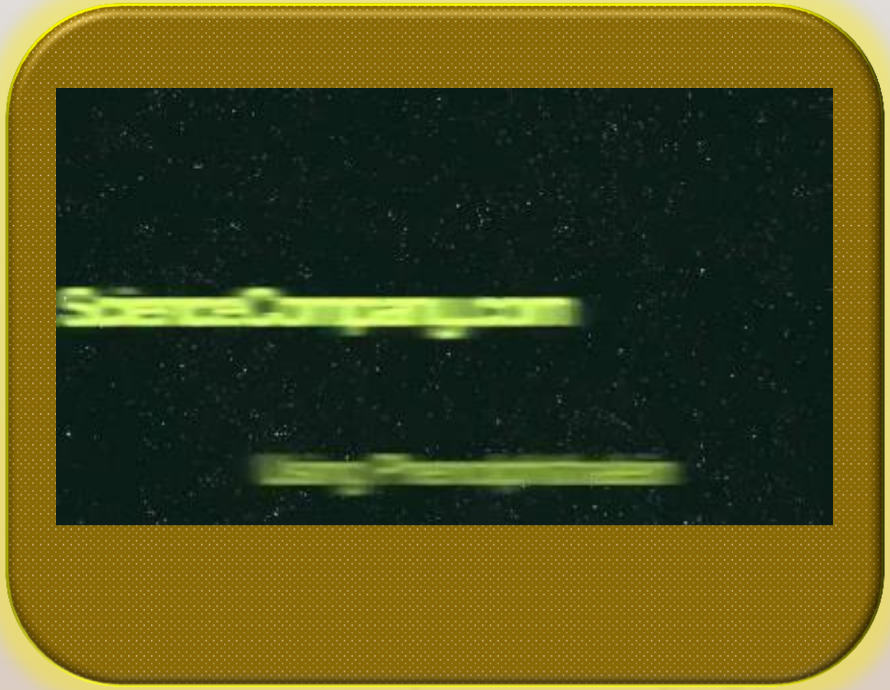
Phenolphthalein is another commonly used indicator for titrations, and is another weak acid :

How indicators work (Phenolphthalein)

$$\boxed{H\text{-}phph_{(aq)}} \underset{H^+}{\overset{OH^-}{\rightleftharpoons}} H^+_{(aq)} + \boxed{phph^-_{(aq)}}$$

In this case, the weak acid is colorless and its ion is bright pink. Adding extra hydrogen ions shifts the position of equilibrium to the left, and turns the indicator colorless. Adding hydroxide ions removes the hydrogen ions from the equilibrium which tips to the right to replace them -– turning the indicator pink.

The half-way stage happens at pH 9.3. Since a mixture of pink and colorless is simply a paler pink, this is difficult to detect with any accuracy!



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Indicator's Range

Indicator Range

At a low pH, a weak acid indicator is almost entirely in the HIn form, the color of which predominates (acidic color) . As the pH increases - the intensity of the color of HIn decreases and the equilibrium is pushed to the right. Therefore the intensity of the color of In^- increases (basic color). The human eye can distinguish the acidic color if :

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

Accordingly :

$$K_{HIn} = \frac{[H^+][In^-]}{[HIn]} = \frac{[H^+]X1}{10}$$

$$[H^+] = K_{HIn} X 10$$

Multiplying the last equation by – log : $pH_{acidcolor} = pK_{HIn} - 1$

Indicator's Range

This means that the acidic color of the indicator will be predominant starting from $pH = pK_{In} - 1$ and downwards . Likewise , human eye is able to distinguish the basic color If :

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

$$K_{HIn} = \frac{[H^+][In^-]}{[HIn]} = \frac{[H^+]\ X\ 10}{1}$$

$$[H^+] = K_{HIn}\ X\ \frac{1}{10}$$

$$pH_{basecolor} = pK_{HIn} + 1$$

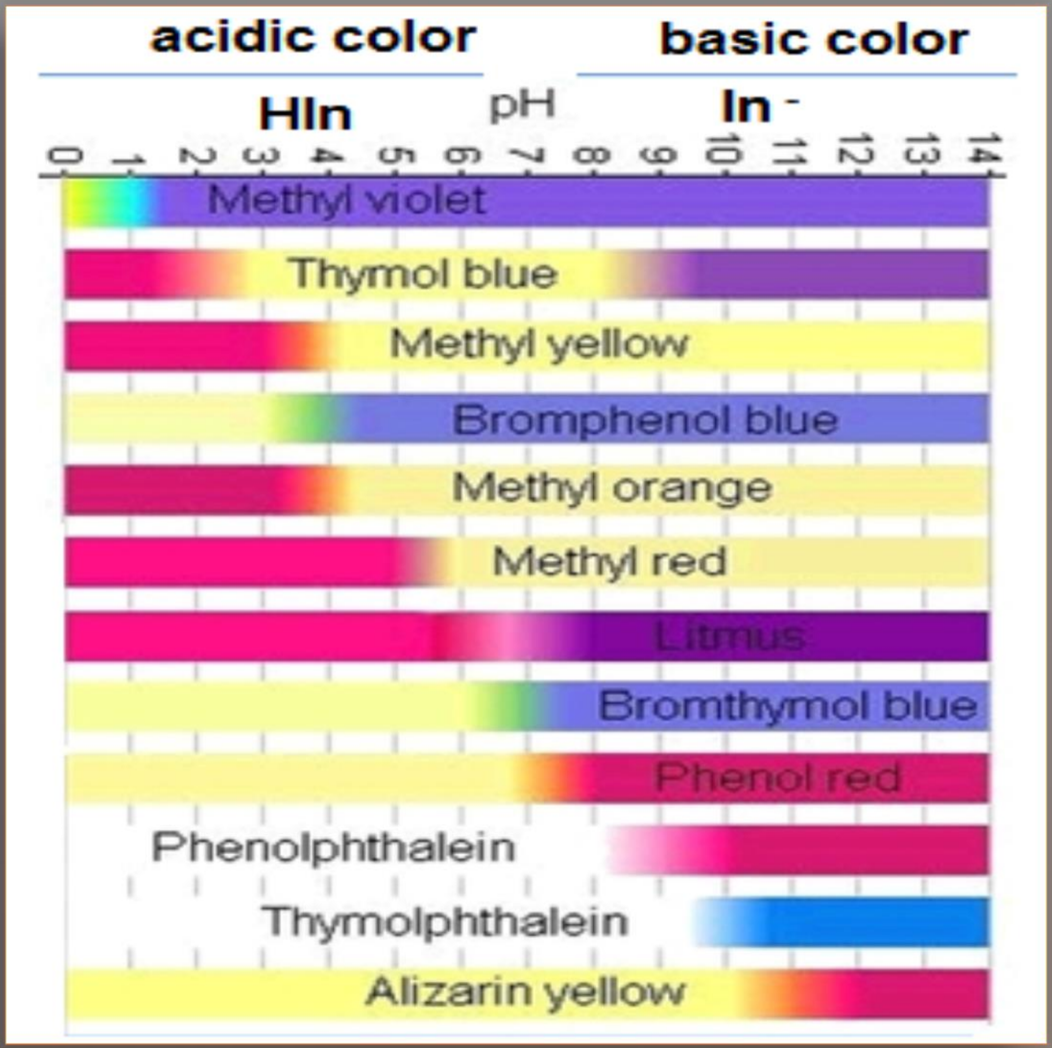
This means that the basic color of the indicator will be predominant starting from $pH = pK_{In} + 1$ and upwards .

Indicator’s Range

For most indicators the range at which the indicator change its color is approximately within ±1 of the pK_{ln} value: -

$$\Delta pH_{In} = pK_{HIn} \pm 1$$

See the table below for examples of some common indicators. The graph to the right is a model of the acidic and basic forms of each indicator – with the color of the solution at the turning point.



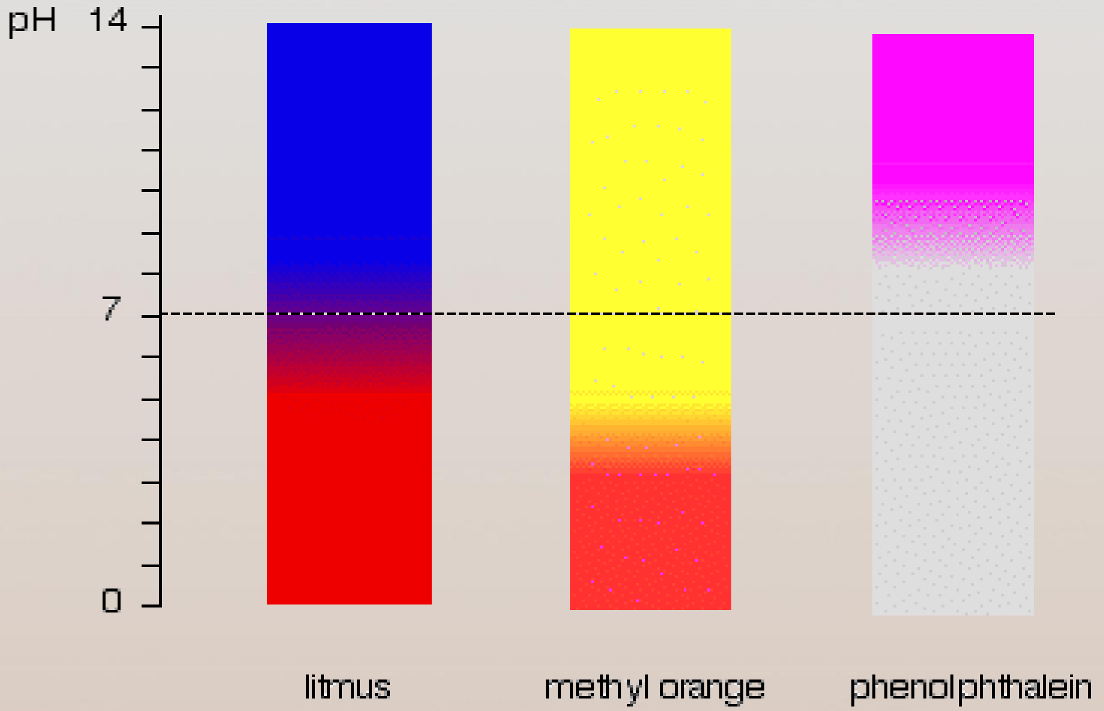
Indicator's Range

Indicator	Color		pK_{In}	pH range
	Acid	Base		
Thymol Blue – 1st change	red	yellow	1.5	1.2 – 2.8
Methyl Orange	red	yellow	3.7	3.2 – 4.4
Bromocresol Green	yellow	blue	4.7	3.8 – 5.4
litmus	red	blue	6.5	5 - 8
Bromothymol Blue	yellow	blue	7.0	6.0 – 7.6
Phenol Red	yellow	red	7.9	6.8 – 8.4
Thymol Blue – 2nd change	yellow	blue	8.9	8.0 – 9.6
Phenolphthalein	colourless	pink	9.4	8.2 – 10.0

Indicator’s Range

Suppose you had methyl orange in an alkaline solution so that the dominant color is yellow. Now start to add acid so that the equilibrium begins to shift. At some point there will be enough of the red form of the methyl orange present that the solution will begin to take on an orange tint. As you go on adding more acid, the red will eventually become so dominant that you can no longer see any yellow. There is a gradual smooth change from one color to the other, taking place over a range of pH of around $pK_{HIn} \pm 1$. The exact values for the three indicators we've looked at are : The litmus color change happens over an unusually wide range, but it is useful for detecting acids and alkalis in the lab because it changes color around pH 7. There is a gradual smooth change from one color to the other, taking place over a range of pH. As a rough "rule of thumb", the visible change takes place about 1 pH unit either side of the pK_{in} value.

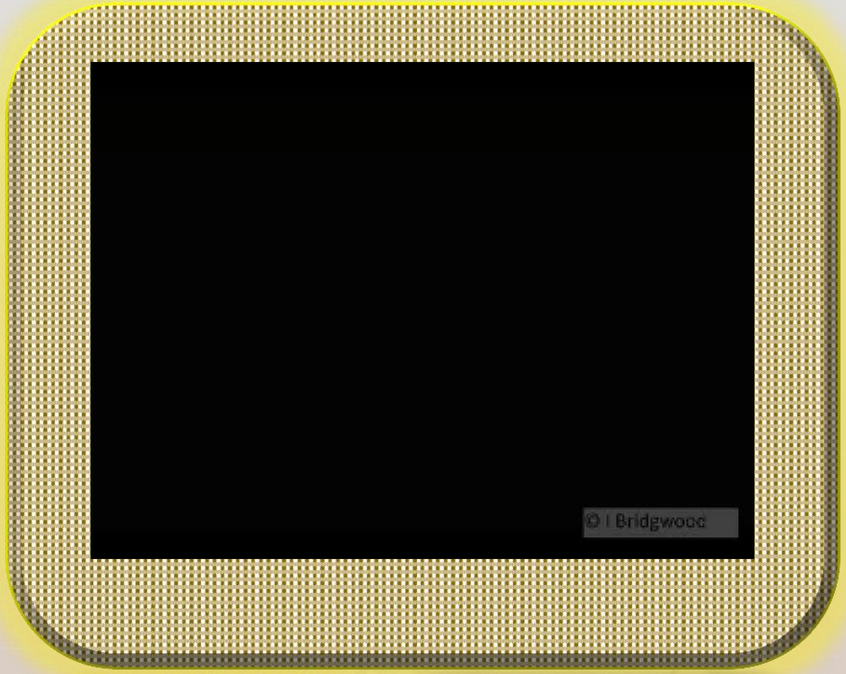
Indicator's Range



For example, methyl orange would be yellow in any solution with a pH greater than 4.4. It couldn't distinguish between a weak acid with a pH of 5 or a strong alkali with a pH of 14.

Choosing Suitable Indicators Via Titration Curves

Remember that the equivalent point of a titration is where you have mixed the titrant and analyte in exactly equation proportions. You obviously need to choose an indicator which changes color as close as possible to that equivalent point. That varies from titration to titration.



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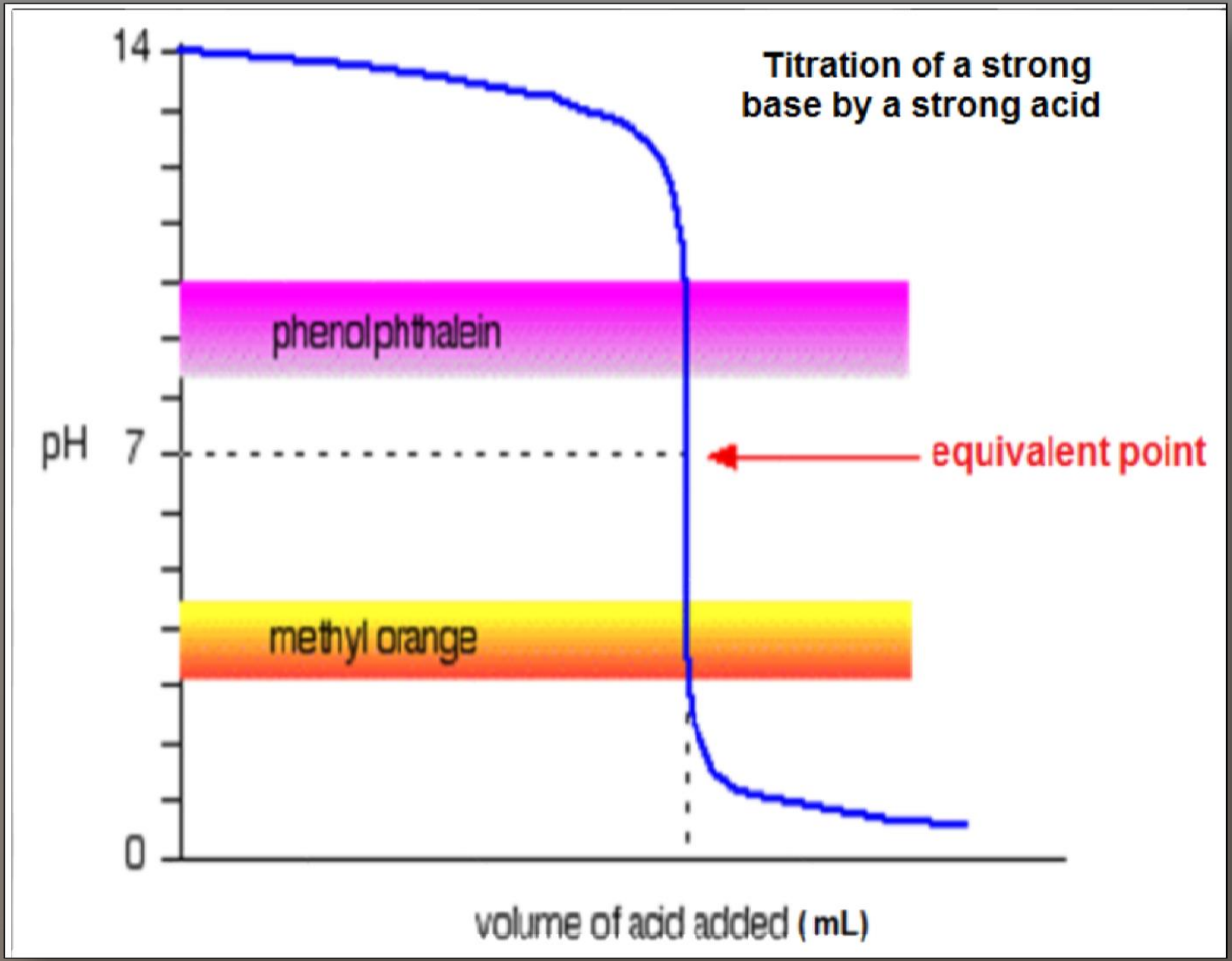
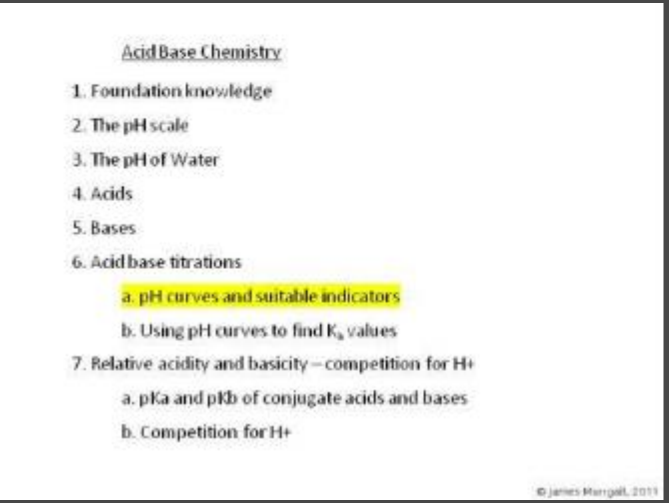
Strong base by strong acid :

The next diagram shows the pH curve for adding a strong acid to a strong base. Superimposed on it are the pH ranges for methyl orange and phenolphthalein

Choosing Suitable Indicators Via Titration Curves





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Choosing Suitable Indicators Via Titration Curves

You can see that neither indicator changes color exactly at the equivalent point. However, the graph is so steep at that point that there will be virtually no difference in the volume of acid added whichever indicator you choose. However, it would make sense to titrate to the best possible color with each indicator.

If you use phenolphthalein, you would titrate until it just becomes colorless (at pH 8.3) because that is as close as you can get to the equivalent point (pH = 7) .

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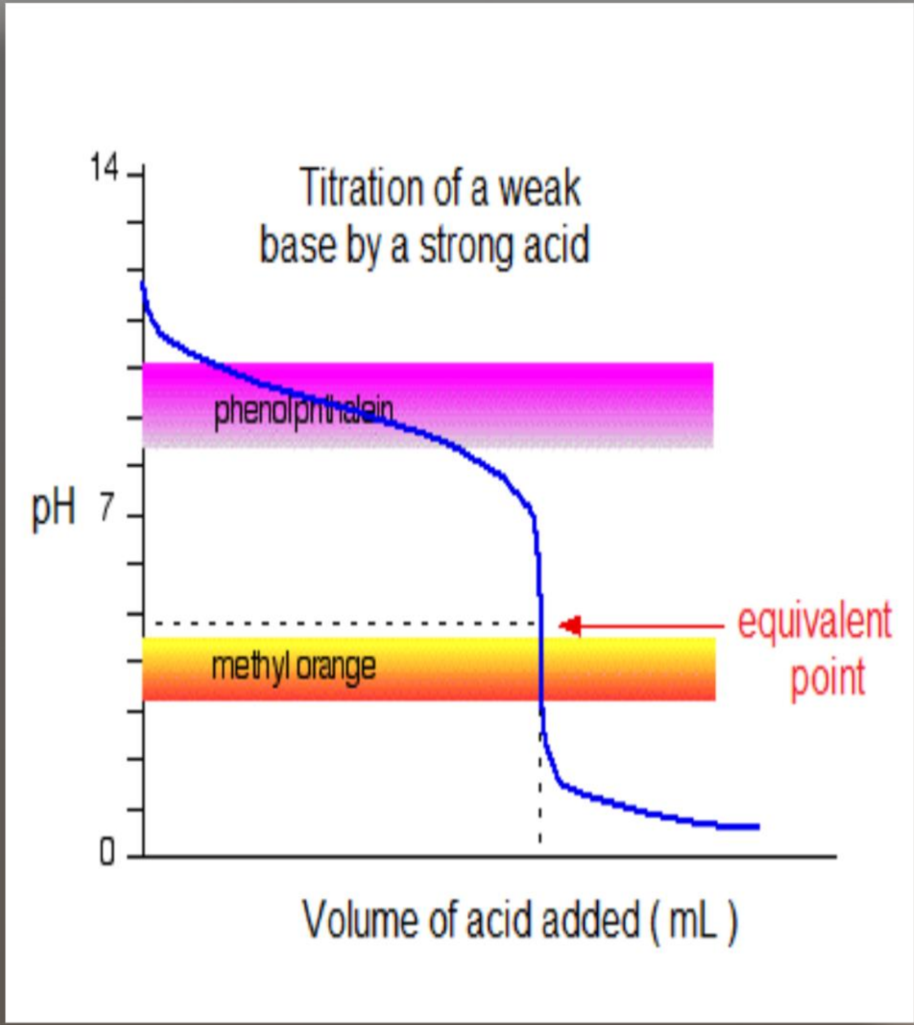
Choosing Suitable Indicators Via Titration Curves

On the other hand, using methyl orange, you would titrate until there is the very first trace of orange in the solution. If the solution becomes red, you are getting further from the equivalent point.

Weak base by strong acid :

This time it is obvious that phenolphthalein would be completely useless showing earlier endpoint . However, methyl orange starts to change from yellow towards orange very close to the equivalence point.

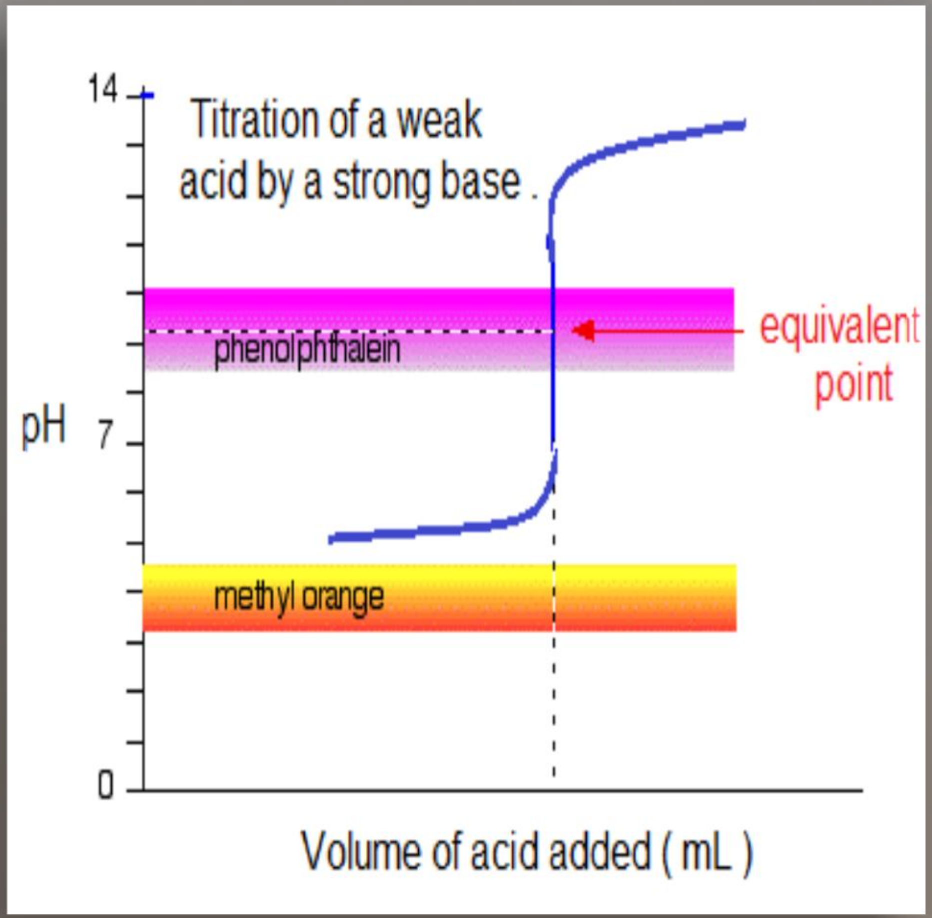


Choosing Suitable Indicators Via Titration Curves

Strong acid by strong base : This is exactly the same as the previous titration of strong base by strong acid except that the pH here increasing while there decreasing during titration .

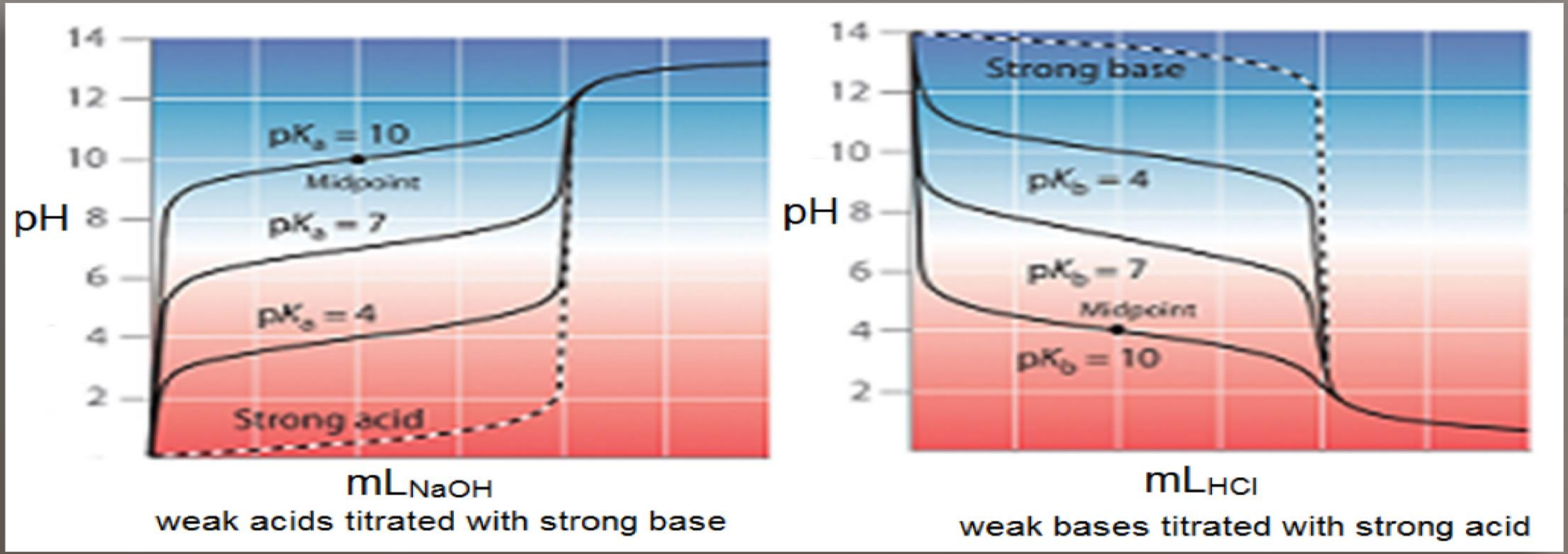
Weak acid by strong base :

This time it is obvious that methyl orange would be completely useless showing earlier endpoint . However, phenolphthalein starts to change from colorless towards pink very close to the equivalent point . You have to choose an indicator which changes color on the steep bit of the curve . The



Choosing Suitable Indicators Via Titration Curves

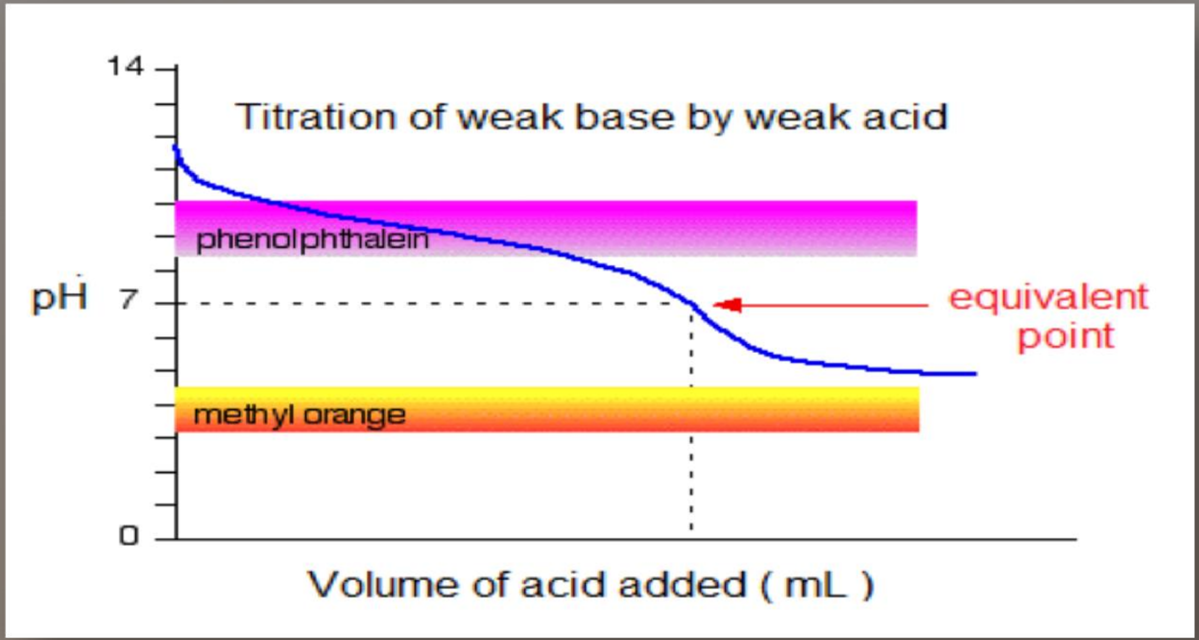
shape of the curve depends on the strength of the titrated acid or base as shown in the following graph .Go back to the previous indicators table and choose the suitable indicators for each weak acid or base listed in the this graph ?

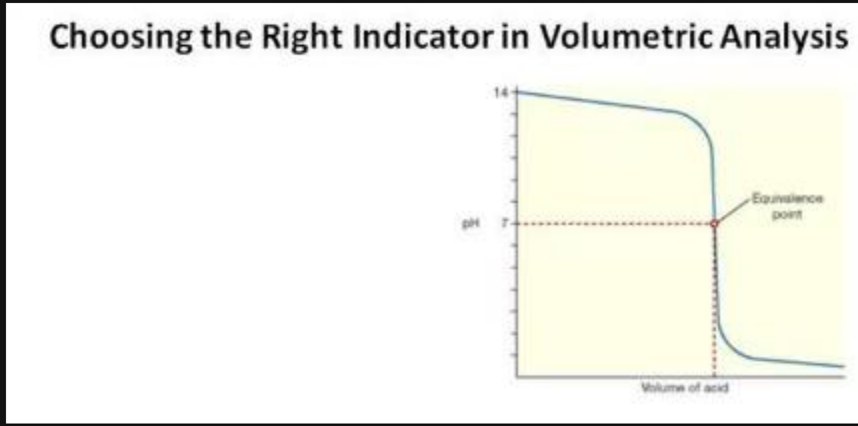


Choosing Suitable Indicators Via Titration Curves

Weak base by weak acid :

The curve is for a case where the base and acid are both equally weak for example, ammonia and acetic acid solution.





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Choosing Suitable Indicators Via Titration Curves

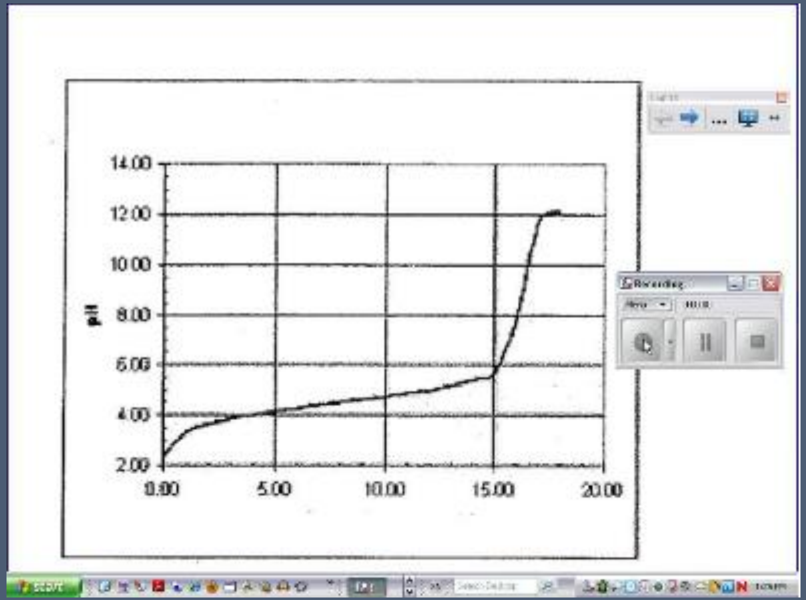
You can see that neither indicator is any use. Phenolphthalein will have finished changing well before the equivalence point, and methyl orange falls off the graph altogether.

It may be possible to find an indicator which starts to change or finishes changing at the equivalence point, but because the pH of the equivalence point will be different from case to case, you can't generalize . On the whole, you would never titrate a weak acid by a weak base or vice versa in the presence of an indicator.

There are two ways by which one can select the suitable indicator for certain titration :

Choosing Suitable Indicators Via Titration Curves

First : If the titration curve is available then we can by looking at it and the range of the indicator we can decide wither this indicator will be suitable or will give a late or earlier endpoint as we previously discussed



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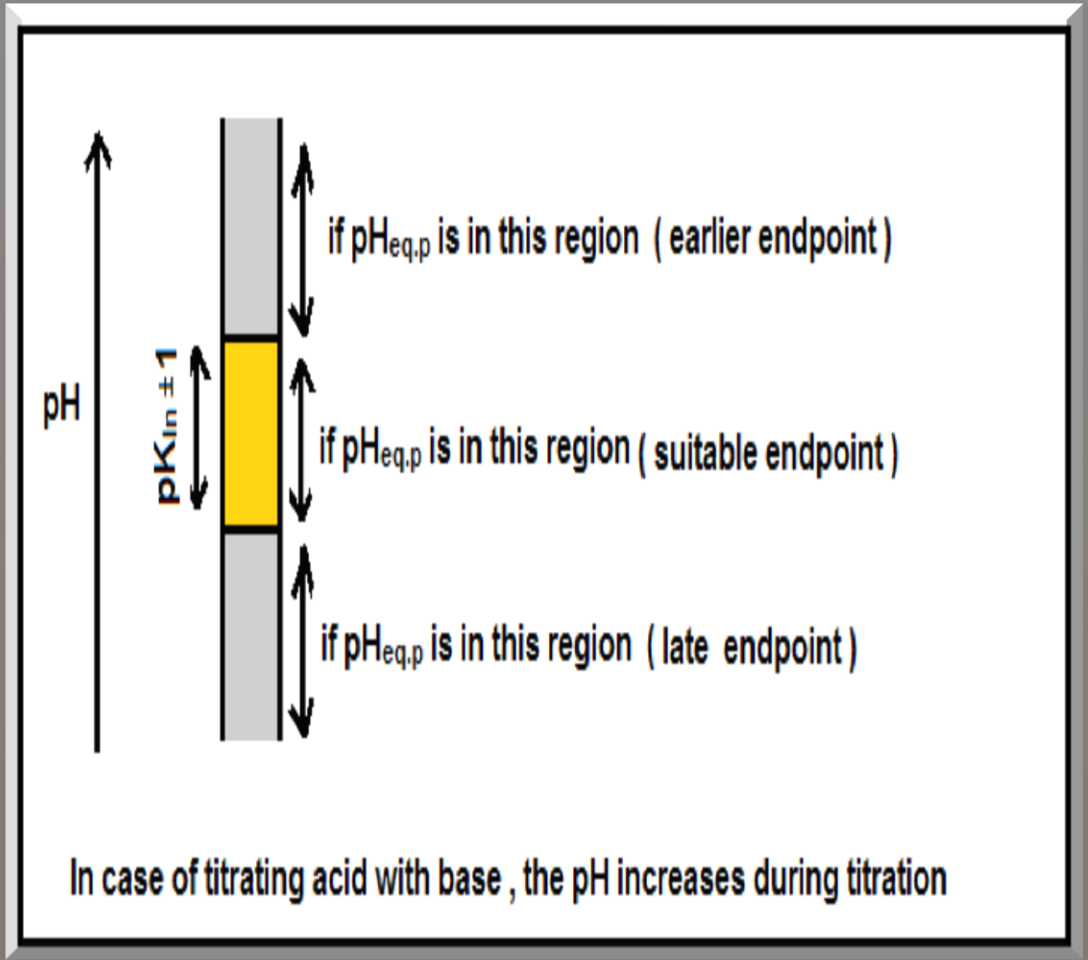
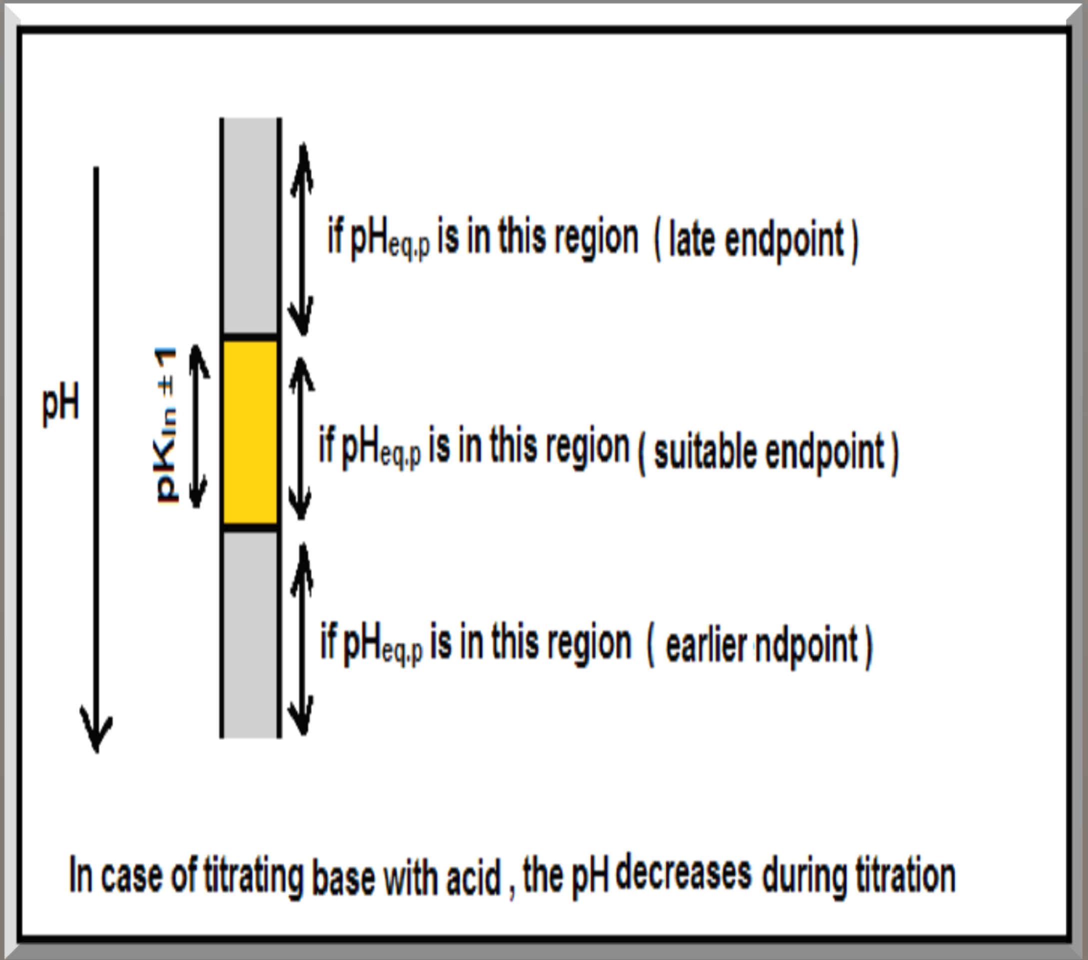
Choosing Suitable indicators Via $pH_{eq.p.}$

Second : If the titration curve is not available , we calculate the pH at the equivalent point of the titration ($pH_{eq.p.}$) as we learned in unit 7 and compare it with the indicator range as follows :

- The pH at the equivalent point of a titration ($pH_{eq.p}$) must lie within the range of the indicator ($pK_{In} \pm 1$) in order for this indicator to be suitable for this titration
- if the $pH_{eq.p}$ lies before the indicator range , then this indicator will give late equivalent point .
- if the $pH_{eq.p}$ lies after the indicator range , then , the indicator will give earlier equivalent point . See the following graphs

Choosing Suitable indicators Via $pH_{eq.p.}$





Choosing Suitable indicators Via $pH_{eq.p.}$

Example : How do the following indicators behave with the titration of 10 mL of 0.05 M of the weak acid HA ($K_a = 1 X 10^{-5}$) with 0.1 M NaOH :
(1) $pK_{In} = 7$ (2) $pK_{In} = 9$ (3) $pK_{In} = 11$?

Solution : We write the titration reaction equation :
$NaOH + HA \leftrightarrow NaA + H_2O$
Then , we calculate the $pH_{eq.p.}$ for the titration :

$$pOH_{eq.p} = -\log \sqrt{\frac{1x10^{-14}[(10\,X\,0.05)/15}{1X10^{-5}}} = 4.7 \therefore pH_{eq.p} = 9.3$$

Since we are adding the base from burette to the acid in the conical flask , then , the pH of the conical flask solution is going to increase during titration :

Choosing Suitable indicators Via $pH_{eq.p.}$

(1) $pK_{In} \pm 1 = 7 \pm 1$: this means the color of the indicator starts to change at pH = 6 and completes the change at pH = 8 . This occurs before reaching the equivalent point at pH = 9.3 . Therefore , this indicator will give with this titration an earlier endpoint (negative error i.e low $mL_{eq.p}$) .

(2) $pK_{HIn} \pm 1 = 9 \pm 1$: this means the color of the indicator starts to change at pH = 8 and completes the change at pH = 10 . Since the equivalent point is at pH = 9.3 which is within the indicator range . Therefore , this indicator is suitable for this titration.

(3) $pK_{HIn} \pm 1 = 11 \pm 1$: this means that the color of the indicator starts to change at pH = 10 and completes the change at pH = 12 . This occurs after passing the equivalent point at pH = 9.3 . Therefore , this indicator will give with this titration a late endpoint (positive error i.e high $mL_{eq.p}$) .

Choosing Suitable indicators Via $pH_{eq.p.}$

Example : How do the following indicators behave with the titration of 20 mL of 0.1 M of NH_3($K_b \approx 2 \times 10^{-5}$) with 0.4 M HCl : (1) $pK_{In} = 3$ (2) $pK_{In} = 5$ (3) $pK_{In} = 7$?

Solution : We write the titration reaction equation :

$$HCl + NH_3 \leftrightarrow NH_4Cl$$

Then we calculate the $pH_{eq.p.}$ for the titration :

$$pH_{eq.p.} = -\log \sqrt{\frac{1 X 10^{-14}[(20 X 0.1)/25}{2 X 10^{-5}}} = 5.2$$

Since we are adding the acid from burette to the base in the conical flask , then , the pH of the conical flask solution is going to decrease during titration :

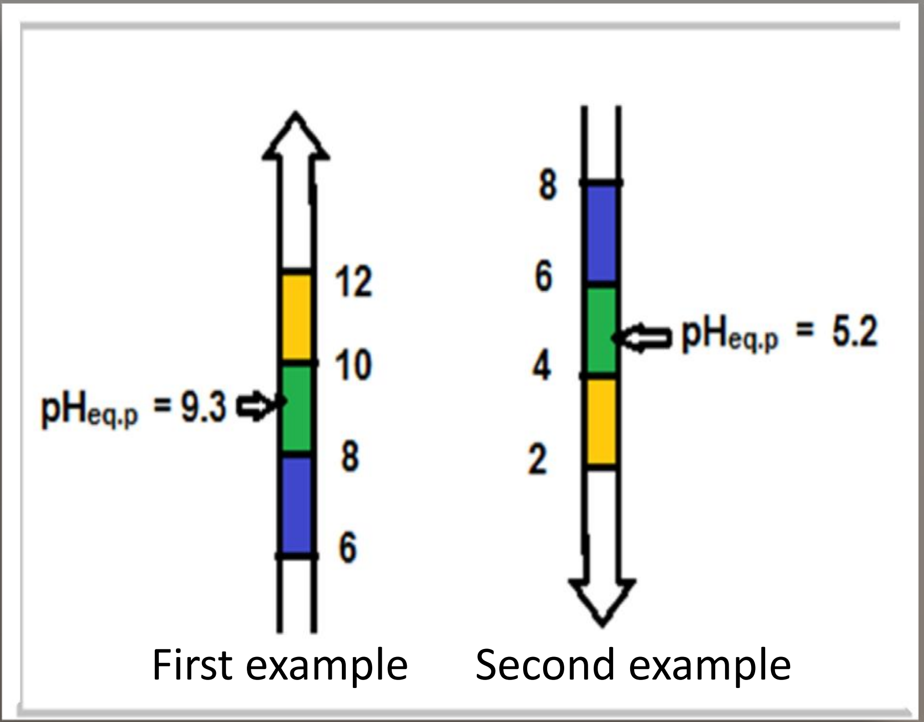
Choosing Suitable indicators Via $pH_{eq.p.}$

(1) $pK_{HIn} \pm 1 = 3 \pm 1$: this means the color of the indicator starts to change at pH = 4 and completes the change at pH = 2 . This occurs after passing the equivalent point at pH = 5.2 . Therefore , this indicator will give with this titration a late endpoint (positive error i.e high $mL_{eq.p}$) .

(2) $pK_{HIn} \pm 1 = 5 \pm 1$: this means the color of the indicator starts to change at pH = 6 and completes the change at pH = 4 . Since the equivalent point is at pH = 5.2 which is within the indicator range . Therefore , this indicator is suitable for this titration .

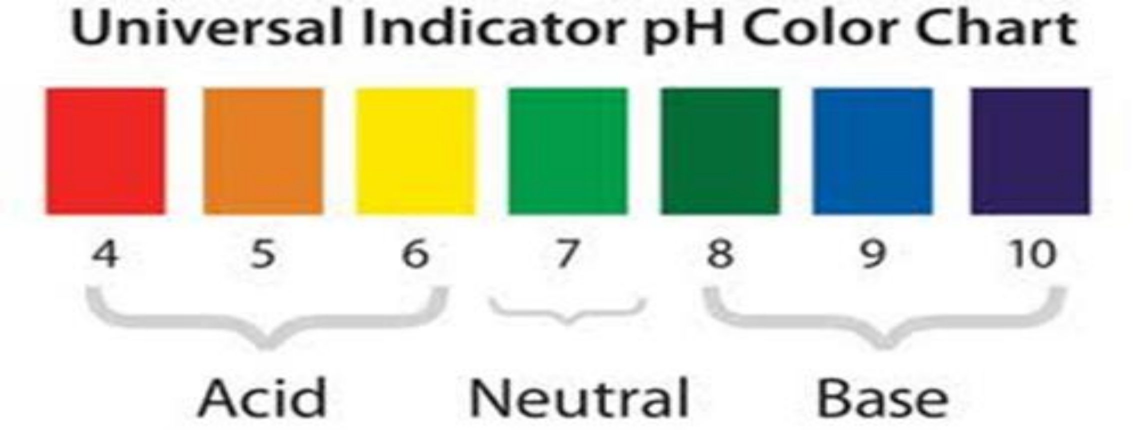
Choosing Suitable indicators Via $pH_{eq.p.}$

(3) $pK_{HIn} \pm 1 = 7 \pm 1$: this means that the color of the indicator starts to change at pH = 8 and completes the change at pH = 6 . This occurs before reaching the equivalent point at pH = 5.2. Therefore , this indicator will give with this titration an earlier endpoint (negative error i.e low $mL_{eq.p}$) .The graph on the right illustrates the idea of these two examples



Universal Indicator

A Universal Indicator is a mixture of indicators which give a gradual change in color over a wide pH range . The pH of a solution can be approximately identified when a few drops of universal indicator are mixed with the solution . There are different types of universal indicators .



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Indicator's Errors

There are three common indicator errors :

1- If you add large amount of an indicator , you will need several drops of titrant to reach the endpoint which mean late endpoint . Remember the ratio 1 :10 previously mentioned . So better use as little as possible of indicator.

2- Suppose you are using an indicator which give a little late equivalent point (indicator error) . Let us say that a blank gave you 0.1 mL at the endpoint . To correct for this error you should subtract 0.1 mL from the volume required for the unknown sample to reach the endpoint .

Indicator’s Errors

But if the indicator gives a little earlier equivalent point in this case we add 0.1 mL (blank) to the volume required for the unknown sample to reach the endpoint .

3- Error resulting from the inability of the analyst to distinguish color recursively . This error can be avoided by using a standard solution of the same analyte where we can theoretically calculate the volume of the titrant required at the equivalent point . the color of the standard solution is kept aside as a reference .

Relative Precision (R.P.)

We've already mentioned that the titration will be more accurate and successful if the change in the pH at the equivalent point region is sharp (vertically) to reduce the titration error and large to enable several indicators to suit the titration . This can be achieved if the used concentration and the equilibrium constant are high as we have previously mentioned . This can also be mathematically expressed by what we call the relative precision of the titration which can be defined as the fraction of the equivalent amount of titrant needed to raise or lower the pH by 0.1 unit above or under $pH_{eq.p}$.

Relative Precision (R.P.)

Note that the smaller the value of the relative precision the more successful the titration . The following equations are used to evaluate a titration :

Titration of strong acid by strong base or vice versa : $$r.p. = \sqrt{\frac{K_w}{C}}$$

Titration of weak acid by strong base : $$r.p. = \sqrt{\frac{K_w}{K_a \cdot C}}$$

Titration of weak base by strong acid : $$r.p. = \sqrt{\frac{K_w}{K_b \cdot C}}$$

Where C is the concentration of the analyte .

Relative Precision (R.P.)

Example : Calculate the relative precision of titrating 0.05 M acetic acid ($K_a = 2 X 10^{-5}$) by NaOH solution ?

Solution :

$$r.p. = \sqrt{\frac{1 X 10^{-14}}{2 X 10^{-5} X 0.05}} = 1 X 10^{-4} = 0.1 X 10^{-3}$$

This means that 0.1 part from one thousand parts represents the equivalent amount of titrant NaOH required for reaction with acetic acid to raise the pH by 0.1 unit above the equivalent point . The small relative precision value indicates that the accuracy of the titration is good.

Acid Base Titration in Non Aqueous Media

In general any substance that owns acidic property can be titrated with standard solution of strong base and vice versa, where any substance owns basic property can be titrated with standard solution of strong acid providing that Ka or Kb $>1x10^{-8}$. Volumetric analysis has a very wide applications in the fields of medicine , geology , pharmacology , forensic analysis , environmental analysis …etc.

There are many acids and bases which are very weak in aqueous medium (K_a or K_b $<1x10^{-8}$) for that reason can not be titrated in water . However, the strength of these weak acids can be increase by using an organic solvent which it's basic property more than water and also the strength of the weak base can be increase by using organic solvent more acidic than water.

Summary

This unit has the answers of questions like : What are the acid – base indicators ? How do they work ? How to find the pH color range during which the indicator changes its color ? How to select the appropriate indicator for a certain titration in case the titration curve is available and in case it is not available ? How do we calculate the relative precision of a titration ? What are the common indicator errors and how to avoid it ? Why sometimes do the acid – base titration in non aqueous media ? . The provided pictures , graphs and videos help in understanding these questions .

ACID – BASE INDICATORS

Tutorial

Exercise 1 : In the titration of 20 mL of 0.05 M CH_3COOH(K_a=1.8X10^{-5}) with 0.1 M NaOH which of the following indicators is more suitable for this titration :
(1) pK_{In} = 7 (2) pK_{In} = 5 (3) pK_{In} = 3 ?

Your answer :

Our answer next slide

Tutorial

Answer 1 : We write the titration reaction equation :

Then , we calculate the $pH_{eq.p.}$ for the titration :

$NaOH$	+	CH_3COOH	$\rightarrow$	CH_3COONa	+	H_2O	
10X0.1 = 1.0		20 X 0.05 = 1.0		0		0	(mmole)(I)
0		0		1.0		1.0	(mmole)(C)

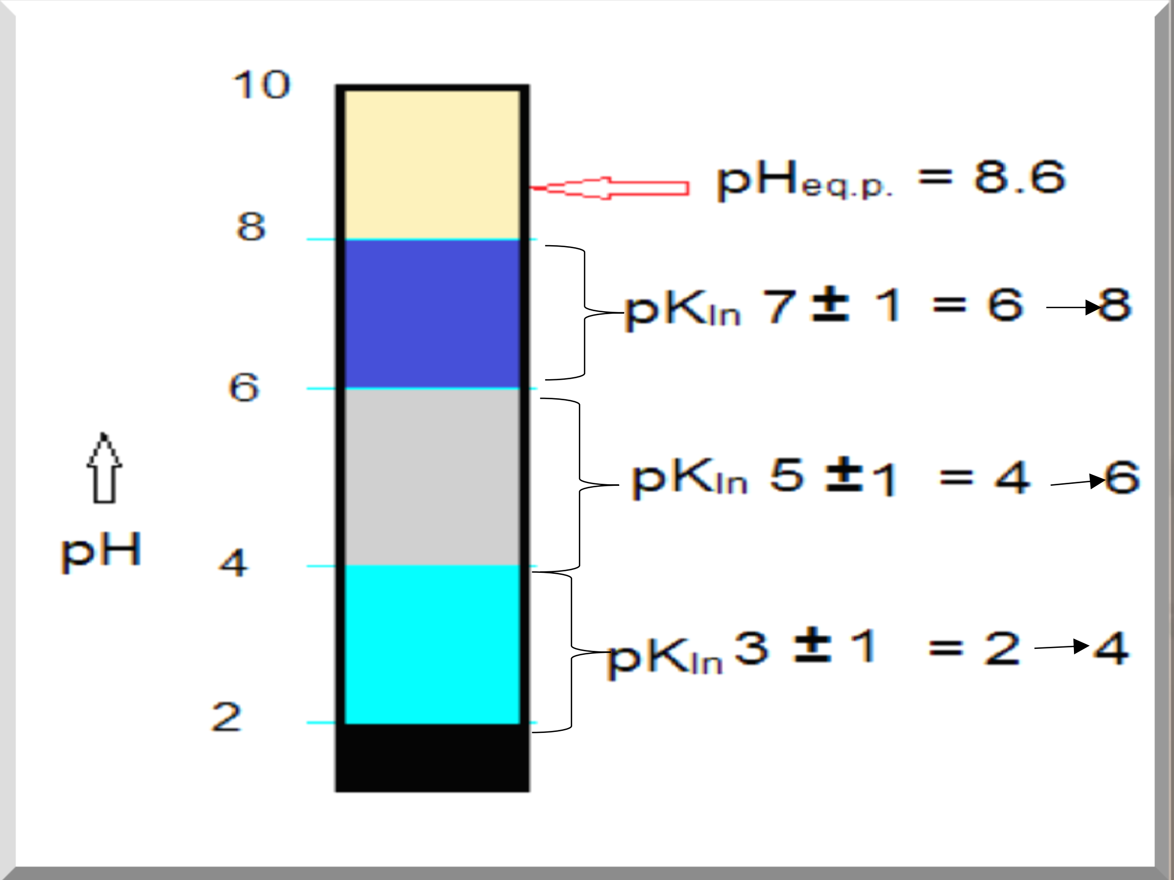
$$pOH_{eq.p} = -\log \sqrt{\frac{1x10^{-14}\ X\ \dfrac{1.0}{20+10}}{1.8X10^{-5}}} \approx 5.4 \quad \therefore\ pH_{eq.p.} = 8.6$$

Since we are adding the base from burette to the acid in the conical flask , then , the pH of the conical flask solution is going to increase during titration .

Tutorial

Follow answer 1 :

It is clear from this graph that all the indicators change it's color before the equivalent point , therefore , all give earlier equivalent point (negative error , low $V_{eq.p.}$) .



Tutorial

Exercise 2 : Calculate the pH at which , the color of the following indicator is red and at which is blue ?

$$HIn \leftrightarrow H^{+} + In^{-} \qquad K_{in} = 1X10^{-5}$$

(Red) (blue)

Your answer :

Our answer next slide

Tutorial

Answer 2 : $pK_{In} = -\log 1X10^{-5} = 5$

$pK_{In} \pm 1 = 5 \pm 1 = 4 \quad 6$

This means that the acidic color of the indicator (HIn) which is red will be dominant from pH = 4 downwards while the basic color (In^-) which is blue will be dominant from pH = 6 upwards . Note that between pH =4 up to 6 , the color is reddish blue .

Tutorial

Exercise 3 : Show by calculation whether the following indicator :

$$HIn \leftrightarrow H^+ + In^- \qquad K_{In} = 1 \times 10^{-8}$$

Is suitable or give earlier or late equivalent point for the titration of an acid with a base whose it's equivalent point at pH = 10.2 ?

Your answer :

Our answer next slide

Tutorial

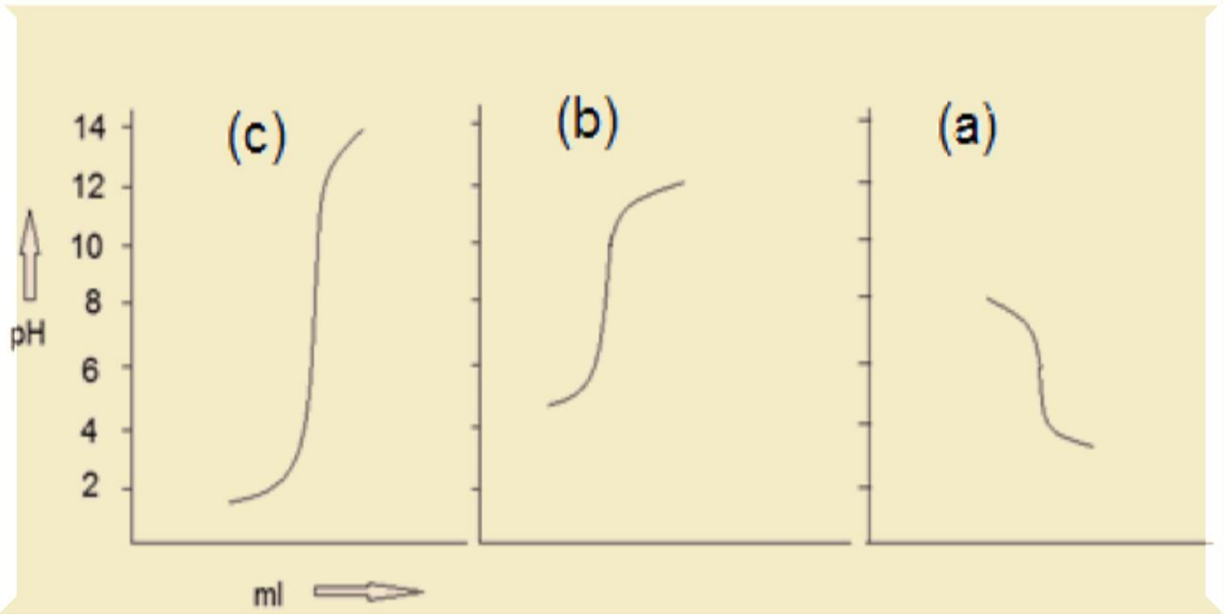
Answer 3 :

The color turn range of the indicator is 8 ± 1 that's from 7 up to 9 or from 9 down to 7 for the titration of acid with base or base with acid respectively .Since we are titrating an acid with a base , the pH is increasing during titration so the indicator will change it's color from 7 up to 9 which is before reaching the equivalent point at pH = 10.2 . Therefore , this indicator will give an earlier equivalent point with this titration .

Tutorial

Exercise 4 : How do the following indicators behave with the titrations (a) , (b) and (c) in the graph below : (1) $pK_{In} = 3$, (2) $pK_{In} = 5$, (3) $pK_{In} = 7$?

Your answer :



Our answer next slide

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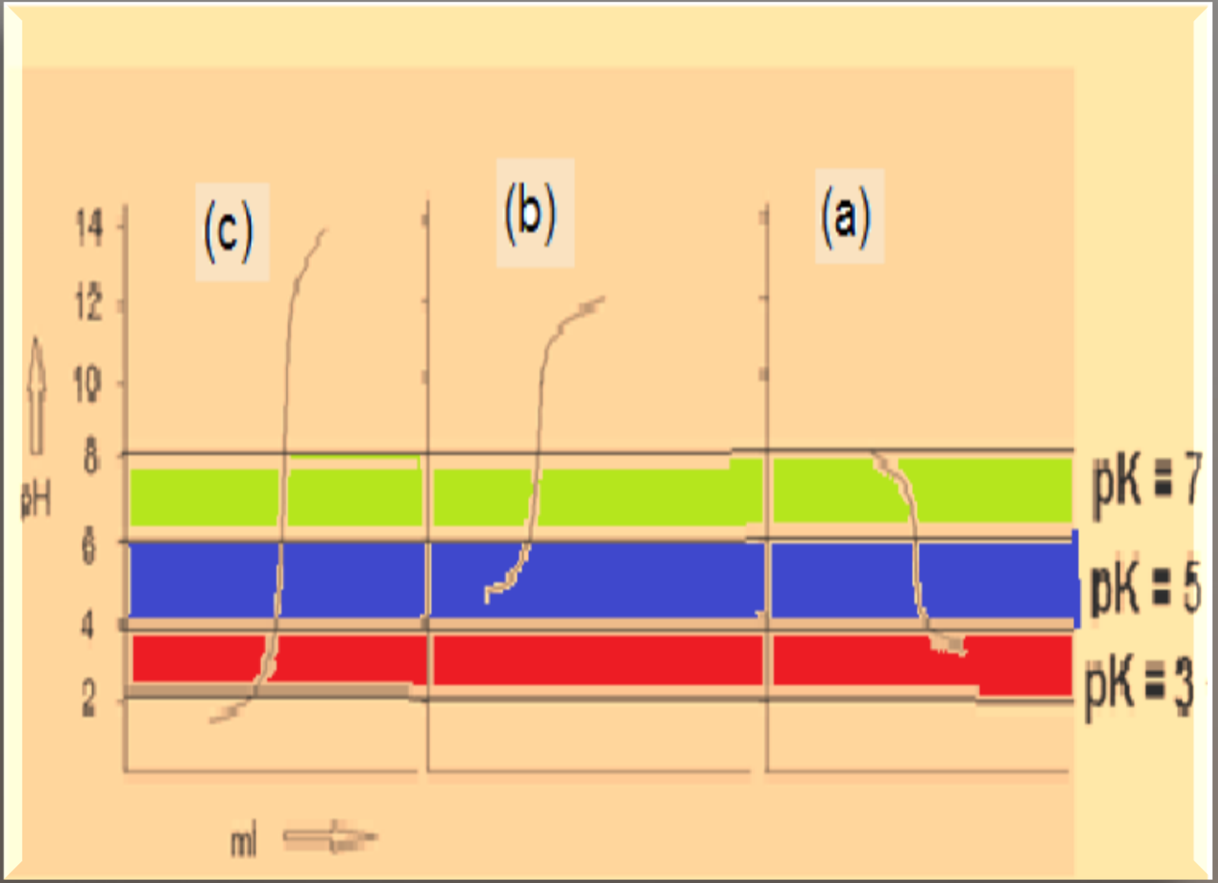
Answer 4 : It is clear from the below graph that all the three indicators are suitable to the titration (c) although indicator pK_{In} = 3 may give a little earlier equivalent point . With the titration (b) only the indicator pK_{In} = 7 is suitable ,the other two indicators give earlier equivalent point . With respect to titration (a) , only indicator pK_{In} = 5 is suitable where as indicator pK_{In} = 7 gives an earlier equivalent point and indicator pK_{In} = 3 gives a late equivalent point .



Tutorial

Exercise 5 : Calculate the relative precision of the titration of 0.1 M NH_3 ($K_b = 1.75X10^{-5}$) with HCl and comment on your result ?

Your answer :

Our answer next slide

ACID – BASE INDICATORS

Tutorial

Answer 5 :

$$R.P. = \sqrt{\frac{K_w}{K_b X\, C_b}} = \sqrt{\frac{1X10^{-14}}{1.75X10^{-5}\ X\ 0.1}} = 7.6X10^{-5}$$

Since the relative precision is very small so we expect the titration to have good precision .

على الراغبين الاستماع الى محاضرات الاستاذ الدكتور/ ابراهيم زامل الزامل باللغة العربية عن هذا الموضوع الرجوع الى الروابط التالية :

أدلة معايرات الحموض و القواعد

أدلة معايرات الحموض و القواعد ٢