

**common ion effect.** It can be defined as a shift in equilibrium on adding a substance that provides more of an ionic species already present in the dissociation equilibrium. Thus, we can say that common ion effect is a phenomenon based on the Le Chatelier's principle discussed in section 7.8.

In order to evaluate the pH of the solution resulting on addition of 0.05M acetate ion to 0.05M acetic acid solution, we shall consider the acetic acid dissociation equilibrium once again,

$\text{HAc(aq)} \rightleftharpoons \text{H}^{\text{+}}(\text{aq}) + \text{Ac}^{\text{-}}(\text{aq})$
Initial concentration (M)
0.05                  0                  0.05
Let x be the extent of ionization of acetic acid.
Change in concentration (M)
-x                      +x                  +x
Equilibrium concentration (M)
0.05-x              x                  0.05+x

Therefore,

$$K_a = [\text{H}^{\text{+}}][\text{Ac}^{\text{-}}] / [\text{HAc}] = \{(0.05+x)(x)\} / (0.05-x)$$

As  $K_a$  is small for a very weak acid,  $x \ll 0.05$ .

$$\text{Hence, } (0.05 + x) \approx (0.05 - x) \approx 0.05$$

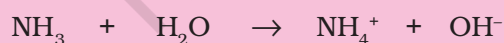
Thus,

$$\begin{aligned} 1.8 \times 10^{-5} &= (x) (0.05 + x) / (0.05 - x) \\ &= x(0.05) / (0.05) = x = [\text{H}^{\text{+}}] = 1.8 \times 10^{-5} \text{ M} \\ \text{pH} &= -\log(1.8 \times 10^{-5}) = 4.74 \end{aligned}$$

#### Problem 7.24

Calculate the pH of a 0.10M ammonia solution. Calculate the pH after 50.0 mL of this solution is treated with 25.0 mL of 0.10M HCl. The dissociation constant of ammonia,  $K_b = 1.77 \times 10^{-5}$

#### Solution



$$K_b = [\text{NH}_4^{\text{+}}][\text{OH}^{\text{-}}] / [\text{NH}_3] = 1.77 \times 10^{-5}$$

Before neutralization,

$$[\text{NH}_4^{\text{+}}] = [\text{OH}^{\text{-}}] = x$$

$$[\text{NH}_3] = 0.10 - x \approx 0.10$$

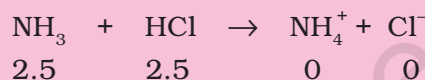
$$x^2 / 0.10 = 1.77 \times 10^{-5}$$

$$\text{Thus, } x = 1.33 \times 10^{-3} = [\text{OH}^{\text{-}}]$$

$$\begin{aligned} \text{Therefore, } [\text{H}^{\text{+}}] &= K_w / [\text{OH}^{\text{-}}] = 10^{-14} / \\ &(1.33 \times 10^{-3}) = 7.51 \times 10^{-12} \end{aligned}$$

$$\text{pH} = -\log(7.5 \times 10^{-12}) = 11.12$$

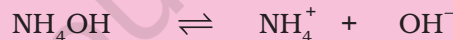
On addition of 25 mL of 0.1M HCl solution (i.e., 2.5 mmol of HCl) to 50 mL of 0.1M ammonia solution (i.e., 5 mmol of  $\text{NH}_3$ ), 2.5 mmol of ammonia molecules are neutralized. The resulting 75 mL solution contains the remaining unneutralized 2.5 mmol of  $\text{NH}_3$  molecules and 2.5 mmol of  $\text{NH}_4^{\text{+}}$ .



At equilibrium

$$\begin{array}{ccccccc} 0 & & 0 & & 2.5 & & 2.5 \end{array}$$

The resulting 75 mL of solution contains 2.5 mmol of  $\text{NH}_4^{\text{+}}$  ions (i.e., 0.033 M) and 2.5 mmol (i.e., 0.033 M) of unneutralised  $\text{NH}_3$  molecules. This  $\text{NH}_3$  exists in the following equilibrium:



$$0.033\text{M} - y \qquad \qquad y \qquad \qquad y$$

where,  $y = [\text{OH}^{\text{-}}] = [\text{NH}_4^{\text{+}}]$

The final 75 mL solution after neutralisation already contains 2.5 mmol  $\text{NH}_4^{\text{+}}$  ions (i.e. 0.033M), thus total concentration of  $\text{NH}_4^{\text{+}}$  ions is given as:

$$[\text{NH}_4^{\text{+}}] = 0.033 + y$$

As y is small,  $[\text{NH}_4\text{OH}] \approx 0.033 \text{ M}$  and  $[\text{NH}_4^{\text{+}}] \approx 0.033\text{M}$ .

We know,

$$\begin{aligned} K_b &= [\text{NH}_4^{\text{+}}][\text{OH}^{\text{-}}] / [\text{NH}_4\text{OH}] \\ &= y(0.033) / (0.033) = 1.77 \times 10^{-5} \text{ M} \end{aligned}$$

Thus,  $y = 1.77 \times 10^{-5} = [\text{OH}^{\text{-}}]$

$$[\text{H}^{\text{+}}] = 10^{-14} / 1.77 \times 10^{-5} = 0.56 \times 10^{-9}$$

Hence,  $\text{pH} = 9.24$

#### 7.11.9 Hydrolysis of Salts and the pH of their Solutions

Salts formed by the reactions between acids and bases in definite proportions, undergo ionization in water. The cations/anions formed

on ionization of salts either exist as hydrated ions in aqueous solutions or interact with water to reform corresponding acids/bases depending upon the nature of salts. The later process of interaction between water and cations/anions or both of salts is called hydrolysis. The pH of the solution gets affected by this interaction. The cations (e.g.,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Ba}^{2+}$ , etc.) of strong bases and anions (e.g.,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{NO}_3^-$ ,  $\text{ClO}_4^-$  etc.) of strong acids simply get hydrated but do not hydrolyse, and therefore the solutions of salts formed from strong acids and bases are neutral i.e., their pH is 7. However, the other category of salts do undergo hydrolysis.

We now consider the hydrolysis of the salts of the following types :

- (i) salts of weak acid and strong base e.g.,  $\text{CH}_3\text{COONa}$ .
- (ii) salts of strong acid and weak base e.g.,  $\text{NH}_4\text{Cl}$ , and
- (iii) salts of weak acid and weak base, e.g.,  $\text{CH}_3\text{COONH}_4$ .

In the first case,  $\text{CH}_3\text{COONa}$  being a salt of weak acid,  $\text{CH}_3\text{COOH}$  and strong base,  $\text{NaOH}$  gets completely ionised in aqueous solution.



Acetate ion thus formed undergoes hydrolysis in water to give acetic acid and  $\text{OH}^-$  ions

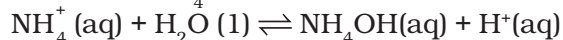


Acetic acid being a weak acid ( $K_a = 1.8 \times 10^{-5}$ ) remains mainly unionised in solution. This results in increase of  $\text{OH}^-$  ion concentration in solution making it alkaline. The pH of such a solution is more than 7.

Similarly,  $\text{NH}_4\text{Cl}$  formed from weak base,  $\text{NH}_4\text{OH}$  and strong acid,  $\text{HCl}$ , in water dissociates completely.



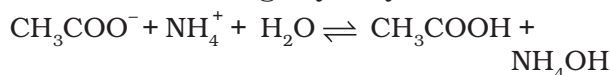
Ammonium ions undergo hydrolysis with water to form  $\text{NH}_4\text{OH}$  and  $\text{H}^+$  ions



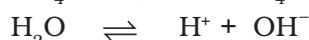
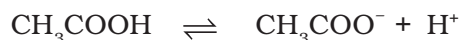
Ammonium hydroxide is a weak base ( $K_b = 1.77 \times 10^{-5}$ ) and therefore remains almost unionised in solution. This results in

increased of  $\text{H}^+$  ion concentration in solution making the solution acidic. Thus, the pH of  $\text{NH}_4\text{Cl}$  solution in water is less than 7.

Consider the hydrolysis of  $\text{CH}_3\text{COONH}_4$  salt formed from weak acid and weak base. The ions formed undergo hydrolysis as follow:



$\text{CH}_3\text{COOH}$  and  $\text{NH}_4\text{OH}$ , also remain into partially dissociated form:



Without going into detailed calculation, it can be said that degree of hydrolysis is independent of concentration of solution, and pH of such solutions is determined by their pK values:

$$\text{pH} = 7 + \frac{1}{2} (\text{p}K_a - \text{p}K_b) \quad (7.38)$$

The pH of solution can be greater than 7, if the difference is positive and it will be less than 7, if the difference is negative.

### Problem 7.25

The  $\text{p}K_a$  of acetic acid and  $\text{p}K_b$  of ammonium hydroxide are 4.76 and 4.75 respectively. Calculate the pH of ammonium acetate solution.

### Solution

$$\begin{aligned} \text{pH} &= 7 + \frac{1}{2} [\text{p}K_a - \text{p}K_b] \\ &= 7 + \frac{1}{2} [4.76 - 4.75] \\ &= 7 + \frac{1}{2} [0.01] = 7 + 0.005 = 7.005 \end{aligned}$$

## 7.12 BUFFER SOLUTIONS

Many body fluids e.g., blood or urine have definite pH and any deviation in their pH indicates malfunctioning of the body. The control of pH is also very important in many chemical and biochemical processes. Many medical and cosmetic formulations require that these be kept and administered at a particular pH. **The solutions which resist change in pH on dilution or with the addition of small amounts of acid or alkali are called Buffer Solutions.** Buffer solutions