(viii) *Which one of the following is true for any diprotic acid, H_2X ?*

(A) $K_{a_2} > K_{a_1}$ **(B)** $K_{a_1} > K_{a_2}$ **(C)** $K_{a_2} = \dfrac{1}{K_{a_1}}$ **(D)** $K_{a_2} = K_{a_1}$

(ix) K_{sp} *of* $Mg(OH)_2$ *is* 1×10^{-12}. 0.01 *M* $MgCl_2$ *will be precipitating at the limiting pH* :

(A) 8 **(B)** 9 **(C)** 10 **(D)** 12

(x) *The solubility products of MA, MB, MC and MD are* 1.8×10^{-10}, 4×10^{-3}, 4×10^{-8} *and* 6×10^{-5} *respectively. If a* 0.01 *M solution of MX is added dropwise to a mixture containing* A^-, B^-, C^- *and* D^- *ions then the one to be precipitated first will be*:

(A) *MA* **(B)** *MB* **(C)** *MC* **(D)** *MD*

(xi) *For a sparingly soluble salt* $A_p B_q$, *the relationship of its solubility product* (L_S) *with its solubility* (S) *is* :

(A) $L_S = S^{p+q} \,.\, p^p \,.\, q^q$ **(B)** $L_S = S^{p+q} \,.\, p^q \,.\, q^p$

(C) $L_S = S^{pq} \,.\, p^p \,.\, q^q$ **(D)** $L_S = S^{pq} \,(pq)^{p+q}$

(xii) *When equal volumes of the following solutions are mixed, precipitation of AgCl* ($K_{sp} = 1.8 \times 10^{-10}$) *will occur only with :*

(A) 10^{-4} *M* (Ag^+) *and* 10^{-4} *M* (Cl^-) **(B)** 10^{-5} *M* (Ag^+) *and* 10^{-5} *M* (Cl^-)

(C) 10^{-6} *M* (Ag^+) *and* 10^{-6} *M* (Cl^-) **(D)** 10^{-10} *M* (Ag^+) *and* 10^{-10} *M* (Cl^-)

ACID BASE TITRATIONS Section - 6

pH of Mixtures of Acids and Bases

Let us take x millimoles of acid (HA) and y millimoles of base (BOH). Note that acid is monobasic and base is monoacidic.

(a) Strong acid and strong base

- If $x = y$, then complete neutralization takes place and we get x (= y). Millimoles of salt (BA) of strong acid and strong base which means no hydrolysis takes place and pH of solution = 7.
- If $x > y$, then there is an excess of strong acid and resulting solution is acidic with millimoles of acid left in excess $= x - y$. Now if V (in cc) be the volume of mixture, then :

  $\Rightarrow$ $\mathrm{M} = \dfrac{x-y}{\mathrm{V}}$. Now calculate pH using the equation $\mathrm{pH} = -\log_{10}[\mathrm{H}^+]$
- If $x < y$, then there is an excess of strong base and resulting solution is basic with millimoles of base left in excess $= y - x$. Now if V (in cc) be the volume of mixture, then :

  $\Rightarrow$ $\mathrm{M} = \dfrac{y-x}{\mathrm{V}}$. Now calculate pH using the equation $\mathrm{pH} = 14 - \log_{10}[\mathrm{OH}^-]$

(b) Strong base and weak acid

- If $x = y$, first of all neutralization takes place to give x (= y) millimoles of salt (BA). The salt will now undergo *hydrolysis* to give an alkaline solution. Calculate pH by using the standard result :

$$\text{pH} = 7 + \frac{1}{2}(\text{pK}_a + \log_{10} c) \qquad ; \qquad \text{c is concentration expressed in M (mol/L)}$$

- If $x > y$, there is excess of weak acid whose millimoles = $x - y$ and y millimoles of salt is formed. This will give an *acidic buffer solution*. Calculate pH of buffer solution using *Henderson's Equation*.

$$\text{pH} = \text{pK}_a + \log_{10}\frac{[\text{salt}]}{[\text{acid}]} = \text{pK}_a + \log_{10}\frac{y}{x-y}$$

- If $x < y$, the solution in this case contains excess of strong base whose millimoles are $y - x$.

$$\text{M} = \frac{y-x}{\text{V}} \qquad \text{Calculate pH using the equation pH} = 14 - \log_{10}[\text{OH}^-]$$

(c) Strong acid and weak base

- If $x = y$, first of all complete neutralisation takes place to produce x (= y) millimoles of salt (BA). The salt (BA) is of strong acid and weak base, hence *hydrolysis* takes place to give an acidic solution. Calculate its pH by using standard result.

$$\text{pH} = 7 - \frac{1}{2}(\text{pK}_b + \log_{10} c) \qquad ; \qquad \text{c : mol/L}$$

- If $x > y$, then solution contain excess of strong acid whose millimoles = $x - \text{y}$.

$$\text{M} = \frac{x-y}{\text{V}} \qquad \text{Now calculate pH using the equation pH} = -\log_{10}[\text{H}^+]$$

- If $x < y$, then there is an excess of weak base whose millimoles are $y - x$ and millimoles of salt (BA) are x. This will give a *basic buffer solution*. Calculate the pH by using Henderson's *Equation*.

$$\text{pH} = 14 - \text{pK}_b - \log_{10}\frac{[\text{salt}]}{[\text{base}]} = 14 - \text{pK}_b - \log_{10}\frac{x}{y-x}$$

(d) Weak acid and weak base

- If $x = y$, neutralisation takes place completely with the formation of x (= y) millimoles of salt (BA) of weak acid and weak base. So hydrolysis takes place. Calculate the pH by using :

$$\text{pH} = 7 + \frac{1}{2}(\text{pK}_a - \text{pK}_b)$$

Indicators

Definition : An “indicator” is a dye (or substance) which changes color over a short pH range.

Example: Methyl orange changes color in the pH range of 3.1 to 4.5

Indicator	1 2 3 4 5 6 7 8 9 10 11 12 13		
Methyl Orange	Pink	3.1 – 4.5	Yellow
Methyl Red	Pink	4.2 – 6.2	Yellow
Phenolphthalein	Colourless	8.3 – 10	Pink
Thymolphthalein	Colourless	9.3 – 10.5	Pink
Bromothymol Blue	Orange	6.0 – 7.5	Blue
Bromocresol Green	Yellow	3.8 – 4.6	Blue

pH Range and color change of some common Acid-base Indicators

End Point : It is the point at which the reaction between an acid and a base is “*observed*” to be complete i.e. the pH at which an indicator changes its color.

Equivalence Point: It is the point at which the reaction between an acid and a base is “*theoretically*” complete (as per the balanced equation for the reaction).

Note :

- At “*equivalence point*”, meq. of acid = meq. of base but the “*end point*” can only be detected by measuring the pH at different points of time during the titration. It is usually more convenient to add an indicator to the solution and detect the “*observed end*” of the reaction through a color change in the solution.
- An indicator is usually a weak acid or a weak base for acid-base titration. The color change occurs when protons are transferred to form a conjugate base or a conjugate acid of a different color.

Let us represent an indicator as HIn (Weak Acid)

$$\underset{\substack{\text{Acid}\\\text{(color 1)}}}{\text{HIn}} + H_2O \rightleftharpoons H_3O^+ + \underset{\substack{\text{Conjugate Base}\\\text{(color 2)}}}{\text{In}^-}$$

or simply,

$$\underset{\text{(color 1)}}{\text{HIn}} \rightleftharpoons H^+ + \underset{\text{(color 2)}}{\text{In}^-}$$

Necessary property of Indicator : Color of ionised form must be remarkably different from that of unionized form.

Now, K_{In} = Equilibrium Constant for the dissociation of the indicator $= \dfrac{[H^+][In^-]}{[HIn]}$

$$\Rightarrow \quad pH = pK_{In} + \log_{10}\frac{[In^-]}{[HIn]}$$

Note :

- An indicator changes color over a pH range (the so called “*transition range*”). It is the range over which color change in the solution is detectable by the “*observer*”.
- The smaller the transition range, the better the indicator in detecting “*equivalence point*”. (*Equivalence Point ≠ End Point*)

With indicator in which both the forms, ionized and unionized form are colored, generally one colour is visible if the ratio of the concentration of the two forms is 10 : 1.

Thus, when only the color of un-ionized (HIn) form is seen : $\dfrac{\left[\text{HIn}\right]}{[\text{In}^-]} = \dfrac{10}{1}$

$\Rightarrow$ $\quad \text{pH}_1 = \text{pK}_a + \log_{10}\dfrac{1}{10} = \text{pK}_a - 1$

and when only the color of ionized (In^-) form is seen : $\dfrac{[\text{In}^-]}{\left[\text{HIn}\right]} = \dfrac{10}{1}$

$\Rightarrow$ $\quad \text{pH}_2 = \text{pK}_a + \log_{10}\dfrac{10}{1} = \text{pK}_a + 1$

Thus, pH change required in going from one color to other is $\Delta\text{pH} = \text{pH}_2 - \text{pH}_1 = 2$

In the midway between the two colors (i.e. in the transition range), one can assume that $[\text{HIn}] = [\text{In}^-]$

$\Rightarrow$ $\quad \text{pH} = \text{pK}_a + \log_{10} 1 = \text{pK}_a \quad \Rightarrow \quad \text{pH} = \text{pK}_a$

$\Rightarrow$ The pK_a of the indicator should be close to the pH of the equivalence point

For weak-base indicators, same transition range is observed and $\text{pOH} = \text{pK}_b$ at the midway.

(i) Phenophthalein : It is a weak acid represented by PhH.

$$\underset{\textit{Colorless}}{\text{PhH}} \rightleftharpoons \underset{\textit{Pink in base}}{\text{Ph}^- + \text{H}^+} \qquad \text{....(i)}$$

- Phenolphthalein is colorless in acid solution and pink in basic solution.
- When a strong base like NaOH is added, it displaces the equilibrium (I) towards right direction and there is a color change.

(ii) Methyl Orange : It is a weak base represented as MeOH.

$$\underset{\textit{Yellow in base}}{\text{MeOH}} \rightleftharpoons \underset{\textit{Red in acid}}{\text{Me}^+ + \text{OH}^-} \qquad \text{....(ii)}$$

- When a strong acid is added, equilibrium (II) is shifted towards right and color change to red is detected.

***Illustrating the concept* :**

(a) *What is the equivalence point of* 0.1 *M* NH_4Br *solution* ?

$[(\text{pK}_b)_{\text{NH}_4\text{OH}} = 4.74]$

When a strong acid reacts with a strong base, equivalence point is the neutralisation point (i.e pH of the solution = 7 if both of acid and base have same meq.) but when a strong acid reacts with a weak base or vice-versa, pH at the equivalence point ≠ 7 as the salt formed will get hydrolysed and pH of the solution > 7 or < 7 at the equivalence point. NH_4Br is a salt of Strong acid and Weak base.

$$\Rightarrow \quad \text{pH} = 7 - \frac{1}{2}\left(\text{pK}_b + \log_{10} c\right) = 7 - \frac{1}{2}\left(4.74 + \log_{10} 0.1\right) = 5.13$$

(b) *What will be the color of the mehtyl red indicator in the solution of* NH_4Br *in part (a) ? At pH* < 3.1, *the indicator methyl red is colored pink, at pH* > 6.3, *it is yellow and at the intermediate values of the pH it is orange.*

Since the pH of NH_4Br solution is 5.13 and it lies in the intermediate range of methyl orange, its color will be orange. $(3.1 < \text{pH} < 6.3)$

(c) *An acid indicator has* $pK_{In} = 5.3$. *In a certain solution, this indicator is found to be* 80% *ionised. What is the pH of the solution ?*

$$\begin{array}{cccc} HIn & \rightleftharpoons & H^+ & + \; In^- \\ 1 & & 0 & 0 \\ 1-x & & x & x \end{array}$$

Indicator is 80% ionized in acid form : $\Rightarrow x = 0.8$

$$\Rightarrow \quad pH = pK_a + \log_{10}\frac{[In^-]}{[HIn]} \quad \Rightarrow \quad pH = 5.3 + \log_{10}\frac{0.8}{0.2} = 5.9$$

Acid Base titration curves :

Titration Curve : It is a curve in which pH of the solution is titrated against volume of the titrate added.

(i) Strong Acid and Strong Base :

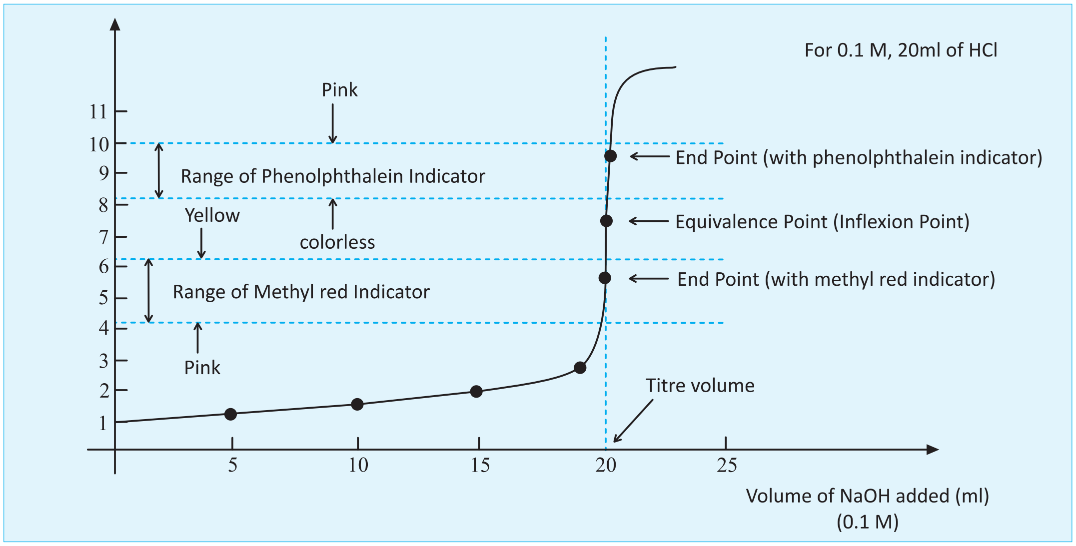
(HCl) (NaOH)

In this case, both the titrants are completely ionized.

$$HCl + NaOH \rightleftharpoons NaCl + H_2O$$

As OH^- is added to an acid solution, $[H^+]$ decreases and $[OH^-]$ increases $\Rightarrow$ pH goes on increasing. As the equivalence point is reached, $[H^+]$ is rapidly reduced. Above this point, $[OH^-]$ increases rapidly from 10^{-7} M and after that pH of the solution remains fairly constant. Thus, there is an inflexion point at the equivalence point.

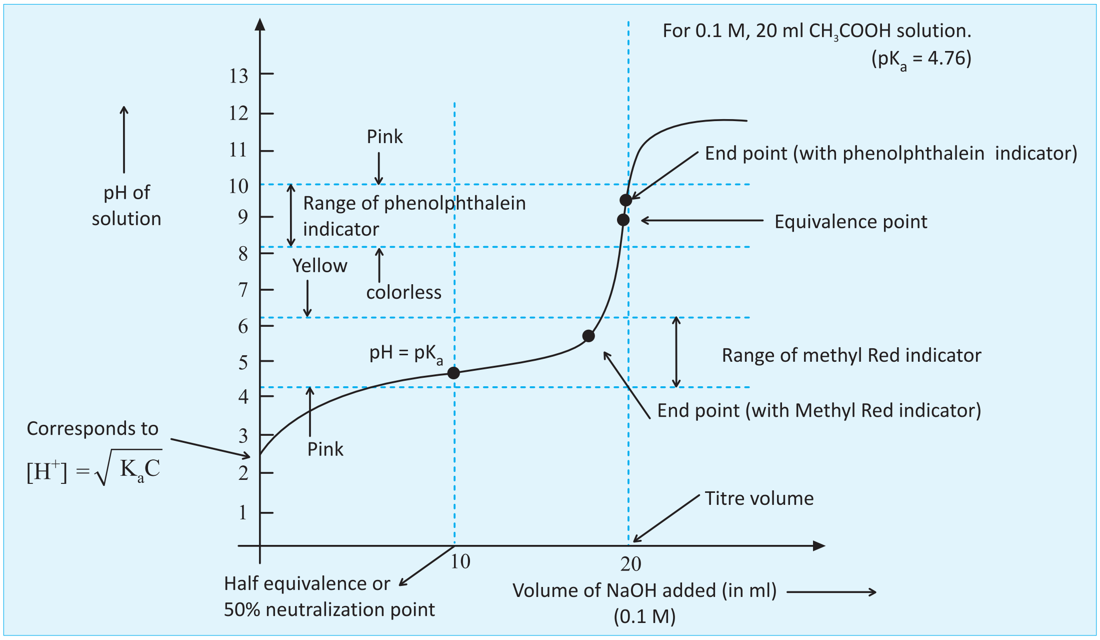
The difference in the volume of NaOH solution between the *end point* and the *equivalence point* is not significant for most of the commonly used indicators as there is a large change in the pH value around the equivalence point and most of them change their color across this pH change.



(ii) Weak Acid and Strong Base :

(CH_3COOH) (NaOH)

Initially, when a few drops of OH^- are added to the weak acid, it forms an acidic buffer CH_3COOH/CH_3COONa and thus, pH of the solution changes slowly. At the equivalence point, solution will be alkaline. If OH^- addition is continued after the equivalence point, $[OH^-]$ will increase rapidly.



$$(pH) \text{ at equivalence point} = 7 + \frac{1}{2}\left(4.76 + \log_{10} c\right) = 7 + \frac{1}{2}\left(4.76 + \log_{10} 0.05\right) = 8.72$$

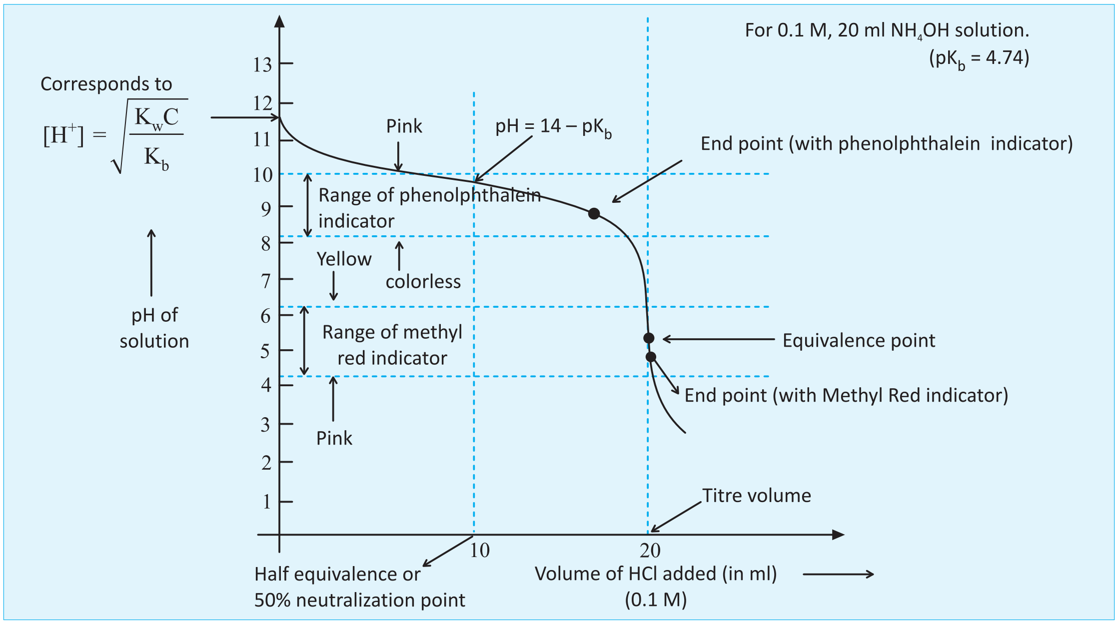
[Here c = concentration of the salt formed at equivalence point]

Thus, methyl red, methyl orange are inappropriate for use in the detection of the end point between a weak acid and a strong base. Also note that the buffer capacity of the buffer solution will be maximum at 50% equivalence point i.e. when the volume of NaOH is 10 ml.

(iii) Strong Acid and Weak Base :

(HCl) (NH_4OH)

Initially, when a few drops of H^+ are added to the weak acid, it forms a basic buffer NH_4OH/NH_4Cl and thus, pH of the solution changes slowly. At the equivalence point, solution will be acidic. If H^+ addition is continued after the equivalence point, $[H^+]$ will increase rapidly.



Thus, phenolphthalein, thymolphthalein are quite inappropriate to be used as an indicator to detect the end point between a strong acid and weak base neutralization.

Also note that the buffer capacity of the buffer solution will be maximum at 50% equivalence point i.e. when the volume of HCl is 10 ml.

Note : The selection of an indicator therefore is determined by the pH of the solution at the equivalence point.

Illustration - 21 *0.1 M NaOH is titrated with 0.1 M, 20 ml HA till the end point.* $K_a(HA) = 6 \times 10^{-6}$ *and degree of dissociation of HA is negligible (small) as compared to unity. Calculate the pH of the resulting solution at the end point* [Use $\log_{10} 6 \sim 0.8$]

SOLUTION :

	NaOH +	HA	$\longrightarrow$	NaA +	H_2O
At end point (mmoles)	2	2 (≡ 0.1 × 20)		-	
	-	-		2	-

Note : 20ml of NaOH is required for the complete neutralisation of HA.

NaA is a salt of strong base and weak acid. Thus, will undergo hydrolysis and solution will become basic.

Here $c = [NaA] = \dfrac{2}{20+20} = 0.05\,M$

and $pK_a = -\log_{10}(6 \times 10^{-6}) = 5.2$

$$pH_{\text{at end point}} = 7 + \frac{1}{2}\left(pK_a + \log_{10} c\right)$$

$$= 7 + \frac{1}{2}\left(5.2 + \log_{10} 0.05\right) = 8.95$$

Illustration - 22 *The equivalence point in a titration of* 40.0 *mL of a solution of a weak monoprotic acid occurs when* 35.0 *mL of a* 0.10 *M NaOH solution has been added. The pH of the solution is* 5.5 *after the addition of* 20.0 *mL of NaOH solution. What is the dissociation constant of the acid ?*

SOLUTION :

Let x millimoles of HA are taken initially. Find x :

Consider the equation of neutralisation :

HA +	NaOH	$\longrightarrow$	NaA +	H_2O
x	y		–	
$x-y$	–		y	

At equivalent point, millimoles of acid = millimoles of NaOH [i.e. $x = y$]

$\Rightarrow$ millimoles HA $= x = 3.5$ [35 ml of 0.1 M NaOH]

At pH = 5.5, millimoles of NaOH added $= 2 = y$ [20 ml of 0.1 M NaOH]

$\Rightarrow$ millimoles of HA left $= x - y = 1.5$

and millimoles of NaA formed $= 2$

Now such a solution will behave as an acidic buffer, whose pH is given as :

$$[H^+] = \frac{K_a\,[\text{acid}]}{[\text{salt}]} \Rightarrow 10^{-5.5} = K_a \frac{1.5}{2}$$

$$\Rightarrow \quad K_a = 4.22 \times 10^{-6} \quad [10^{-5.5} = \sqrt{10} \times 10^{-6}]$$

IN-CHAPTER EXERCISE - E

1. Calculate the pH of the following mixtures. (pK_a of acetic acid = 4.74 = pK_b of NH_4OH)

(i) 50 mL of 0.1 M NaOH and 50 mL of 0.1 M CH_3COOH

(ii) 50 mL of 0.1 M NaOH and 50 mL of 0.05 M CH_3COOH

(iii) 50 mL of 0.05 M NaOH and 50 mL of 0.1 M CH_3COOH

(iv) 50 mL of 0.1 M NH_4OH and 50 mL of 0.05 M HCl

(v) 50 mL of 0.05 M NH_4OH and 50 mL of 0.1 M HCl

(vi) 50 mL of 0.05 M NH_4OH and 50 mL of 0.05 M CH_3COOH

2. Calculate the pH at which an acid indicator ($K_a = 1.0 \times 10^{-5}$) changes colour when the indicator is 1.0×10^{-3} M. (Hint : The mid-point of the colour change range of an indicator is the point at which its acid and conjugate base forms are present in equal concentration)

3. At what pH does an indicator change colour if the indicator is a weak acid with $K_{ind} = 4.0 \times 10^{-4}$. For which of the following neutralizations would the indicator be useful ?

(i) NaOH + CH_3COOH **(ii)** HCl + NH_3 **(iii)** HCl + NaOH

4. **Choose the correct alternative. Only one choice is correct :**

(i) In the titration of NH_4OH versus HCl, the pH of the solution at equivalence point is :

(A) about 5.5 **(B)** about 7 **(C)** about 8.5 **(D)** about 9.5

(ii) The pH indicators are :

(A) salts of strong acids and strong bases **(B)** salts of weak acids and weak bases

(C) either weak acids or weak bases **(D)** either strong acids or strong bases

(iii) In which of the following acid-base titration, pH is greater than 8 at the equivalence point ?

(A) Acetic acid versus ammonia **(B)** Acetic acid versus sodium hydroxide

(C) Hydrochloric acid versus ammonia **(D)** Hydrochloric acid versus sodium hydroxide

(iv) Why are strong acids generally used as standard solutions in acid-base titrations ?

(A) The pH at the equivalent point will always be 7

(B) They can be used to titrate both strong and weak bases

(C) Strong acids form more stable solutions than weak acids

(D) The salts of strong acid do not hydrolyze

(v) The best indicator for detection of end point in titration of a weak acid and a strong base is:

(A) methyl orange (3 to 4) **(B)** methyl red (5 to 6)

(C) bromothymol blue (6 to 7.5) **(D)** phenolphthalein (8 to 9.6)