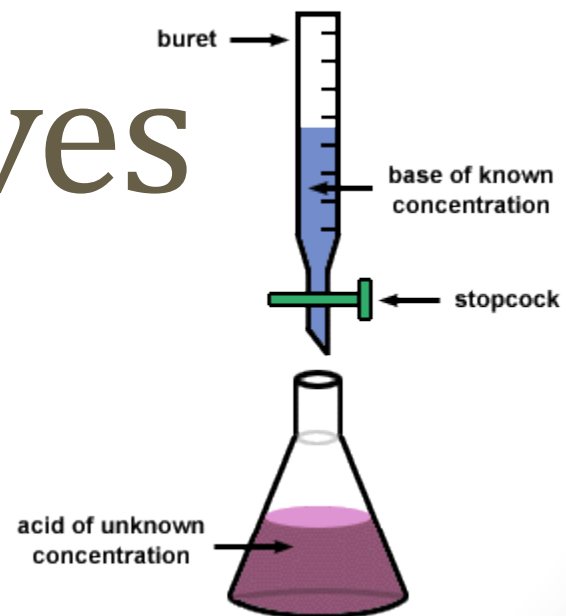


# Titration curves



# Titration of a strong acid

- When a strong acid is titrated with a strong base the pH at any point is determined solely by **the concentration of un-titrated acid or excess base**.
- The conjugated base that is formed has **no effect on pH**.

# Titration of a weak acid

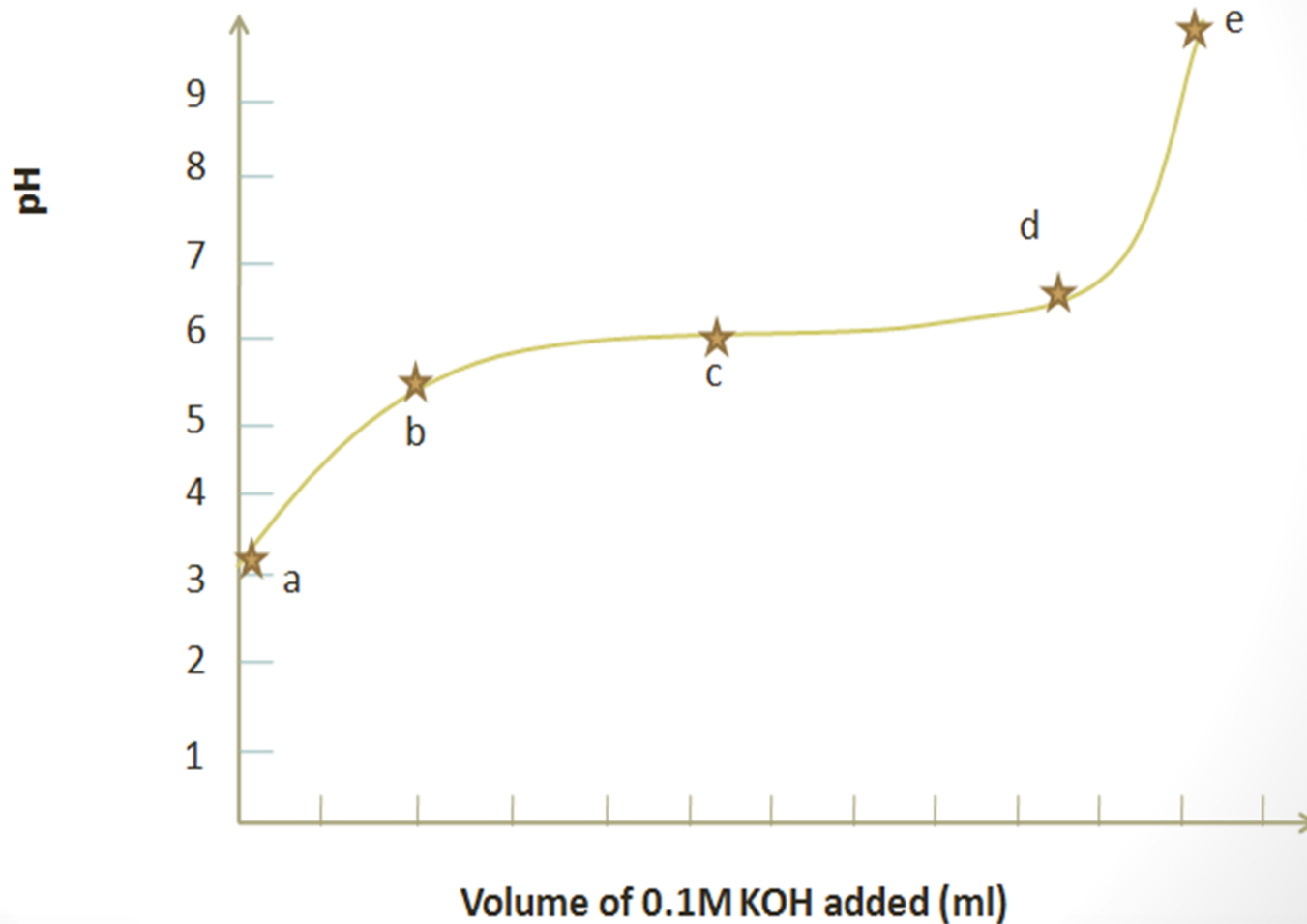
- When a weak acid is titrated with a strong base, the weak acid dissociates to yield a small amount of  $\text{H}^+$ .
- Weak acids or bases ***do not dissociate completely***, therefore an equilibrium expression with  $K_a$  must be used.



- When  $\text{OH}^-$  ions are added during titration it is neutralized by  $\text{H}^+$  ions to produce  $\text{H}_2\text{O}$ .
- The removal of the  $\text{H}^+$  ions disturbs the equilibrium thus more HA molecules will ionize to produce  $\text{H}^+$  ions to re-establish the equilibrium.
- This process will continue until all the HA molecules are ionized.

**Thus the no. of moles of HA will be equal to the no. of moles of proton.**

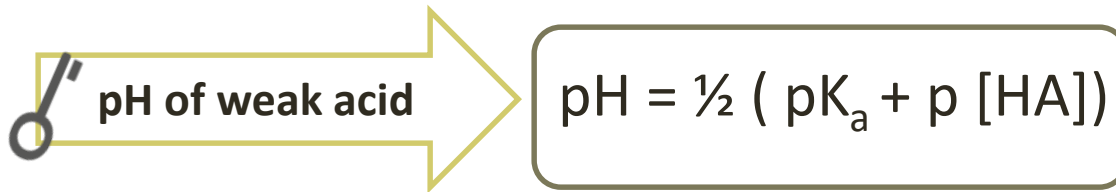
# Titration curve of a monoprotic weak acid



# Example (1)

- Calculate the appropriate pH values and draw the curve for the titration of 500 ml of 0.1 M weak acid HA with 0.1 M KOH,  $pK_a = 5$ ?

**A) At the start point:** Before the addition of any base



pH of weak acid

$$pH = \frac{1}{2} ( pK_a + p [HA])$$

$$pH = \frac{1}{2} [(5 + (-\log 0.1))]$$

$$pH = 3$$

**NOTE:** at *any point during the titration (after any addition of a base)*, the pH

should be calculated using **Henderson-Hasselbalch equation**

$$\text{pH} = \text{pK}_a + \log \frac{[\text{A}^-]}{[\text{HA}]}$$

• **Here we will use the no. of moles instead of molarity;** because when we calculate the volume it will give the same ratio at the end



## B) pH after the addition of 100 ml of KOH

-The no. of moles of HA *originally* present =  $0.1 \times 0.5 = 0.05$  mole

-The no. of moles  $\text{OH}^-$  *added* =  $M \times V = 0.1 \times 0.1 = 0.01$  mole

-Thus 0.01 moles of KOH will *react* with 0.01 mole of HA to **produce 0.01 mole  $\text{A}^-$**

- Moles of HA *remaining* = moles of HA *originally* present – moles of HA *titrated to salt*

$$= 0.05 - 0.01 = \mathbf{0.04 \text{ mole}}$$

$$-\text{pH} = \text{pK}_a + \text{Log} ([\text{A}^-] / [\text{HA}])$$

$$-\text{pH} = 5 + \text{Log} (0.01/0.04)$$

$$-\text{pH} = 4.4$$

Used after any addition of base to calculate moles of HA remaining

### C) pH after the addition of 250 ml of KOH

The no. of moles  $\text{OH}^-$  **added** =  $M \times V = 0.1 \times 0.25 = 0.025$  mole

Thus 0.025 moles of KOH will **react** with 0.025 mole of HA to **produce 0.025 mole  $\text{A}^-$**

no. of HA **remaining** = moles of HA **originally** present – moles of HA **titrated to salt**

$$= 0.05 - 0.025 = \mathbf{0.025 \text{ mole}}$$

$$\text{pH} = \text{pK}_a + \text{Log} ([\text{A}^-] / [\text{HA}])$$

$$\text{pH} = 5 + \text{Log} (0.025/0.025)$$

$$\text{pH} = 5$$

Here the  $[\text{A}^-] = [\text{HA}]$  thus, **pH = pKa  $\rightarrow$  acts as a buffer**





### D) the pH after the addition of 375 ml of KOH

The no. of moles  $\text{OH}^-$  **added** =  $M \times V = 0.1 \times 0.375 = 0.0375$  mole

Thus 0.0375 moles of KOH will **react** with 0.0375 mole of HA to produce

**0.0375 mole  $\text{A}^-$**

The no. of moles of HA **remaining** =  $0.05 - 0.0375 = \mathbf{0.0125}$  mole

$$\text{pH} = \text{pK}_a + \text{Log} ([\text{A}^-] / [\text{HA}])$$

$$\text{pH} = 5 + \text{Log} (0.0375/0.0125)$$

$$\text{pH} = 5.48$$

### E) When 500 ml of KOH is added

🔑 pH of weak base

$$\text{pOH} = \frac{1}{2} ( \text{pK}_b + \text{p} [\text{A}^-] )$$

The no. of moles  $\text{OH}^-$  **added** =  $M \times V = 0.1 \times 0.5 = 0.05$  mole

Thus 0.05 moles of KOH will **react** with 0.05 mole of HA to produce **0.05 mole  $\text{A}^-$**

Molarity of  $\text{A}^-$  = no. of moles / vol. in L

**The total volume of whole solution = 1000 ml = 1 L** 🔑

Molarity of  $\text{A}^-$  = no. of moles / vol. in L

Molarity of  $\text{A}^-$  =  $0.05 / 1 = 0.05$  M

$$\text{p} [\text{A}^-] = - \log [\text{A}^-]$$

$$\text{p} [\text{A}^-] = - \log 0.05$$

$$\text{p} [\text{A}^-] = 1.3$$

$$\text{pK}_w = \text{pK}_a + \text{pK}_b$$

$$\text{pK}_b = \text{pK}_w - \text{pK}_a = 14 - 5 = 9$$

$$\text{pOH} = \frac{1}{2} ( \text{pK}_b + \text{p} [\text{A}^-] )$$

$$\text{pOH} = \frac{1}{2} ( 9 + 1.3 )$$

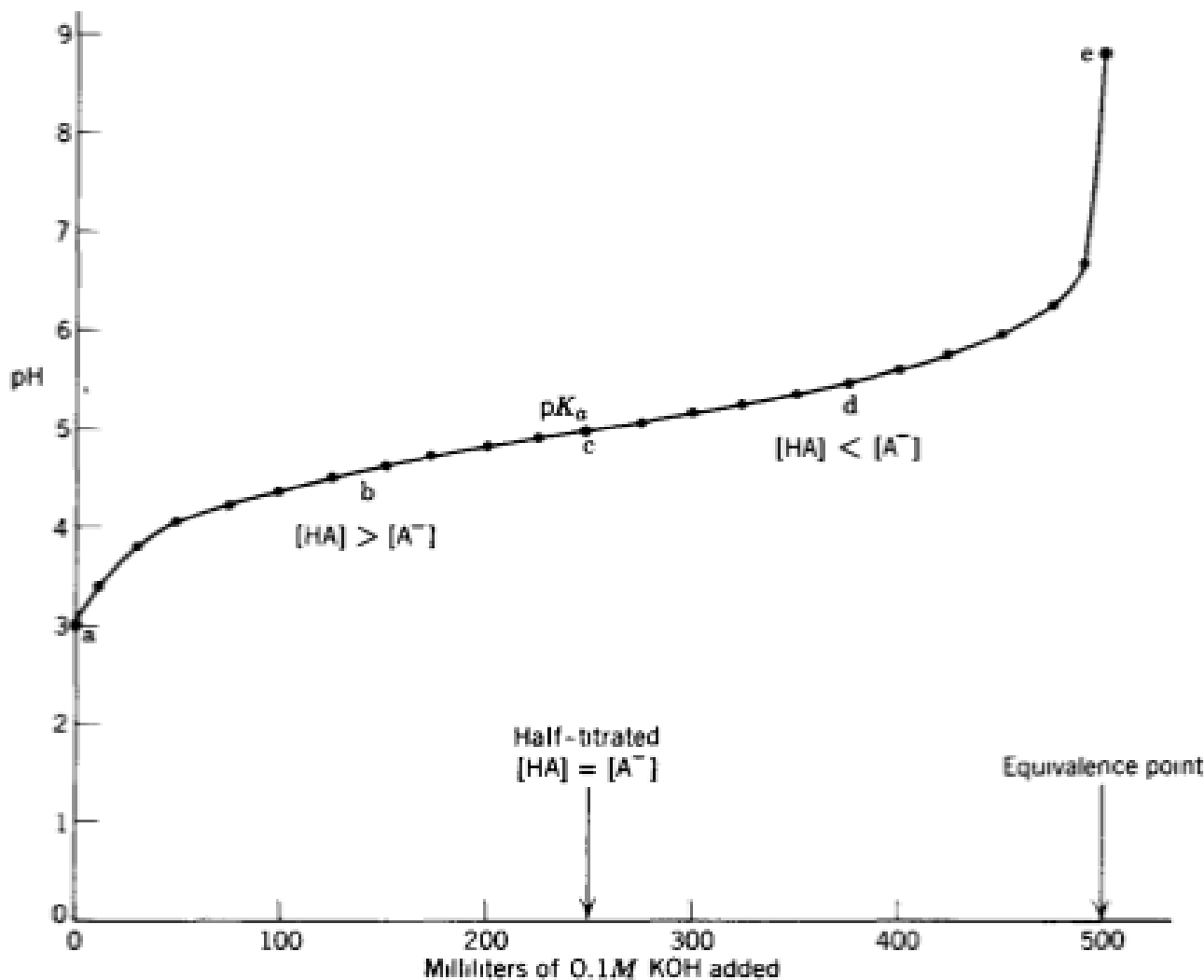
$$\text{pOH} = 5.15$$

$$\text{pK}_w = \text{pH} + \text{pOH}$$

$$\text{pH} = \text{pK}_w - \text{pOH}$$

$$\text{pH} = 14 - 5.15 = 8.85$$

# Titration Curve of 500ml of 0.1 M HA



- The components of each point in the titration curve from the previous example is :

A) **All** HA is in the form of CH<sub>3</sub>COOH

B) [CH<sub>3</sub>COOH] > [CH<sub>3</sub>COO<sup>-</sup>]

C) [CH<sub>3</sub>COOH] = [CH<sub>3</sub>COO<sup>-</sup>]

D) [CH<sub>3</sub>COOH] < [CH<sub>3</sub>COO<sup>-</sup>]

E) **All** as CH<sub>3</sub>COO<sup>-</sup>

## NOTICE:

- When the acid is *less* than half titrated the pH is less than  $\text{pK}_a$
- When the acid is *half* titrated the  $\text{pH} = \text{pK}_a$
- When the acid is *more* than half titrated the pH is greater than  $\text{pK}_a$

## How to calculate the pH at different points of titration curve!

- At starting point (Weak acid only is present) →

$$\text{pH} = (\text{pK}_a + \text{p}[\text{HA}]) / 2$$

- At any point within the curve (Weak acid and its conjugate base) →

$$\text{pH} = \text{pK}_a + \log[\text{A}^-] / [\text{HA}]$$

-Henderson-Hasselbalch equation-

- At end point (conjugate base only is present) →

$$\text{pOH} = (\text{pK}_b + \text{p}[\text{A}^-]) / 2$$

$$\text{pH} = \text{pK}_w - \text{pOH}$$

# Example (2)

The  $K_a$  for a **weak acid**, is  $1.6 \times 10^{-6}$ . The molarity of acid is  $10^{-3}$  M. What are the:

A) pH.

B) Calculate  $pK_a$  and  $pK_b$ .

A)

$$pH = \frac{1}{2} (pK_a + p[HA])$$

$$pK_a = -\log K_a$$

$$pK_a = -\log K_a = -\log 1.6 \times 10^{-6}$$

$$\rightarrow pK_a = 5.796$$

$$p[HA] = -\log [HA] = -\log 10^{-3}$$

$$\rightarrow p[HA] = 3$$

-apply it to “pH of weak acid”-

$$pH = \frac{1}{2} (5.79 + 3)$$

$$pH = 4.398$$

B)

$$\text{pK}_a = -\log K_a$$

$$\text{pK}_a = -\log K_a = -\log 1.6 \times 10^{-6}$$

$$\text{pK}_a = 5.796$$

$$\text{pK}_a + \text{pK}_b = 14$$

$$\text{pK}_b = 14 - \text{pK}_a = 14 - 5.796$$

$$\text{pK}_b = 8.204$$



# Titration curve

*of **poly**protic acids*

# Dissociation of polyprotic acids

- A polyprotic acid has more than one proton per molecule, thus it **ionizes in successive steps**.
- Example:  $\text{H}_2\text{A}$  a “polyprotic acid”, diprotic acid



$$K_{a1} = \frac{[\text{H}^+][\text{HA}^-]}{[\text{H}_2\text{A}]}$$

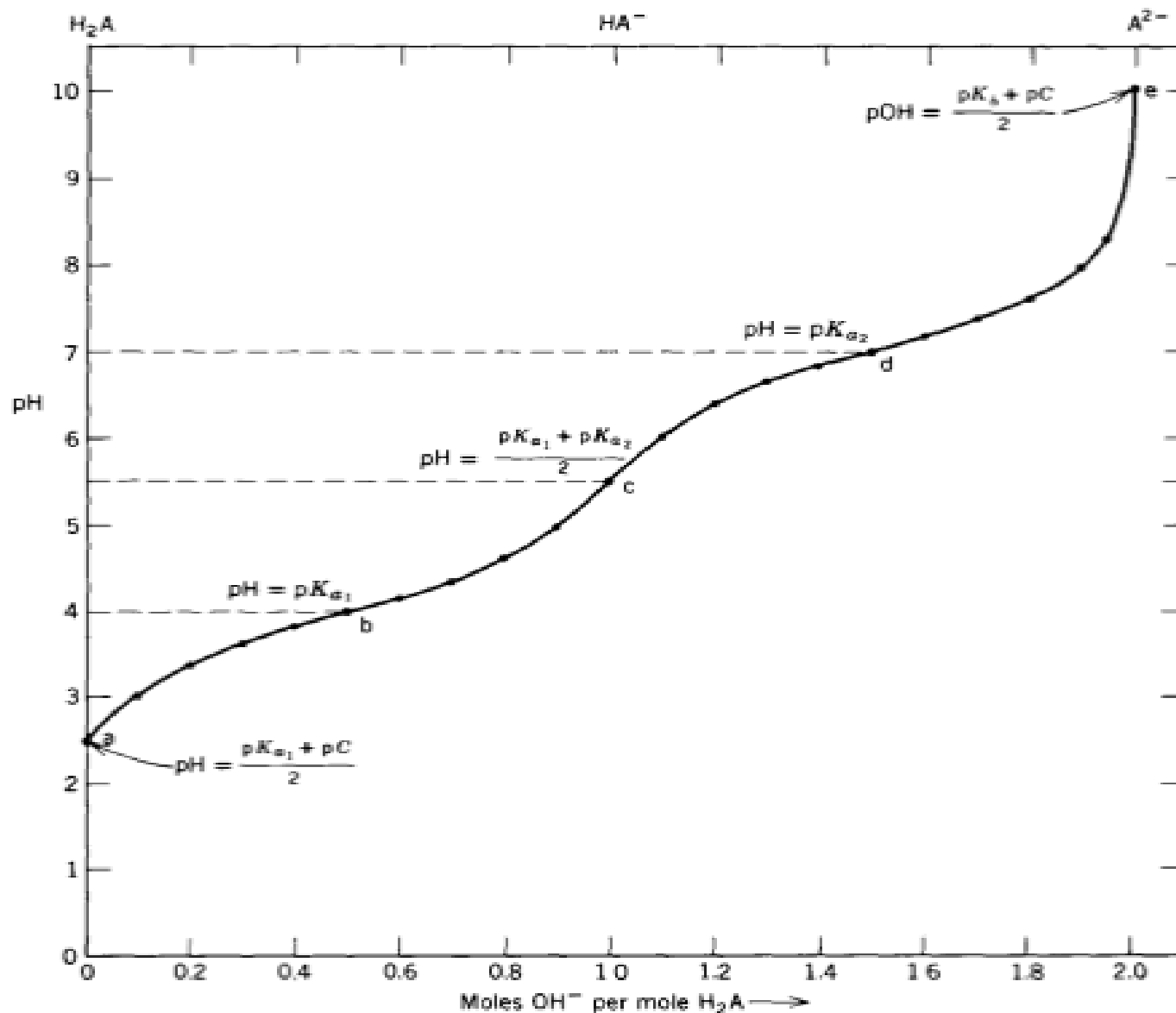
$$K_{a2} = \frac{[\text{H}^+][\text{A}^{2-}]}{[\text{HA}^-]}$$

For most common weak diprotic acids:

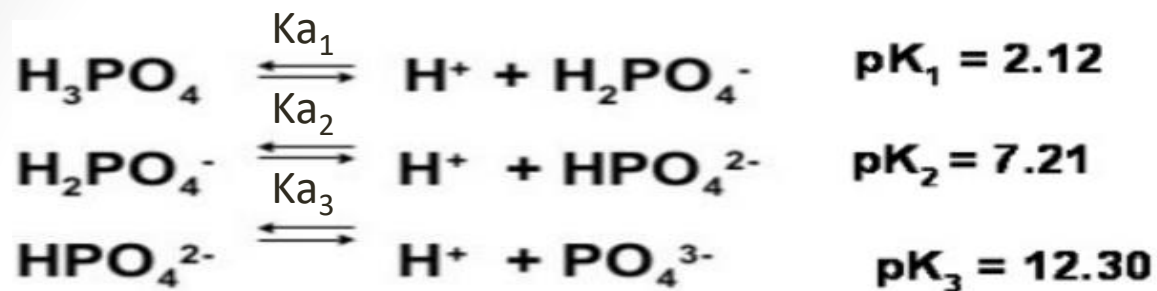
$K_{a1}$  is larger than the  $K_{a2}$

The pH of  $\text{H}_2\text{A}$  solution is **mainly dependent on the first ionization step**.

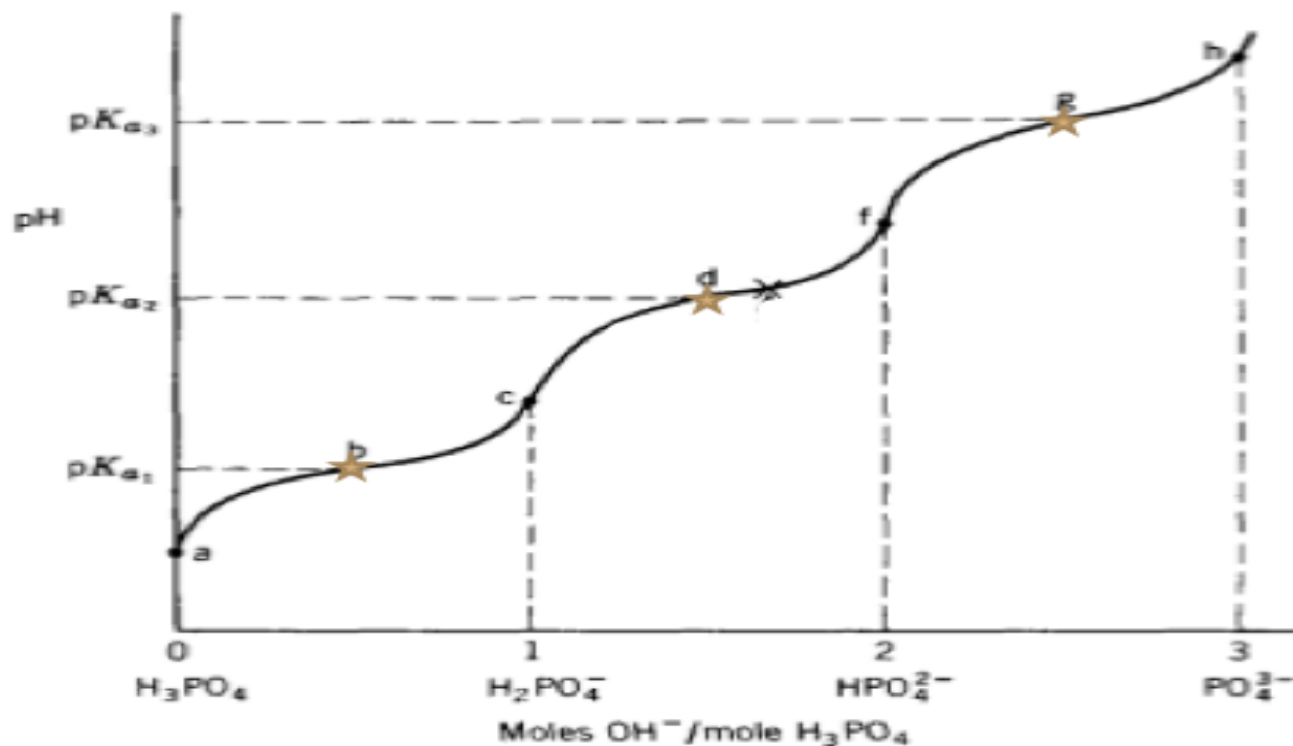
# Titration of a weak diprotic acid with strong base



# Titration curve of $\text{H}_3\text{PO}_4$ (a polyprotic acid)



For  $\text{H}_3\text{PO}_4$ :  $K_{a1} > K_{a2} > K_{a3}$



## Example (1):

- How many ml of 0.1 M NaOH are required to titrate 100 ml of 0.1 M  $\text{H}_3\text{PO}_4$ ?

No. of moles of  $\text{H}_3\text{PO}_4(\text{H}^+) = V \times M(n) = 0.1 \times 0.1(3) = 0.03$  mole

**Thus:** we need 0.03 moles of NaOH to titrate the acid

$$M = \text{no. of moles} / V$$

$$V = \text{no. of moles} / M$$

$$V = 0.03 / 0.1$$

$$V = 0.3 \text{ L} = 300 \text{ ml}$$

# Buffers

# Buffer



- It is a solution which resists large changes in the pH by partially absorbing addition of limited amounts of  $H^+$  or  $OH^-$  ions to the system.
- Buffer pH **Do change** upon the addition of  $H^+$  or  $OH^-$  **BUT** the change is much less than that would occur in the absence.

# There are two types of buffers

```
graph TD; A[There are two types of buffers] --> B[Acidic Buffer]; A --> C[Basic Buffer]
```

## Acidic Buffer

Are made from weak acid and its conjugated base [ its salt ].

### Example:

1.  $\text{CH}_3\text{COOH} / \text{CH}_3\text{COONa}$  (Pka)

→  $\text{CH}_3\text{COOH}$  (Weak acid)

→  $\text{CH}_3\text{COONa}$  (conjugated base –its salt-)

2.  $\text{NaH}_2\text{PO}_4 / \text{Na}_2\text{HPO}_4$  (Pka)

## Basic Buffer

Are made from weak base and its conjugated acid [ its salt ].

### Example:

1.  $\text{NH}_3 / \text{NH}_4\text{Cl}$  (Pkb)

→  $\text{NH}_3$  (Weak base)

→  $\text{NH}_4\text{Cl}$  (conjugated acid –its salt-)



# Mechanism of Action of Buffers

## How does a buffer resist changes in pH?

*For Example:* In the acetate buffer which is made of acetic acid ( $\text{CH}_3\text{COOH}$ ) and sodium acetate ( $\text{CH}_3\text{COONa}$ )

- When  $\text{H}^+$  are added it will react with the salt:



→ Thus the buffer converted the free  $\text{H}^+$  into acetic acid which does not affect the pH **because it is a weak acid.**

- When  $\text{OH}^-$  are added it will react with the acetic acid:



→ Thus the buffer converted the free  $\text{OH}^-$  in the **into water and salt** which does not affect the pH.

**NOTE:** It resists pH changes as long as it does not run out of one of its components.

# Buffer Capacity

- Quantitative measure of the buffer's ability to resist changes in the pH is referred to as a **buffer capacity**.
- **It is defined as either:**
  - The no. of moles of  $\text{H}^+$  that must be added to one liter of the buffer in order to decrease the pH by one unit.

**OR**

- The no. of moles of  $\text{OH}^-$  that must be added to one liter of the buffer in order to increase the pH by one unit.

- The buffer capacity is expressed as  $\beta$  and can be from Henderson-Hasselbalch equation:

$$\beta = \frac{2.3 K_a [H^+][C]}{(K_a + [H^+])^2}$$

From the equation → the buffer capacity is **directly proportional** to the buffer concentration.

- **Where:**

- $\beta$  = buffer capacity
- $[H^+]$  = hydrogen ion concentration of the buffer
- $K_a$  = acid dissociation constant
- $[C]$  = total concentration of buffer components =  $[HA] + [A^-]$  .

# Handerson-Hasselbalch Equation

- It is often used to preform:
  1. To calculate the pH of the buffer.
  2. To prepare buffer.
  3. To calculate the pH in any point within the titration curve (Except starting and ending point)
- It is derived from the dissociation constant.

$$\text{pH} = \text{pK}_a + \log \frac{[\text{A}^-]}{[\text{HA}]} = \text{pK}_a + \log \frac{[\text{base}]}{[\text{acid}]} \quad \text{acid form}$$

$$\text{pOH} = \text{pK}_b + \log \frac{[\text{HB}^+]}{[\text{B}]} = \text{pK}_b + \log \frac{[\text{acid}]}{[\text{base}]} \quad \text{base form}$$

# Henderson-Hasselbalch Equation

- The buffer capacity is optimal when the ratio of the weak acid/weak base to its salt is 1:1; that is, when,  $\text{pH} = \text{pK}_a$  **OR**  $\text{pOH} = \text{pK}_b$

$$\text{pH} = \text{pK}_a + \log 1$$

$$\text{pH} = \text{pK}_a + 0$$

$$\boxed{\text{pH} = \text{pK}_a}$$

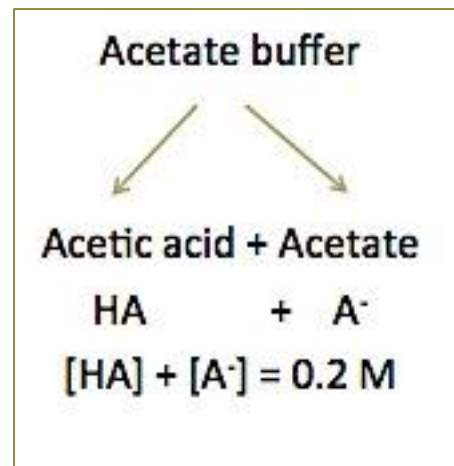
- For a good buffer, the pH of the solution must be within one unit of the pK ( $\text{pH} = \text{pK} \pm 1$ ).

# Preparation of buffers

## Example 1:

What is the concentration of acetic acid and acetate in 0.2 M acetate buffer, and which has a  $\text{pH} = 5$  and  $\text{pK}_a = 4.77$

- Assume  $[\text{A}^-] = y$  thus,  $[\text{HA}] = 0.2 - y$
- $\text{pH} = \text{pK}_a + \log[\text{A}^-]/[\text{HA}]$
- $5 = 4.77 + \log y/0.2 - y$
- $\text{antilog} 0.23 = y/0.2 - y$
- $1.7 = y/0.2 - y$
- $y = 0.34 - 1.7y$
- $y = 0.34/2.7$
- $y = 0.126 \text{ molar}$ .
- Since  $[\text{HA}] = 0.2 - y$  then  $[\text{HA}] = 0.2 - 0.126 = 0.074$  molar.



## Example 2:

Describe the preparation of 3 L of 0.2 M acetate buffer. Starting from solid sodium acetate trihydrate ( $A^-$ ), Mwt = 136 and a 1 M solution of acetic acid (HA); the  $pK_a = 4.77$ .

- From the previous example, the concentration of:

$[A^-] = 0.126 \text{ M}$ ,  $[HA] = 0.074 \text{ M}$  in 0.2 M solution in 1 L.

- SINCE** the concentration of  $[A^-] = 0.126 \text{ M}$  in 1 L; the **Total** no. of moles in buffer of 3 L =  $0.126 \times 3 = 0.378$  moles
- SINCE** the concentration of  $[HA] = 0.073 \text{ M}$  in 1 L; the **Total** no. of moles in buffer of 3 L =  $0.073 \times 3 = 0.222$  moles
- SINCE**  $A^-$  is solid the wt needed = no. of moles  $\times$  Mwt =  $0.378 \times 136 = 51.4 \text{ g}$
- The **volume** of HA needed = no. of moles / M =  $0.222 / 1 = 0.222 \text{ L} = 222 \text{ ml}$

51.4 g of solid sodium acetate trihydrate is added to 222 ml of acetic acid and the volume is brought up to 3 L.

### Example 3:

1.025 g of anhydrous sodium acetate is dissolved in 100 ml of 0.25 M acetic acid  $\text{CH}_3\text{COOH}$ . Calculate:

A) The pH of the final solution.

B) The molarity of the final solution (resulting buffer)

Knowing: Mwt of anhydrous sodium acetate = 82;  $\text{pK}_a = 4.7$

A)  $\text{pH} = \text{pK}_a + \log ([\text{A}^-] / [\text{HA}])$

$$\begin{aligned}\text{no. of moles of } \text{A}^- \text{ in buffer} &= \text{wt} / \text{Mwt} \\ &= 1.025 / 82 = 0.0125 \text{ moles}\end{aligned}$$

$$\begin{aligned}\text{Molarity of } \text{A}^- &= \text{no. of moles} / \text{V in L} \\ &= 0.0125 / 0.1 \\ &= 0.125 \text{ M}\end{aligned}$$

$$\begin{aligned}\text{no. of moles of } \text{HA} \text{ in buffer} &= \text{M} \times \text{V} \\ &= 0.25 \times 0.1 = 0.025 \text{ moles}\end{aligned}$$

$$\begin{aligned}\text{Molarity of } \text{HA} &= \text{no. of moles} / \text{v in L} \\ &= 0.025 / 0.1 = 0.25 \text{ M}\end{aligned}$$

$$\begin{aligned}\text{pH} &= 4.7 + \log (0.125 / 0.25) \\ &= 4.39\end{aligned}$$



**B) The molarity of the buffer = the molarity of HA + the molarity of A<sup>-</sup>**

$$\text{Buffer molarity} = 0.25 + 0.125 = 0.375 \text{ M}$$

**OR**

**No. of moles of buffer = no. of moles of HA + the no. of moles of A<sup>-</sup>**

$$\text{No. of moles of buffer} = 0.025 + 0.0125 = 0.0375 \text{ moles}$$

$$\text{Molarity of buffer} = \text{no. of moles} / V \text{ in L}$$

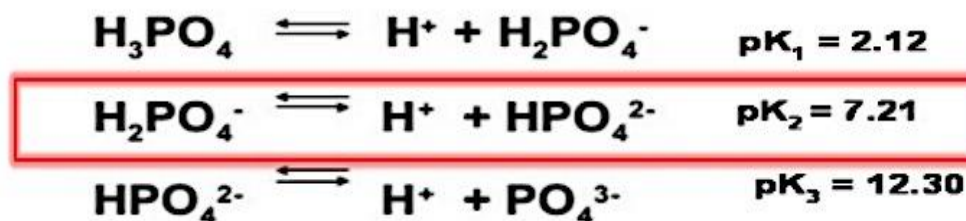
$$= 0.0375 / 0.1 = 0.375 \text{ M}$$

### Example 4:

**Describe the preparation of 10 liters of 0.045M potassium phosphate buffer, pH= 7.5?  $pK_{a1}= 2.12$  ,  $pK_{a2}= 7.21$  ,  $pK_{a3}= 12.32$ ?**

**1<sup>st</sup> →** Write the equations of phosphoric acid dissociation and the pKa of corresponding ones.

**2<sup>nd</sup> →** Choose the pKa value which is near the pH value of the required buffer, to be able to know the ionic species involved in your buffer:

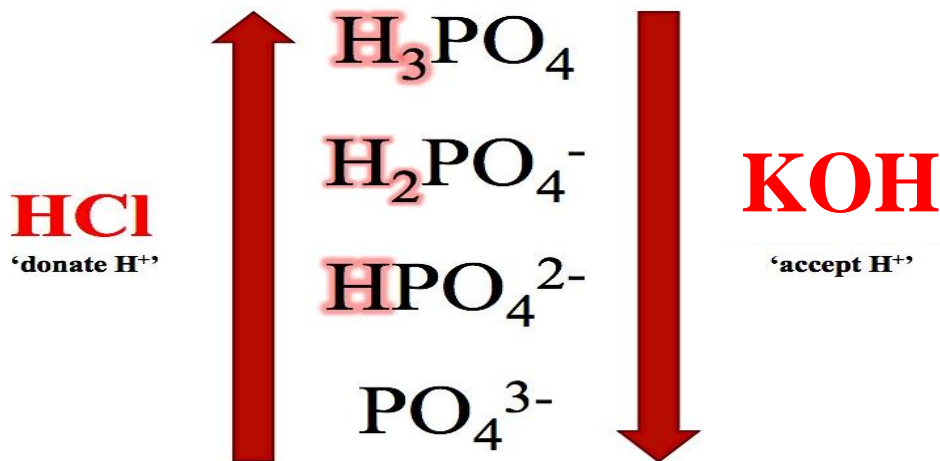


The pH of the required buffer [pH =7.5] is near the value of  $pK_{a2}$ . consequently , **the two major ionic species present are  $\text{H}_2\text{PO}_4^-$  ( conjugate acid ) and  $\text{HPO}_4^{2-}$  (conjugate base),** with the  $\text{HPO}_4^{2-}$  predominating {since the pH of the buffer is slightly basic}.

**3<sup>rd</sup> →** calculate No. of moles for the two ionic species in the buffer

## The buffer can be prepared by several ways as:

1. By mixing  $\text{KH}_2\text{PO}_4$  and  $\text{K}_2\text{HPO}_4$  in proper proportions.
2. By starting with  $\text{KH}_2\text{PO}_4$  and converting a portion of it into  $\text{K}_2\text{HPO}_4$  by adding  $\text{KOH}$ .
3. By starting with  $\text{K}_2\text{HPO}_4$  and converting a portion of it into  $\text{KH}_2\text{PO}_4$  by adding strong acid as  $\text{HCl}$ .
4. From concentrated  $\text{H}_3\text{PO}_4$  and solution of  $\text{KOH}$



Regardless of which method is used, first calculate the proportion and amounts of the 2 ionic species in the buffer.

- $\text{pH} = \text{pK}_{\text{a}_2} + \log \left[ \frac{\text{HPO}_4^{2-}}{\text{H}_2\text{PO}_4^-} \right] \rightarrow$  Note that :  $[\text{A}^-] = \text{HPO}_4^{2-}$ ,  $[\text{HA}] = \text{H}_2\text{PO}_4^-$
- Since the buffer concentration is **0.045M**, so assume  $\rightarrow [\text{A}^-] = y$ ,  $[\text{HA}] = 0.045 - y$
- $7.5 = 7.2 + \log (y / 0.045 - y)$
- $7.5 - 7.2 = \log (y / 0.045 - y)$
- $0.3 = \log (y / 0.045 - y)$  *{antilog for both sides}*
- $2 = (y / 0.045 - y) \rightarrow y = 0.09 - 2y \rightarrow 3y = 0.09 \rightarrow y = 0.09/3 = \underline{\underline{0.03\text{M}}} \rightarrow$  conc. of  $[\text{HPO}_4^{2-}]$
- So, conc. of  $[\text{H}_2\text{PO}_4^-] = [\text{HA}] = 0.045 - y \rightarrow = 0.045 - 0.03 = \underline{\underline{0.015\text{ M}}}$

Now find the number of mole for the two ionic species in the buffer:

- No. of moles of  $\text{HPO}_4^{2-} (\text{A}^-) = M \times V = 0.03 \times 10 = 0.3$  moles.
- No. of moles of  $\text{H}_2\text{PO}_4^- (\text{HA}) = M \times V = 0.015 \times 10 = 0.15$  moles.

Note that Total no. of moles of phosphate buffer =  $M \times V$   
 $= 0.045 \times 10 = 0.45$  moles.

- From solid  $\text{KH}_2\text{PO}_4$  (HA) and  $\text{K}_2\text{HPO}_4$  ( $\text{A}^-$ ):

$$\text{wt}_g \text{ of } \text{K}_2\text{HPO}_4 = \text{no. of moles} \times \text{MW}$$

$$= 0.3 \times 174 = \mathbf{52.2g}$$

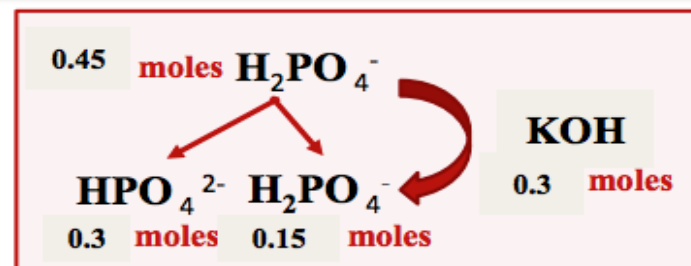
$$\text{wt}_g \text{ of } \text{KH}_2\text{PO}_4 = \text{no. of moles} \times \text{MW}$$

$$= 0.15 \times 136 = \mathbf{20.4g}$$

Dissolve the two solutes in some water and make up the volume to 10L by water.

- From solid  $\text{KH}_2\text{PO}_4$  and solid KOH:

Start with 0.45 mole (same as buffer's total no. of moles) of  $\text{KH}_2\text{PO}_4$  (HA) and add 0.3 moles of KOH to convert  $\text{KH}_2\text{PO}_4$  to give  $\text{K}_2\text{HPO}_4$  ( $\text{A}^-$ )



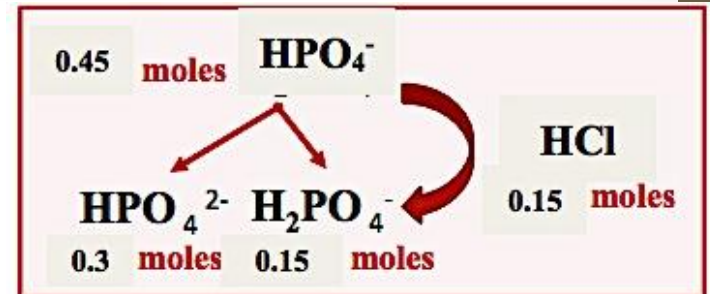
$$\text{wt}_g \text{ of } \text{KH}_2\text{PO}_4 \text{ needed} = \text{no. of moles} \times \text{MW} = 0.45 \times 141.98 = 63.8 \text{ g}$$

$$\text{wt}_g \text{ of KOH needed} = \text{no. of moles} \times \text{MW} = 0.3 \times 40 = 12 \text{ g}$$

→ So, dissolve the 63.8g of  $\text{KH}_2\text{PO}_4$  and 12g of KOH in some water, mix ; then add sufficient water to bring the final volume to 10 liters and check the pH.

- From solid  $\text{K}_2\text{HPO}_4(\text{A}^-)$  and 2M HCl:

Start with 0.45 mole (same as buffer's total no. of moles) of  $\text{K}_2\text{HPO}_4(\text{A}^-)$  and add 0.15 moles of HCl to convert  $\text{K}_2\text{HPO}_4$  to give  $\text{KH}_2\text{PO}_4(\text{HA})$



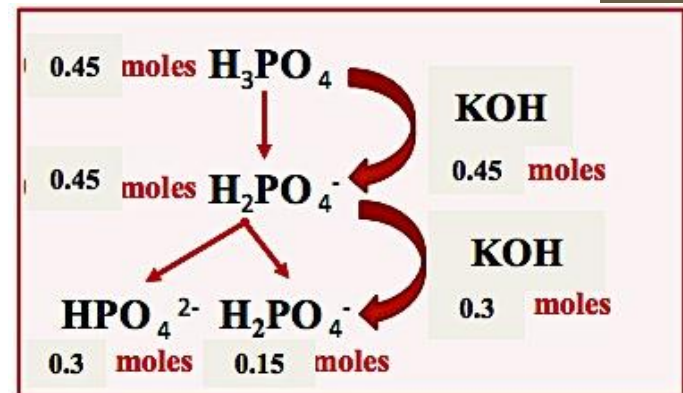
$$\begin{aligned} \text{wt}_g \text{ of } \text{K}_2\text{HPO}_4 &= \text{no. of moles} \times \text{MW} \\ &= 0.45 \times 174 = 78.3\text{g.} \end{aligned}$$

$$\begin{aligned} M &= \text{No. of moles} / V_{(L)} \text{ thus, } V_{(L)} = \text{No. of moles} / M \\ &= 0.15 / 2 \\ &= 0.075\text{L} \end{aligned}$$

Dissolve 78.3g of the  $\text{K}_2\text{HPO}_4$  in a little water then add 75ml of the 2M HCl and make up the volume up to 10 liters with water.

- From concentrated (15M)  $\text{H}_3\text{PO}_4$  and solution of 1.5 M KOH:

Start with 0.45 mole (same as buffer's total no. of moles) of  $\text{H}_3\text{PO}_4$  and add 0.45 moles of **KOH** to convert  $\text{H}_3\text{PO}_4$  to give  $\text{KH}_2\text{PO}_4$  (HA), **THEN** add 0.3 moles of **KOH** to convert  $\text{KH}_2\text{PO}_4$  to give  $\text{K}_2\text{HPO}_4$  ( $\text{A}^-$ )



**No. of moles needed of KOH=  $0.45+0.3= 0.75$  moles**

Volume of **KOH** needed= no.of moles / M =  $0.75/ 1.5 = 0.5 \text{ L} = \mathbf{500 \text{ ml}}$

Volume of  $\text{H}_3\text{PO}_4$  needed =no.of moles / M =  $0.45/ 15 =0.03 \text{ L} = \mathbf{30 \text{ ml}}$

→So, Add 500ml of KOH to the 30ml of concentrate  $\text{H}_3\text{PO}_4$  , mix ; then add sufficient water to bring the final volume to 10 liters, and check the pH.

# SELF SOLVE EXAMPLE

- 5 L of 0.1 M phosphate buffer with a pH = 12.32 was prepared from  $\text{Na}_3\text{PO}_4$  and  $\text{Na}_2\text{HPO}_4$ .

Calculate the weight in grams of each component which was used to prepare the buffer,  $\text{pK}_a = 12$ .



# Importance of Buffers in Physiological Systems:

- pH plays an important role in almost all biological processes.
- Small change in pH i.e. decreased or high pH can cause metabolic implications in human body like acidosis and alkalosis that can cause death within minutes.
- **Important buffers that are dominant in human body are:**
  1. Bicarbonate buffers
  2. Phosphate buffers
  3. Protein buffers

# Bicarbonates buffers (Buffering in blood)

- Blood is a biological fluid in which Carbonic acid and Hydrogen carbonate buffer system plays an important role in maintaining pH around 7.4.
- In this buffer, carbonic acid ( $\text{H}_2\text{CO}_3$ ) act as a weak acid and hydrogen carbonate ion ( $\text{HCO}_3^-$ ) act as conjugate base of a weak acid or salt of weak acid.



- When there is excessive amount of  $\text{H}^+$  in the blood it is consumed by  $\text{HCO}_3^-$  forming carbonic acid that is a weak acid which does not alter the blood pH so much and when there is excessive amount of  $\text{OH}^-$  in the blood it is consumed by  $\text{H}_2\text{CO}_3$  as it will release the  $\text{H}^+$  ions upon excess amount of  $\text{OH}^-$  in the blood forming  $\text{H}_2\text{O}$ .

# Phosphate buffer

## (Buffering of internal cell fluids)

- This buffer system consists of dihydrogen phosphate ions ( $\text{H}_2\text{PO}_4^-$ ) as a weak acid and hydrogen phosphate ions ( $\text{HPO}_4^{2-}$ ) as a conjugate base of weak acid.



- If additional hydrogen ions enter the cellular fluid, they are consumed in the reaction with  $\text{HPO}_4^{2-}$ , and the equilibrium shifts to the left.
- If additional hydroxide ions enter the cellular fluid, they react with  $\text{H}_2\text{PO}_4^-$ , producing  $\text{HPO}_4^{2-}$ , and shifting the equilibrium to the right.

# Protein buffer

## (Buffering in Cells and Tissues)

- Proteins are mainly composed of amino acids. These amino acids contain functional groups that act as weak acid and bases ( $\text{COOH}$  and  $\text{NH}_2$ ) when there are sharp changes in pH in order to stabilize the pH within the body cells.
- **At a near neutral pH, like the pH of blood:**
  - The carboxyl group is actually  $\text{COO}^-$  instead of  $\text{COOH}$ . Then, if a protein finds itself in a more acidic solution, the carboxyl group will be able to take on the extra hydrogen ions and return to the  $\text{COOH}$  configuration.
  - The amino group is actually  $\text{NH}_3^+$  rather than just  $\text{NH}_2$ . Then, if a protein finds itself in a more basic environment, its amino groups on its amino acids can actually release their hydrogen ions and return to  $\text{NH}_2$ .