Buffer solution

❖**Common ion effect:-**The suppression of degree of ionization of a weak electrolyte by the addition of some strong electrolyte having a common ion is called the common ion effect. For example:-

$$NH_4OH \rightleftharpoons \boxed{NH_4^+} + OH^-$$
$$NH_4Cl \rightarrow \boxed{NH_4^+} + Cl^-$$

Common ion

❖**Le Chatelier's principle** :- It states that when a system experiences a disturbance (such as concentration, temperature, or pressure changes), it will respond to restore a new equilibrium state.

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Buffer solution

- A buffer solution is the solution which can resist the change in pH on addition of small amount of acid or base.
- Depending upon the pH values, buffer solution are divided into two types.

a. Acidic buffer
b. Basic buffer

Acidic buffer

- The mixture of weak acid and its salt with strong base(conjugated base) is called acidic buffer.
- If the pH value of the buffer solution is less than 7, it is called acidic buffer solution.
- A weak acid together with a salt of same acid with a strong base. These are called acidic buffer.
- For example:-

a. Acetic acid and Sodium acetate ($CH_3COOH + CH_3COONa$)
b. Oxalic acid and Lithium oxalate ($C_2O_4H_2 + C_2O_4Li_2$)
c. Carbonic acid and Sodium carbonate ($H_2CO_3 + Na_2CO_3$)
d. Phosphoric acid and Potassium phosphate(H_3PO_4+ K_3PO_4)
e. Formic acid and Sodium formate ($HCOOH + HCOONa$)

Basic buffer

- The mixture of weak base and its salt with strong acid(conjugated acid) is called basic buffer.
- If the pH value of the buffer solution is greater than 7, it is called basic buffer.
- A weak base together with a salt of same base with a strong acid. These are called basic buffer.
- For example:-

a. Ammonia solution and ammonium nitrate($NH_4OH + NH_4NO_3$)
b. Ammonia solution and ammonium chloride($NH_4OH + NH_4Cl$)

Buffer capacity and buffer range

- The important characteristics of a buffer is buffer capacity and buffer range(pH range).
- Buffer capacity is defined as the number of moles of acid or base added per liter of the buffer required to cause a unit change in pH .
- Buffer capacity is the amount of acid or base that a buffer can neutralize before the pH beings the change extremely.

$$\textit{Buffer Capacity} = \frac{(\textit{number of moles of } OH^- \textit{ or } H_3O^+ \textit{ added})}{(\textit{pH change})(\textit{volume of buffer in L})}$$

- The buffer range is the pH range where a buffer effectively neutralizes added acids and bases, while maintaining a relatively constant pH.
- Buffer range is the pH range over which a buffer works effectively.
- Buffer range is related to the ratio of buffer component concentrations.
- In real practice, the maximum buffer range is reached when one component is 10 times more concentrated than other component.

$$pH = pK_a + \log \frac{[\text{conjugate base}]}{[\text{acid}]}$$

- For conjugated base : acid ratio of 10:1 , pH = pKa + 1
- For conjugated base : acid ratio of 1:10 , pH = pKa – 1
- Thus, maximum buffer range for acidic buffer ,pH = pKa ± 1
- The maximum buffer range for basic buffer, pOH = pKb ± 1

Mechanism of buffer action

- A buffer solution maintains its pH value by consuming H^+ and OH^- ions added to it in a small amount.

Mechanism of acidic buffer action:-

- To understand the mechanism of acidic buffer action, let us consider acidic buffer solution containing acetic acid and sodium acetate.
- The ionization reaction of following buffer is

$$CH_3COOH(aq) \rightleftharpoons CH_3COO^-(aq) + H^+(aq)$$

(partially/feebly/weakly ionized)

$$CH_3COONa(aq) \longrightarrow CH_3COO^-(aq) + Na^+(aq)$$

(strongly ionized)

- ***Suppose, a few drops of HCl(acid) are added to this buffer solution,***

$$HCl \longrightarrow H^+ + Cl^-$$ *This would provide H^+ ion*

These H^+ ions would combine with CH_3COO^- ions to form unionized CH_3COOH molecule as given below.

$$CH_3COO^-(aq) + H^+(aq) \longrightarrow CH_3COOH(aq)$$

from buffer ***from acid***

Since the additional H^+ ions are balanced by CH_3COO^- ions in the solution, there will be no change in its pH value.

- ***Suppose, a few drops of NaOH(Base) are added to this buffer solution,***

$$NaOH \longrightarrow Na^+ + OH^-$$ ***It would provide OH⁻ ions***

These OH^- ions will combine with H^+ ions present in buffer solution to form unionized water molecules.

$$\underset{\text{From buffer}}{H^+(aq)} + \underset{\text{from base}}{OH^-(aq)} \longrightarrow H_2O(aq)$$

These would result in the decrease of H^+ ions in the system which disturb the equilibrium state .

Thus the reaction shifts towards right hand side to maintain the equilibrium state(le-chateliar principle) i.e. more acetic acid ionizes to give H^+ ions.

And in this way, pH of the solution remains unchanged.

Mechanism of buffer action

Acetate buffer

$CH_3COONa \longrightarrow CH_3COO^- + Na^+$ H^+

$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$ OH^-

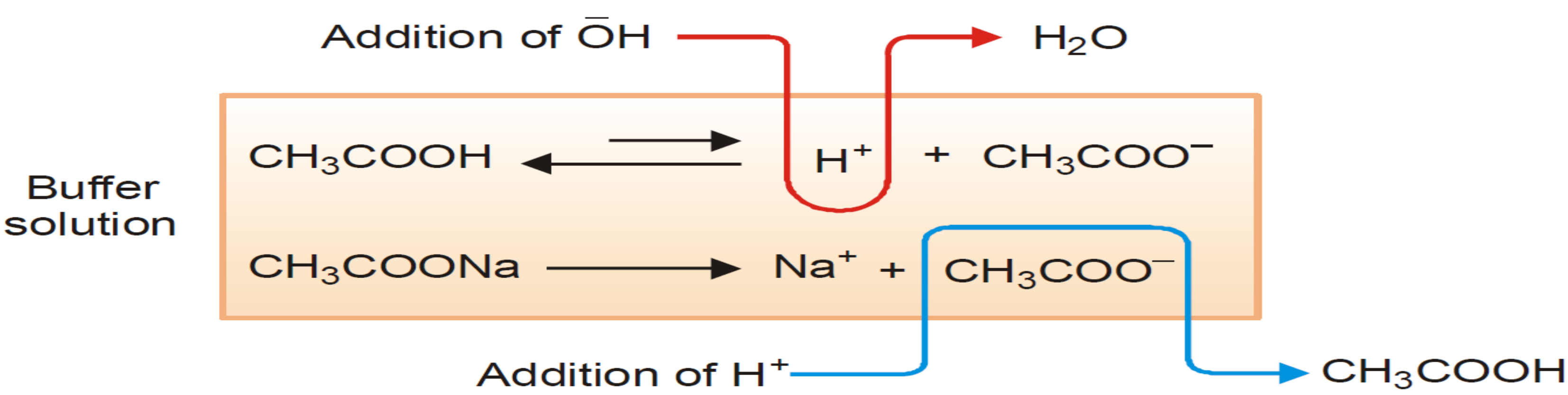
+ 1 mole NaOH — 1 mole

$CH_3COOH + OH^- \rightleftharpoons CH_3COO^- + H_2O$

+1 mole HCL — (weak electrolite)

$CH_3COO^- + H^+ \rightleftharpoons CH_3COOH$

1 mole (weak electrolite)



Mechanism of basic buffer action

- Let us consider a basic buffer solution containing ammonium solution and ammonium chloride.

The ionization reaction of following reaction is

$$NH_4OH(aq) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

(weakly ionized)

$$NH_4Cl(aq) \longrightarrow NH_4^+(aq) + Cl^-(aq)$$

(strongly ionized)

- ***When an acid is added to it in a small amount,***

$$HCl \longrightarrow H^+ + Cl^-$$

It would provide H^+ ions

These H^+ ions would combine with OH^- ions to form undissociated water molecule.

$$H^+(aq) + OH^-(aq) \longrightarrow H_2O(aq)$$

From acid *from buffer*

As some of OH^- ions from NH_4OH combine with H^+ ions from the acid, it would result in the greater ionization of NH_4OH to restore OH^- ion concentration.

- ***When an base is added to it in a small amount,***

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

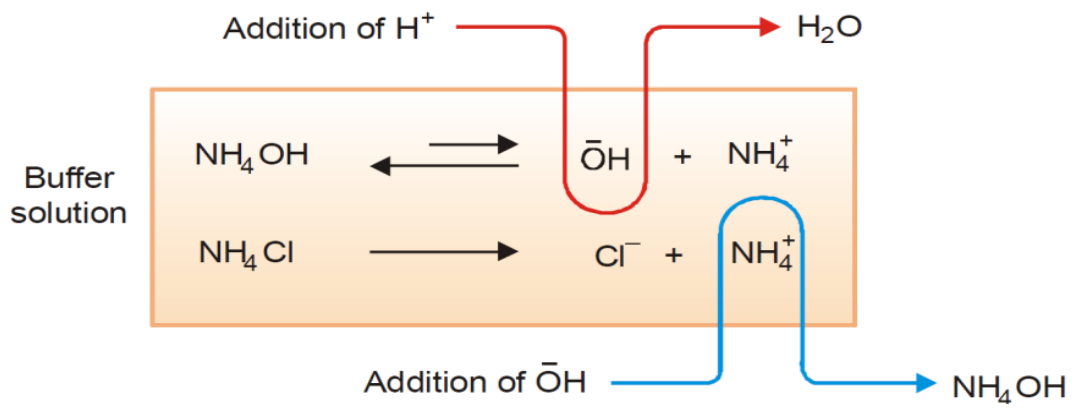
It would provide OH^- ions

These OH^- ions will combine with NH_4^+ ions to form unionized NH_4OH to maintain the amount of OH^- ions in the system.

$$NH_4^+(aq) + OH^-(aq) \longrightarrow NH_4OH$$

From buffer ***from base***

Hence, the pH of the mixture almost remains unchanged after the addition of small amount of acid and base.



Calculation of pH of buffer (Henderson – Hasselbalch equation)

- pH of acidic buffer:-

  Consider a buffer solution(acidic) containing a weak acid HA and its highly ionized salt NaA.

  Ionization reaction is as follows,

  $HA + H_2O \longrightarrow H_3O^+ + A^-$(weakly ionized)

  $NaA + HO$ Na $+A^-$(completely ionized)

  The ionization of weak electrolyte is given by,

$$K_a = \frac{[H_3O][A^-]}{[HA]} \qquad i)$$

where K_a = ionization constant of weak acid

Due to common ion effect, the ionization of weak electrolyte(weak acid HA) is greatly suppressed.

Hence its concentration remains same. Similarly, the concentration of common ion can be assumed equal to the concentration of salt as the concentration from acid is negligible.

$$[HA] = [acid] \quad \text{and} \quad [A^-] = [salt]$$

Then, equation (i) becomes:-

$$K_a = \frac{[H_3O^+][Salt]}{[Acid]} \longrightarrow \quad (ii)$$

$$[H_3O^+] = \frac{K_a\,[acid]}{[salt]}$$

Taking negative log on both sides,

$$-\log [H_3O^+] = -\log K_a \frac{[acid]}{[salt]}$$

$$-\log [H_3O^+] = -\log K_a - \log \frac{[acid]}{[salt]}$$

pH = - log [H_3O^+]
pK_a= -log K_a

$$\boldsymbol{pH = pK_a + \log \frac{[salt]}{[acid]}} \longrightarrow \quad (iii)$$

This equation (iii) is known as Henderson – Hasselbalch equation for acidic buffer solution.

pH of basic buffer

- Consider a basic buffer solution containing a weak base BOH and its salt BCl. These electrolytes undergo ionization as follows:-

  $$BOH \rightleftharpoons B^+ + OH^- \text{(weakly ionized)}$$

  $$BCl \longrightarrow B^+ + Cl^- \text{(completely ionized)}$$

  The ionization of weak electrolyte is given by,

  $$Kb = \frac{[B^+][OH^-]}{[BOH]}$$

  Where Kb is ionization constant of weak base.

Due to the common ion effect, concentration of base remains same. Similarly concentration of common ion can be assumed equal to the concentration of salt, as the concentration from base is negligible.

So, $[B^+] = [salt]$ and $[BOH] = [Base]$

Now equation (i) becomes,

$$Kb = \frac{[salt]\,[OH^-]}{[Base]}$$

$$[OH^-] = \frac{Kb\,[Base]}{[salt]} \longrightarrow \text{(ii)}$$

Taking –ve log on both side in equation (ii)

$$-\log [OH^-] = -\log Kb \frac{[Base]}{[salt]}$$

$$pOH = -\log Kb - \log \frac{[Base]}{[salt]}$$

pOH = - log [OH⁻]
pKb= -log Kb

$$\boldsymbol{pOH = pKb + \log \frac{[salt]}{[Base]}} \longrightarrow \text{(iii)}$$

This equation (iii) is called Henderson – Hasselbalch equation for basic buffer.

We known that, pH + pOH = 14

$$\boldsymbol{pH = 14 - pOH}$$

Related numerical

- **Some important formula,**

1. **Molarity** $= \dfrac{\text{no of moles}}{\text{volume in litre}}$
2. **Number of moles** $= \dfrac{\text{weight in gram}}{\text{molecular weight}}$
3. **Normality** $= \dfrac{\text{gm/litre}}{\text{equivalent weight}}$
4. **If question says**
5. **i) a litre of solution contains x mole of base or acid or salt then molarity = x M**

   For example 0.1 mole per litre means 0.1M

   ii) when wt is provided in gm then,

   $$\text{molarity} = \frac{\text{wt. in gm}}{\text{molecular wt.}} \times \frac{1000}{\text{Volume in ml}}$$

   iii) X gm equivalent of acid or base or salt in V ml then,

   $$\text{normality} = \frac{X}{V} \times 1000$$

   iv) Normality = Molarity [in monobasic and monoacidic case]

Henderson Hasselbalch Equation

$$pH = pK_a + \log \frac{[conjugate\ base]}{[weak\ acid]} \text{ (for weak acid)}$$

$$pOH = pK_b + \log \frac{[conjugate\ acid]}{[weak\ base]} \text{ (for weak base)}$$

Where, pKa and pKb = 4.75 (same for both)
Ka or Kb = 1.8 x 10^{-5}

$pH = -\log_{10}[H^+]$ $[H^+] = 10^{-pH}$ (in mol/L)

$pOH = -\log_{10}[OH^-]$ $[OH^-] = 10^{-pOH}$ (in mol/L)

$pH + pOH = 14$ $[H^+] \times [OH^-] = 10^{-14}$ (in mol^2/L^2)

1. **200ml of 0.1M acetic acid is mixed with 400ml of 0.2M sodium acetate solution. Calculate the pH of the resulting mixture.**

Solution:-Given,

Initial case, volume of acetic acid (CH_3COOH) = 200ml

strength of acetic acid (CH_3COOH) = 0.1M

volume of sodium acetate(CH_3COONa) = 400ml

strength of sodium acetate(CH_3COONa) = 0.2M

pH of the resulting mixture = ?

Here, total volume of the mixture = (200+400)ml

= 600 ml

finally, new strength of acetic acid (CH_3COOH) = $\frac{0.1 \times 200}{600}$

$[CH_3COOH] = 0.033M$

strength of sodium acetate(CH_3COONa) = $\frac{0.2 \times 400}{600}$

$[CH_3COONa] = 0.133M$

$S_1V_1 = S_2V_2$ where, ***S_1= initial strength***

$S_2 = \frac{S_1V_1}{V_2}$ ***V_1= initial volume***

S_2= final strength

V_2= final volume

Using Henderson's equation,

$$pH = pKa + \log\frac{[salt]}{[acid]}$$

$$pH = 4.74 + \log\frac{[0.133]}{[0.033]}$$

$$pH = 4.74 + \log 4$$

$$pH = 4.74 + 0.602$$

$$pH = 5.34$$

Hence, pH of the resulting mixture is 5.34 .

2. ***Calculate the pH of a buffer solution containing 0.1M acetic acid and 0.01M sodium acetate.(pKa = 4.74)***
3. ***Calculate the pH of a buffer solution having the concentration ratio of acid and its salt is 2:1 and pKa = 4.74.***
4. ***The Ka of acetic acid is 1.76 X 10^{-5}. What is the pH of a buffer solution prepared by combining 100ml of 0.5M potassium acetate and 200ml of 0.25M acetic acid?***

5. 1.64g of anhydrous sodium acetate is added to 100ml of 0.02M acetic acid. What is the pH of buffer?

Solution:- Given,

weight of anhydrous CH_3COONa = 1.64g

volume of mixture = 100ml

strength of CH_3COOH = 0.02M

pH of buffer = ?

we know that,

molecular weight of anhydrous CH_3COONa = 82

$$\text{Molarity(strength) of } CH_3COONa = \frac{\text{number of moles}}{\text{vol. in litre}}$$

$$= \frac{\text{wt. in gm}}{\text{molecular weight}} \times \frac{1000}{\text{vol. in ml}}$$

$$= \frac{1.64}{82} \times \frac{1000}{100}$$

$$= 0.2M$$

Concentration of acetic acid(CH_3COOH) = 0.02M

Concentration of sodium acetate(CH_3COONa) = 0.2M

Using Henderson's equation,

$$pH = pKa + \log \frac{[CH_3COONa]}{[CH_3COOH]}$$

$$pH = 4.74 + \log \frac{0.2}{0.02}$$

$$pH = 4.74 + 1$$

$$\mathbf{pH = 5.74}$$

Hence , pH of a buffer solution is 5. 74 .

6. ***2.05g of anhydrous sodium acetate is added to 400ml of 0.32 M acetic acid. What will be the pH of the resulting solution?***
7. ***What is the pH of the solution obtained by mixing 1.5g of acetic acid and 2g of sodium acetate and making volume equal to 100ml. Dissociation constant of acetic acid is 1.75 X 10⁻⁵.***

8. Calculate the pH of 100ml of 0.4M NH_3 solution in which 20ml of 0.5M HCl is added.[pKa = 4.74]

Solution:- Given,

At initial , strength of ammonia solution[NH_4OH]= 0.4M

strength of [HCl] = 0.5M

volume of NH_4OH = 100ml

volume of HCl = 20ml

when they are mixed to each other volume is changed and as a result strength will also be changed. That's why at now,

$$\text{strength of ammonia solution}[NH_4OH] = \frac{0.4 \times 100}{(100 + 20)}$$

$$= 0.33M$$

$$\text{strength of } [HCl] = \frac{0.5 \times 20}{(100 + 20)}$$

$$= 0.083M$$

When HCl is added,

$$NH_3 + HCl \longrightarrow NH_4Cl$$

0.33M	0.083M	0	(At starting of reaction)
(0.33 – 0.083)M	0	0.083M	(At end of reaction)

$[NH_3] = 0.247M$

$[NH_4Cl] = 0.083M$

Using Henderson's equation,

$$pOH = pKb + \log \frac{[salt]}{[base]}$$

$$= 4.74 + \log \frac{[0.083]}{[0.247]}$$

$$= 4.74 + \log (0.336)$$

$$= 4.74 + (-0.474)$$

$$= 4.27$$

Now, $pH = 14 - pOH = 14 - 4.27$

$pH = 9.73$

9. 2.05g of anhydrous sodium acetate is added to 100ml of 0.1M HCl. What will be the pH of the solution?

10. What is pH of resulting mixture obtained by mixing of 100 cc of 0.2N HCl and 50 cc of 0.5M ammonia solution, Kb for ammonia is $1.8 X 10^{-5}$.

11. Calculate the pH of the mixture when 2ml of 0.01M HCl is added into a system having 400 ml of 0.2M NH_4OH and 200ml of 0.5M NH_4Cl solution.

Solution:- At initial,

volume of HCl = 2ml

volume of NH_4OH = 400ml

volume of NH_4Cl = 200ml

strength of HCl = 0.01M

strength of NH_4OH = 0.2M

strength of NH_4Cl = 0.5M

when solution are mixed to each other volume will be changed for each.

As a result strength of each component would be different.

Now, new strength(in mixture) of [HCl] = $S_1V_1/V_2 = \dfrac{0.01 \times 2}{(2+400+200)}$

$$[HCl] = 3.32 \times 10^{-5} M$$

new strength(in mixture) of $NH_4OH = \dfrac{0.2 \times 400}{(400+200+2)}$

$$[NH_4OH] = 0.1328M$$

Strength of $NH_4Cl = \frac{0.5 \times 200}{602}$

$[NH_4Cl] = 0.166M$

when reaction takes place, strength of salt and weak base again changed.

NH_4OH	+	$HCl \longrightarrow$	NH_4Cl	+	H_2O
0.1328M		3.32×10^{-5}M	0.166M		(At starting of reaction)
$[0.1328 – 3.32 \times 10^{-5}]$M		0M	$[0.166 + 3.32 \times 10^{-5}]$M		(At the end of rxn)

Now,

final strength of $[NH_4OH] = [0.1328 – 3.32 \times 10^{-5}]M = 0.1329M$

final strength of $[NH_4Cl] = [0.166 + 3.32 \times 10^{-5}]M = 0.1660M$

Using Henderson's equation, $pOH = Pkb + \log \frac{[NH_4Cl]}{[NH_4OH]}$

$$pOH = 4.74 + \log \frac{[0.1660]}{[0.1329]}$$

$$= 4.74 + \log[1.249]$$

$$= 4.74 + 0.0965 = 4.83$$

We know that, pH = 14- pOH = 14- 4.83 = 9.17 **pH of the mixture = 9.17**

12. A litre of solution contains 0.1 mole of acetic acid and 0.1 mole of sodium acetate. What is the change in pH of the solution after adding 0.02 mole of NaOH .[Ka = 1.8 X 10^{-5}]

solution:- given ,

A litre of solution contains 0.1 mole of acetic acid that means,

strength of [CH_3COOH] = 0.1M (Molarity = no. of moles/litre)

strength of [CH_3COONa] = 0.1M

strength of [NaOH] = 0.02M

Change in pH of solution after addition of NaOH = ?

Now,

Before the addition of NaOH, $pH = pKa + \log\frac{[CH_3COONa]}{[CH_3COOH]}$

$$= -\log(1.8 \times 10^{-5}) + \log\frac{[0.1]}{[0.1]}$$

$$= 4.74 + \log 1 \quad = 4.74 + 0$$

pH = 4.74

After the addition of NaOH,

$$CH_3COOH \quad + \quad NaOH \longrightarrow CH_3COONa \quad + \quad NaCl$$

0.1M	0.02M	0.1M	***No change in volume so initial concentration will be same.***
(0.1 – 0.02)M	0M	(0.1 + 0.02)M	

Now, $[CH_3COOH] = (0.1 - 0.02)M =$ **0.08M**

$[CH_3COONa] = (0.1 + 0.02)M =$ **0.12M**

$$pH = pKa + \log \frac{[CH_3COONa]}{[CH_3COOH]}$$

$$= 4.74 + \log \frac{[0.12]}{[0.08]}$$

$$= 4.74 + 0.176$$

$$= 4.916$$

Change in pH = pH of after addition of NaOH – pH of before addition of NaOH

$$= 4.916 - 4.74$$

Change in pH = 0.176.

13. What amount of sodium acetate should be used to prepare 1200ml of a buffer which is N/10 with respect to acetic acid and has a pH of 5.2 [pKa = 4.74]

Solution:- Given , total volume of solution = 1200ml

strength of acetic acid = N/10 = 0.1N

In case of CH_3COOH , Normality is equal to Molarity.

Thus, molar concentration of $[CH_3COOH]$ = 0.1M

pH of mixture = 5.2

pKa = 4.74

using Henderson's equation,

$$pH = pKa + \log\frac{[CH_3COONa]}{[CH_3COOH]}$$

$$5.2 = 4.74 + \log\frac{[CH_3COONa]}{[0.1]}$$

$$5.2 - 4.74 = \log\frac{[CH_3COONa]}{[0.1]}$$

$$0.46 = \log\frac{[CH_3COONa]}{0.1}$$

$$\frac{[CH_3COONa]}{0.1} = \text{antilog } (0.46)$$

$$[CH_3COONa] = 2.88 \times 0.1$$

$$\mathbf{[CH_3COONa] = 0.288M}$$

we know that, $\text{Molarity} = \frac{\text{wt. in gm}}{\text{mol. Wt}} \times \frac{1000}{\text{vol. in ml}}$

$$0.288 = \frac{\text{wt. in gm}}{82} \times \frac{1000}{1200}$$

$$\text{wt. in gm} = \frac{0.288 \times 82 \times 1200}{1000}$$

$$= 28.33 \text{ gm}$$

Thus, weight of CH_3COONa = 28.33 gm

14. Calculate the pH buffer solution prepared by mixing 100ml of 0.2M NH_4Cl and 200ml of 0.3M ammonia solution which is 3.1% ionized in the solution.