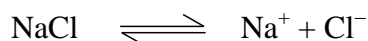
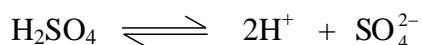


# IONIC EQUILIBRIUM

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## 1. ARRHENIUS THEORY OF ELECTROLYTIC DISSOCIATION

When an electrolyte is dissolved in a solvent (usually water) or is fused, it spontaneously dissociates into oppositely charged particles called ions, to a considerable extent.



The positively charged ions are called cations and the negatively charged ions are called anions.

Since the solution of an electrolyte, as a whole, is electrically neutral, the total charge on the cations is equal to the total charge on the anions.

Electrolytic dissociation or ionization produces equilibrium between unionized molecules and the ions in solution. The degree of dissociation of an electrolyte ( $\alpha$ ) is the fraction of one mole of the electrolyte that has dissociated under the given conditions. The value of  $\alpha$  depends on the nature of the electrolyte, nature of the solvent, the dilution and the temperature.

**(a) Nature of the electrolyte:** Some electrolytes, e.g., mineral acids such as  $\text{H}_2\text{SO}_4$ ,  $\text{HCl}$  and  $\text{HNO}_3$ , alkalis such as  $\text{NaOH}$  and  $\text{KOH}$  and all salts have a very *high degree of ionization* ( $\alpha$  nearly equal to 1) at all reasonable concentrations. They are known as *strong electrolytes*. The *number of ions* in solutions of strong electrolytes is large and thus such solutions have *high conductance*.

Some electrolytes, e.g., organic acids such as acetic acid, propionic acid. etc., and bases like ammonium hydroxide have a *low degree of ionization* in solution. They are called *weak electrolytes*. The *number of ions* in solutions of weak electrolytes is *quite small* and thus such solutions have *low conductance*.

**(b) Nature of the solvent:** A solvent which has a high dielectric constant weakens the attractive force between the cations and anions. Hence a solvent of high dielectric constant favours the dissociation of the electrolyte.

Likewise a solvent which can solvate the ions readily, and can release energy by solvation, favours the dissociation of the electrolyte. Thus, the dissociation of acids in water is favoured by the hydration of the hydrogen ions to form hydronium ions. The enthalpy of hydration of the proton has a very high value.

**(c) Dilution:** For some electrolytes, degree of dissociation increases with dilution as explained by Ostwald's dilution law (explained later)

**(d) Temperature:** Increase of temperature generally increases ionization.

Ionic theory satisfactorily explains the behaviour of weak electrolytes. In solution they contain very few ions; so they are "on an average" far apart and exert no attractive force on one another. But it fails to account for the behaviour of strong electrolytes. The low conductance in fairly concentrated solutions of strong electrolytes is really due to strong attractive forces between ions and not to the small degree of ionization (because  $\alpha$  is nearly 1 for strong electrolytes even in fairly concentrated solutions).

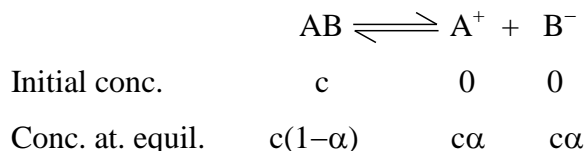
Note that conductance depends on (i) the number of ions "per unit volume", (ii) the speed of ions and (iii) the charge on the ion. In concentrated solutions of strong electrolytes because of inter-ionic attractions, the speed is less and so the conductance is less.

# IONIC EQUILIBRIUM

## 2. OSTWALD'S DILUTION LAW

This law deals with the application of the law of mass action to the equilibrium between the ions and unionized molecules in aqueous solutions of weak binary electrolytes such as acetic acid, propionic acid, HCN,  $\text{NH}_4\text{OH}$ , etc.

Consider a dilute solution of a weak binary electrolyte AB containing  $c$  moles in 1 litre. At any given temperature, there will be equilibrium between the unionized molecules of AB and the ions  $\text{A}^+$  and  $\text{B}^-$ . Let ' $\alpha$ ' be the degree of dissociation of AB at equilibrium.



Then according to the law of mass action, the equilibrium constant  $K_{\text{eq}}$  will be given by

$$K_{\text{eq}} = \frac{[\text{A}^+][\text{B}^-]}{[\text{AB}]} = \frac{c\alpha \times c\alpha}{c(1-\alpha)} = \frac{\alpha^2 c}{1-\alpha}$$

This expression " $K_{\text{eq}} = \frac{\alpha^2 c}{1-\alpha}$ " is called Ostwald's dilution law.  $K_{\text{eq}}$  is called the dissociation (or ionization) constant of the weak electrolyte.

If 1 mole is present in ' $V$ ' litres of solution,  $c = \frac{1}{V}$ .  $\therefore K_{\text{eq}} = \frac{\alpha^2}{V(1-\alpha)}$ . This is another expression for Ostwald's dilution law.

$\alpha$  has a very small value for a weak electrolyte and is therefore negligible in comparison with unity.

$$\therefore 1 - \alpha \approx 1.$$

$$\therefore K_{\text{eq}} = \alpha^2 c$$

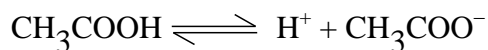
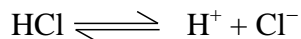
$$\begin{aligned}\alpha &= \sqrt{\frac{K_{\text{eq}}}{c}} \\ &= \sqrt{K_{\text{eq}} \times V}\end{aligned}$$

This law is valid only for weak electrolytes that too in dilute solutions. It is not applicable for strong electrolytes.

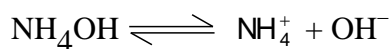
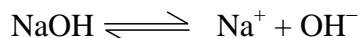
## 3. CONCEPT OF ACID AND BASES

### 3.1 THE ARRHENIUS CONCEPT

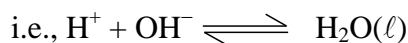
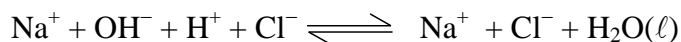
An acid is a substance which in aqueous solution gives hydrogen ions as the only cations. (This definition excludes acid salts). e.g.,



A base is a substance which in aqueous solution gives hydroxyl ( $\text{OH}^-$ ) ions as the only anions.

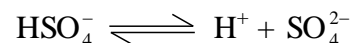
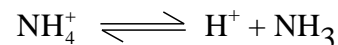
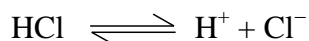


Neutralization is nothing but combination of  $\text{H}^+$  ions of the acid and  $\text{OH}^-$  ions of the base to form unionized water.



### 3.2 THE LOWRY-BRONSTED THEORY

According to this concept, an acid is a substance which has a tendency to lose a proton ( $\text{H}^+$ ), i.e., an acid is a proton donor and a base is a substance, which has a tendency to accept a proton, i.e., it is a proton acceptor. When an acid loses a proton, the residue will have a tendency to regain a proton and hence it is referred as conjugate base

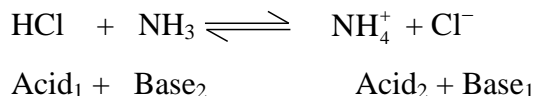


The acid and the conjugate base, which differ by a proton, forms a conjugate pair. For example,  $\text{HCl}$  and  $\text{Cl}^-$  ion form a conjugate pair;  $\text{Cl}^-$  is the conjugate base of  $\text{HCl}$  and  $\text{HCl}$  is the conjugate acid of  $\text{Cl}^-$ . From the examples given above, it is clear that acids and bases may be molecules or ions, but at least one of the members of a conjugate pair should be an ion.

# IONIC EQUILIBRIUM

## Acid–Base Reaction

When an acid and a base are mixed, the acid donates its proton and the base accepts it. Thus, when HCl and  $\text{NH}_3$  react,  $\text{NH}_4^+$  and  $\text{Cl}^-$  ions are produced.



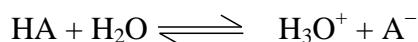
The products  $\text{NH}_4^+$  and  $\text{Cl}^-$  are another acid and base; so the reverse reaction may also take place. So an acid–base reaction may be considered to be equilibrium between two acid–base systems:



where  $\text{acid}_1$  and  $\text{base}_1$  are the conjugate acid and base of one system and  $\text{acid}_2$  and  $\text{base}_2$  are those of the other system.

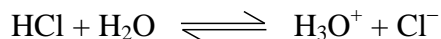
Behaviour of acids and bases in aqueous solution

(i) Acids in water: Water functions as a weak base and accepts a proton from the acid, thus



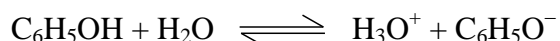
$\text{A}^-$  can be considered as the conjugate base or anion or salt of the acid HA. So an aqueous solution of an acid contains hydronium ( $\text{H}_3\text{O}^+$ ) ions (and not  $\text{H}^+$  ions).

(ii) Strong and Weak acids: (Relationship between a conjugate pair) An acid is considered to be a strong acid, if it can give up its proton readily. In an aqueous solution of HCl, there is equilibrium



Since HCl can give up its proton readily, this equilibrium will lie far to the right. Consequently the base  $\text{Cl}^-$  cannot take up the proton from  $\text{H}_3\text{O}^+$  readily, i.e.,  $\text{Cl}^-$  is a weak base. In general, the conjugate base of a strong acid will be a weak base. Since there is large ionization in aqueous solution of a strong acid, the acid is a strong acid, the solution has a high conductance.

In the case of a weak acid like phenol, the equilibrium

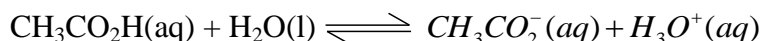


will lie far to the left. So the conjugate base ( $\text{C}_6\text{H}_5\text{O}^-$ ) of a weak acid ( $\text{C}_6\text{H}_5\text{OH}$ ) will be moderately strong. Again there is little ionization in the aqueous solution of a weak acid so the acid is a weak electrolyte and the solution has a low conductance. Based on studies of acids it is established that,



(iii) Relationship between the ionization constants of acids and their conjugate bases

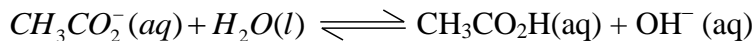
Let us derive a relationship between the ionization constants of acid,  $\text{CH}_3\text{CO}_2\text{H}$  and its conjugate base,  $\text{CH}_3\text{CO}_2^-$ . The equilibrium reaction of  $\text{CH}_3\text{CO}_2\text{H}$  in water is written as



## IONIC EQUILIBRIUM

$$K_{eq}[H_2O] = \frac{[CH_3CO_2^-][H_3O^+]}{[CH_3CO_2H]} = K_a \quad \dots\dots(i)$$

The conjugate base of acetic acid ( $CH_3CO_2^-$ ) acts as base in its reaction with water as



$$K'_{eq}[H_2O] = \frac{[CH_3CO_2H][OH^-]}{[CH_3CO_2^-]} = K_b \quad \dots\dots(ii)$$

As we know,  $[OH^-] = \frac{K_w}{[H^+]}$ . Inserting  $[OH^-]$  in equation (ii) gives

$$\therefore K_b = \frac{[CH_3CO_2H] K_w}{[CH_3CO_2^-][H^+]}$$

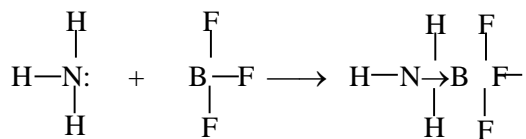
$$K_b = \frac{K_w}{K_a}$$

Thus, stronger the acid (the larger  $K_a$ ), weaker will be its conjugate base (the smaller  $K_b$ ) and vice versa. Therefore, for an acid–conjugate base pair.

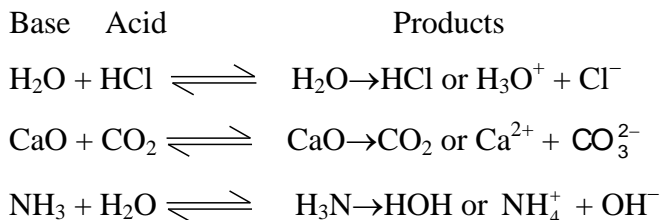
$$K_w = K_a \times K_b$$

### 3.3 LEWIS ELECTRONIC THEORY

According to this theory an acid is any molecule or ion, which can accept an electron pair with the formation of a coordinate bond. For example, in  $BF_3$  the boron atom can accept a pair of electrons; so  $BF_3$  is a Lewis acid. A base must therefore be any molecule or ion, which has a lone pair of electrons, which it can donate. For example, ammonia molecule has a lone pair of electrons; so it is a Lewis base. The reaction between a Lewis base and a Lewis acid is just the formation of a coordinate bond between them.



Other examples of Lewis acid–base neutralization



# IONIC EQUILIBRIUM

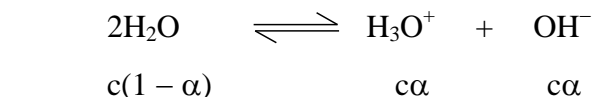
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The concepts and principles underlying chemical equilibrium are also applicable for ionic equilibrium. The fundamental concepts of chemical equilibrium, which are useful in ionic equilibrium are:

- The equilibrium are dynamic in nature.
- The equilibrium constant is independent of the initial concentration of reactants.
- The equilibrium constant depends on temperature and nature of reactants and products.
- The equilibrium can be attained from either side.
- The concentration of pure solids, pure liquids and solvents do not appear in the equilibrium constant expression.
- The equilibrium in solutions will only have equilibrium constant,  $K_C$  and  $K_P$  do not exist for such equilibrium.
- The degree of dissociation of a weak electrolyte is the fraction of a mole of electrolyte that underwent dissociation.
- The equilibrium constant for the overall reaction is given by the product of the equilibrium constants of the individual reactions.
- In order to predict the direction of equilibrium movement, reaction quotient (Q) should be compared with equilibrium constant, K. If  $Q = K$ , reaction is at equilibrium, if  $Q < K$ , reaction will proceed from left to right to achieve equilibrium and if  $Q > K$ , reaction will move from right to left to attain equilibrium.
- According to Le Chatelier principle if an external stress is applied to a system at equilibrium, the system will adjust to partially offset the stress.

## 4. IONIC PRODUCT OF WATER

Water is a weak electrolyte so its ionisation is not complete and undissociated water is in equilibrium with its ions,  $H_3O^+$  and  $OH^-$ . Since water gives  $H_3O^+$  and  $OH^-$  both, it is called **amphiprotic**. Let us take pure water of density 1 g/cc. Its concentration would be  $1000/58 = 55.56$  molar. Let  $\alpha$  be the degree of ionization of water, then



$$[H_2O] = c = \frac{1000}{58} = 55.56 \text{ M}$$

$$K_{eq} = \frac{[H_3O^+][OH^-]}{[H_2O]^2}$$

where  $K_{eq}$  is ionisation (dissociation) constant of water.

Since water is present in large amount, there is no appreciable change in the concentration of water. So concentration of water is taken as constant and it is merged with the  $K_{eq}$  to give  $K_w$ .

$$K_{eq} [H_2O]^2 = [H_3O^+][OH^-]$$

$$K_w = [H_3O^+][OH^-] = (c\alpha)^2$$

## IONIC EQUILIBRIUM

$K_w$  is called ionic product of water. The value of  $K_w$  at  $25^\circ\text{C}$  is  $1 \times 10^{-14}$  and it is temperature dependent.

$$\therefore 1 \times 10^{-14} = [\text{H}_3\text{O}^+] [\text{OH}^-]$$

$1 \times 10^{-14} = [\text{H}_3\text{O}^+]^2 = [\text{OH}^-]^2$  (as water on dissociation give equal number of  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$  ions)

$\therefore [\text{H}_3\text{O}^+] = [\text{OH}^-] = \sqrt{1 \times 10^{-14}} = 1 \times 10^{-7} \text{ M}$ , so water at  $25^\circ\text{C}$  has  $10^{-7} \text{ M}$  of  $\text{H}_3\text{O}^+$  and  $10^{-7} \text{ M}$  of  $\text{OH}^-$  ions. As the number of  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$  are same, so water is neutral.

The product of  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$  concentration for any solution (acidic, basic or neutral) at any temperature is a constant, called ionic product (auto protolysis constant) of water.

For any acidic solution,  $[\text{H}_3\text{O}^+] > [\text{OH}^-]$   
or  $[\text{H}_3\text{O}^+] > 10^{-7} \text{ M}$

For any alkaline solution,  $[\text{H}_3\text{O}^+] < [\text{OH}^-]$   
or  $[\text{OH}^-] > 10^{-7} \text{ M}$ .

$K_w$  is not same as the dissociation constant of water.

$K_w$  is a constant irrespective of the presence of other ions in the solution.

$K_w$  increases with temperature.

Temperature ( $^\circ\text{C}$ )	0	10	20	25	30	40	50
$K_w (\times 10^{-14})$	0.114	0.292	0.681	1.008	1.468	2.919	5.474

## 5. ACIDITY AND pH SCALE

Acidic strength means the tendency of an acid to give  $\text{H}_3\text{O}^+$  or  $\text{H}^+$  ions in water and basic strength means the tendency of a base to give  $\text{OH}^-$  ions in water. So more the tendency of the substance to give  $\text{H}^+$  or  $\text{OH}^-$  ions, more will be the acidic or basic strength of the substance.

Many properties of aqueous solution depend on the concentration of  $\text{H}_3\text{O}^+$  or  $\text{H}^+$  ions in the solutions and therefore there is a need to express these concentrations in some other simpler terms. For this purpose, Sorenson introduced the concept of pH. **pH is negative logarithm of activity of  $\text{H}^+$  ions.**

$$\therefore \text{pH} = -\log a_{\text{H}^+} \text{ (where } a_{\text{H}^+} \text{ is the activity of } \text{H}^+ \text{ ions).}$$

Activity of  $\text{H}^+$  ions is the concentration of free  $\text{H}^+$  ions or  $\text{H}_3\text{O}^+$  ions in a solution. By free, we mean those  $\text{H}^+$  (or  $\text{H}_3\text{O}^+$ ) that are at a large distance from the other  $\text{H}^+$  (or  $\text{H}_3\text{O}^+$ ) ion, so as not to experience its pull. We can infer from this that in dilute solutions, the activity of an ion is same as its concentration since more number of solvent molecules would separate the two ions. But for concentrated solutions, the activity would be much less than the concentration itself. Therefore, the earlier given expression of pH can be modified for dilute solutions as,  $\text{pH} = -\log [\text{H}^+]$ . This assumption can only be made when the solution is very much dilute, i.e.,  $[\text{H}^+] \leq 1\text{M}$ . For higher concentration of  $\text{H}^+$  (or  $\text{H}_3\text{O}^+$ ) ions, one needs to calculate the activity experimentally and then calculate the pH.

# IONIC EQUILIBRIUM

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Thus, for dilute solutions,  $\text{pH} = -\log [\text{H}^+] = -\log [\text{H}_3\text{O}^+]$

and  $\text{pOH} = -\log [\text{OH}^-]$

For pure water,  $\text{pH} = -\log 1 \times 10^{-7} = 7 \log 10 = 7$

Sorenson devised a scale called pH scale for measuring the acidity of a solution. The scale was marked from 0 to 14 with central point at 7.  $\text{pH} = 7$  represents a neutral solution,  $\text{pH} < 7$  represents an acidic solution and  $\text{pH} > 7$  implies alkaline solution. This scale was devised keeping water as solvent at  $25^\circ\text{C}$ . If the temperature and the solvent are changed, the pH range of the scale will also change.

## Illustration 1

What is the hydrogen ion concentration in a solution whose  $\text{pH} = 4.3$ ?

**Solution:**

$$\text{pH} = -\log [\text{H}^+] = 4.3$$

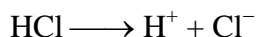
$$\log [\text{H}^+] = -4.3 = \bar{5}.7000$$

$$[\text{H}^+] = \text{antilog } \bar{5}.7000 = 5.012 \times 10^{-5}.$$

## 6. pH CALCULATION

### 6.1 pH CALCULATION OF STRONG ACID

A strong acid completely ionizes in water. For example, HCl ionizes completely to give same concentration of  $\text{H}^+$  and  $\text{Cl}^-$  ions.



Let 'c' be the concentration of HCl. The concentration of  $\text{H}^+$  obtained from HCl would also be 'c'.

$$\therefore \text{pH} = -\log c$$

Now let us calculate the pH of HCl solutions of varied concentrations.

$$10^{-1} \text{ M HCl}, [\text{H}^+] = 10^{-1} \text{ M}; \quad \text{pH} = -\log 10^{-1} = 1$$

$$10^{-2} \text{ M HCl}, [\text{H}^+] = 10^{-2} \text{ M}; \quad \text{pH} = -\log 10^{-2} = 2$$

$$10^{-3} \text{ M HCl}, [\text{H}^+] = 10^{-3} \text{ M}; \quad \text{pH} = -\log 10^{-3} = 3$$

$$10^{-4} \text{ M HCl}, [\text{H}^+] = 10^{-4} \text{ M}; \quad \text{pH} = -\log 10^{-4} = 4$$

$$10^{-5} \text{ M HCl}, [\text{H}^+] = 10^{-5} \text{ M}; \quad \text{pH} = -\log 10^{-5} = 5$$

$$10^{-6} \text{ M HCl}, [\text{H}^+] = 10^{-6} \text{ M}; \quad \text{pH} = -\log 10^{-6} = 6$$

$$10^{-7} \text{ M HCl}, [\text{H}^+] = 10^{-7} \text{ M}; \quad \text{pH} = -\log 10^{-7} = 7$$

The pH calculation of  $10^{-7} \text{ M HCl}$  is not correct, as we know any acid solution cannot behave neutral. We can very well think that the  $[\text{H}^+]$  in any acid solution would always be more than the  $[\text{H}^+]$  in water alone. Let us see, how pH of  $10^{-7} \text{ M HCl}$  is then calculated.



# IONIC EQUILIBRIUM

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## Method I

We already know the concentration of  $\text{H}^+$  (or  $\text{H}_3\text{O}^+$ ) ions from pure water is  $10^{-7}$  M. So all we need to do is to add the  $\text{H}^+$  ion concentration from water and  $\text{H}^+$  (or  $\text{H}_3\text{O}^+$ ) ion concentration from HCl to get the  $[\text{H}^+]_{\text{Total}}$ .

$$(\text{H}^+)_{\text{T}} = (\text{H}^+)_{\text{HCl}} + (\text{H}^+)_{\text{water}} = 10^{-7} \text{ M} + 10^{-7} \text{ M} = 2 \times 10^{-7} \text{ M}$$

$$\text{pH} = -\log (\text{H}^+)_{\text{T}} = -\log 2 \times 10^{-7} = 6.6989$$

Though the method looks correct but there is a mistake in it. In chemical equilibrium we have learnt about Le-Chatelier's Principle, which states that when concentration of a reactant or product is changed the reaction tends to go forward or reverse to finally reestablish equilibrium. We can see that in the present case, by adding  $10^{-7}$  M HCl to water, we are increasing the  $[\text{H}^+]$ . This should make the reaction go in the reverse direction. Therefore the  $[\text{H}^+]$  from water would become less than  $10^{-7}$  M. So the method will yield incorrect result.

## Method II

The statement given above that “the addition of an ion to an equilibrium, having the same ion makes the equilibrium move in a direction to consume that ion” is called the common ion effect. This implies that water would dissociate less in the presence of HCl. Let the amount of water dissociated be  $x'$  in the presence of  $10^{-7}$  M HCl.



$$\text{At equilibrium} \quad (x' + 10^{-7}) \quad x'$$

$$[\text{H}_3\text{O}^+][\text{OH}^-] = 10^{-14}$$

$$(x' + 10^{-7})(x') = 10^{-14}$$

Calculating for  $x'$ , we get  $x' = 0.618 \times 10^{-7}$  M.

Here, we can clearly see the common ion effect in operation. Water which was dissociating to give  $10^{-7}$  M  $\text{H}_3\text{O}^+$  ions, has now experienced the common ion effect and has now yielded only  $0.618 \times 10^{-7}$  M  $\text{H}_3\text{O}^+$  ions.

$$\text{Therefore, } [\text{H}_3\text{O}^+]_{\text{T}} = (10^{-7} + 0.618 \times 10^{-7}) \text{ M}$$

$$\therefore \text{pH} = -\log (1.618 \times 10^{-7}) = 6.7910$$

Now, let us answer the question as to why we take the  $[\text{H}^+]$  from water into account for calculating the pH of  $10^{-7}$  M HCl while for calculating the pH of  $10^{-6}$  M,  $10^{-5}$  M,  $10^{-4}$  M,  $10^{-3}$  M,  $10^{-2}$  M and  $10^{-1}$  M HCl, we have not considered it. It can be seen that the  $\text{H}^+$  ions from water, decreases due to the common ion from HCl. Greater the concentration of the common ion added, greater will be the effect. Therefore, for concentrations higher than  $10^{-6}$  M (and inclusive of  $10^{-6}$  M), the  $\text{H}^+$  from water will be even less than  $0.618 \times 10^{-7}$  M and would be so small in comparison to the  $[\text{H}^+]$  from HCl, that we can ignore it.

Thus, it is concluded that  $[\text{H}_3\text{O}^+]$  from water needs to be considered only if the  $[\text{H}_3\text{O}^+]$  from acid is  $< 10^{-6}$  M and if  $[\text{H}_3\text{O}^+]$  from acid is  $\geq 10^{-6}$  M, the  $[\text{H}_3\text{O}^+]$  from water can be ignored.

## Illustration 2

While calculating the pH of  $10^{-7}$  M HCl, we have taken into account the common ion effect of HCl on water. Why did we not take the common ion effect of water on HCl?

## IONIC EQUILIBRIUM

### Solution:

Let us assumed that the  $K_w$  of water be  $10^{-10}$  at  $25^\circ\text{C}$ . Then in pure water,

$$x^2 = 10^{-10}; x = 10^{-5}$$

Let us now calculate  $[\text{H}_3\text{O}^+]$  from the water in the presence of  $10^{-7}$  M HCl using the same value of  $K_w$ .

$$(x' + 10^{-7}) x' = 10^{-10}$$

$$\therefore x' = 0.995 \times 10^{-5} \text{ M}$$

The percentage decrease in the concentration of  $\text{H}_3\text{O}^+$  of water is  $\frac{10^{-5} - 0.995 \times 10^{-5}}{10^{-5}} \times 100 = 0.5\%$

When the  $K_w$  of water was  $10^{-14}$ , the  $\text{H}_3\text{O}^+$  concentration of pure water was  $10^{-7}$  M while that in the presence of  $10^{-7}$  M HCl was  $0.618 \times 10^{-7}$  M.

The percentage decrease in the  $[\text{H}_3\text{O}^+]$  of water in the presence of  $10^{-7}$  M HCl is  $\frac{10^{-7} - 0.618 \times 10^{-7}}{10^{-7}} \times 100 = 38.2\%$

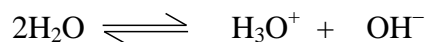
Thus, it can be concluded that larger the value of equilibrium constant of the weak electrolyte, lesser is the common ion effect produced. So, the common ion effect is experienced more by the weak electrolyte (having smaller equilibrium constant) than the strong electrolyte (having larger equilibrium constant).

### Illustration 3

What is the pH of (a)  $5 \times 10^{-8}$  M HCl, (b)  $5 \times 10^{-10}$  M HCl?

### Solution:

(a) If we consider only the contribution of hydrogen ion concentration from HCl, that is  $[\text{H}^+] = 5 \times 10^{-8}$  then the pH would be  $> 7$ . This is not possible because  $[\text{H}_3\text{O}^+]$  of any acid solution, no matter how dilute it is, cannot be less than that of pure water alone. In such cases, we have to take into account the contribution of  $\text{H}_3\text{O}^+$  made by water. Let  $[\text{H}_3\text{O}^+]$  from water be  $x$  moles/litre in the presence of  $5 \times 10^{-8}$  M HCl.



From HCl  $5 \times 10^{-8}$

From water  $x \quad x$

At equilibrium  $(5 \times 10^{-8} + x) \quad x$

$$K_w = [\text{H}_3\text{O}^+] [\text{OH}^-] = (5 \times 10^{-8} + x) (x) = 10^{-14}$$

$$x = 0.78 \times 10^{-7}$$

$$[\text{H}_3\text{O}^+] = 5 \times 10^{-8} + 0.78 \times 10^{-7} = 1.28 \times 10^{-7}$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (1.28 \times 10^{-7}) = -(-7 + 0.11) = \mathbf{6.89}$$

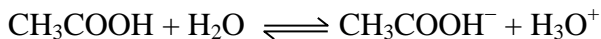
## IONIC EQUILIBRIUM

(b) HCl is so dilute that its contribution to  $[\text{H}_3\text{O}^+]$  is negligible.

$\therefore$  pH will be nearly 7

### 6.2 pH CALCULATION OF WEAK ACID

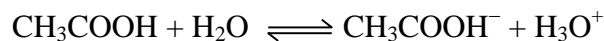
Weak acid is that which dissociate partially in water and soon comes in equilibrium with its ions as



The equilibrium constant is called  $K_a$  (dissociation or ionization constant).

$$K_a = \frac{[\text{CH}_3\text{COO}^-] \times [\text{H}_3\text{O}^+]}{[\text{CH}_3\text{COOH}]}$$

Let the degree of dissociation of weak acid be  $\alpha$ .



Initial conc.	c	0	0
Conc. at equilib.	$c - c\alpha$	$c\alpha$	$c\alpha$

If  $\alpha < 1$  then  $1 - \alpha \approx 1$  (i.e. for  $\alpha$  less than or equal to 0.1)

$$K_a \approx c\alpha^2 \quad \text{or} \quad \alpha = \sqrt{\frac{K_a}{c}}$$

$$[\text{H}_3\text{O}^+] = c\alpha = c \times \sqrt{\frac{K_a}{c}} = \sqrt{K_a \times c}$$

Using the value of  $K_a$  and  $c$ ,  $[\text{H}_3\text{O}^+]$  can be calculated and then pH of the solution can be calculated.

Taking log of both the sides of above equation,

$$\log [\text{H}_3\text{O}^+] = \frac{1}{2} \log K_a + \frac{1}{2} \log c$$

Multiplying both sides by  $-1$ ,

$$-\log [\text{H}_3\text{O}^+] = -\frac{1}{2} \log K_a - \frac{1}{2} \log c$$

$$\text{pH} = \frac{1}{2} \text{p}K_a - \frac{1}{2} \log c = \frac{1}{2} (\text{p}K_a - \log c)$$

#### Illustration 4

Calculate the pH of  $10^{-6}$  M  $\text{CH}_3\text{COOH}$ .  $K_a (\text{CH}_3\text{COOH}) = 1.8 \times 10^{-5}$ .

#### Solution:

##### Method 1:

$[\text{H}_3\text{O}^+]$  due to a weak acid is given by

$$[\text{H}_3\text{O}^+] = \sqrt{K_a \times c} = \sqrt{1.8 \times 10^{-5} \times 10^{-6}} = 4.24 \times 10^{-6}$$

$$\text{pH} = 5.37$$

## IONIC EQUILIBRIUM

Though it seems that we have solved the problem correctly, there is an error in this method. This error can be highlighted by comparing it with the pH of  $10^{-6}$  M HCl. We can see that the pH of  $10^{-6}$  M HCl would be 6. As we know that lesser pH implies higher concentration of  $\text{H}_3\text{O}^+$  ions. So a weak acid having the same concentration as that of a strong acid cannot give higher concentration of  $\text{H}_3\text{O}^+$  ions. The error in pH calculation has occurred because we have assumed that  $\alpha$  is very much small compared to 1 without knowing the value of  $\alpha$ . In fact, if we make this assumption, the  $\alpha$  we get is,

$$\alpha = \sqrt{\frac{K_a}{c}} = \sqrt{\frac{1.8 \times 10^{-5}}{10^{-6}}} = 4.24$$

This value is not possible as  $\alpha$  cannot be more than 1, ever. Therefore, the assumption made by us is not valid and pH of  $10^{-6}$  M  $\text{CH}_3\text{CO}_2\text{H}$  is to be calculated without any assumption.

### Method 2:

$$K_a = \frac{c\alpha^2}{1-\alpha}, 1.8 \times 10^{-5} = \frac{10^{-6} \times \alpha^2}{1-\alpha}$$

Solving for  $\alpha$ ,  $\alpha = 0.95$

Note that the value of  $\alpha$  is quite high, so it cannot be ignored with respect to 1.

$$\therefore [\text{H}_3\text{O}^+] = c\alpha = 0.95 \times 10^{-6} = 9.5 \times 10^{-7}$$

The  $[\text{H}_3\text{O}^+]$  from acetic acid  $< 10^{-6}$  M, so  $[\text{H}_3\text{O}^+]$  from water should also be considered.

$\therefore (x' + 9.5 \times 10^{-7}) x' = 10^{-14}$  (where  $x'$  is the  $[\text{H}_3\text{O}^+]$  coming from water in the presence of  $10^{-6}$  M  $\text{CH}_3\text{COOH}$ ).

$$x' = 1.04 \times 10^{-8}$$

$$[\text{H}_3\text{O}^+]_T = (9.5 \times 10^{-7} + 1.04 \times 10^{-8}) = 9.6 \times 10^{-7}$$

$$\text{pH} = 6.01.$$

The above illustration shows a need to know when the assumption (that  $\alpha$  is very small compared to 1) is valid and when not. Thus, to calculate the pH of a weak acid, we should proceed as

First calculate the value of  $\alpha$  from the expression  $\alpha = \sqrt{\frac{K_a}{c}}$ .

If this value of  $\alpha$  comes out to be less than or equal to 0.1, then the assumption is valid and  $[\text{H}_3\text{O}^+]$  is calculated using the expression,  $[\text{H}_3\text{O}^+] = \sqrt{K_a \times c}$  but if the  $\alpha$  value obtained from the given expression  $> 1$ , then the assumption is not valid and one has to calculate  $\alpha$  using the expression,  $K_a = \frac{c\alpha^2}{1-\alpha}$  and then calculate  $[\text{H}_3\text{O}^+]$  using the expression,  $[\text{H}_3\text{O}^+] = c\alpha$ .

## IONIC EQUILIBRIUM

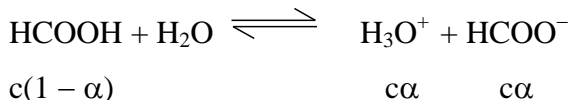
It was suggested that for calculating the pH of weak acid, first calculate  $\alpha$  from the expression,  $\alpha = \sqrt{\frac{K_a}{C}}$  and then compare its value with 0.1. This statement looks a little odd. How can we compare the value of  $\alpha$  (which is obtained after making the assumption) with 0.1 and then claim that it is correct if  $\alpha \leq 0.1$ ? Let us see how the given procedure works.

The actual expression for calculating the value of  $\alpha$  is  $K_a = \frac{c\alpha^2}{1-\alpha}$ . If we make the assumption that  $\alpha$  is very small compared to one and ignore it with respect to 1 in the denominator, we get  $K_a = c\alpha^2$ . By ignoring the  $\alpha$  in the denominator, we increase the value of the denominator. This will consequently increase the value of the numerator (since the ratio is a constant). Thus, the value of  $\alpha$  calculated after the assumption will be greater than the actual value of  $\alpha$ . If this approximated value of  $\alpha$  is less than or equal to 0.1 then it means that the actual value of  $\alpha$  will be even less than 0.1. Therefore, the assumption is valid and if this approximated value of  $\alpha$  is greater than 0.1, then the actual value of  $\alpha$  may be greater than, equal to or less than 0.1. So in the later case, we are unable to predict and so we do not make any assumption and calculate actual value of  $\alpha$  using the expression,  $K_a = \frac{c\alpha^2}{1-\alpha}$ .

### Illustration 5

Formic acid is 4.5% dissociated in 0.1 M solution at 20°C. Calculate the dissociation constant  $K_a$  of the acid at this temperature.

#### Solution:



$$\alpha = 4.5\% = 0.045$$

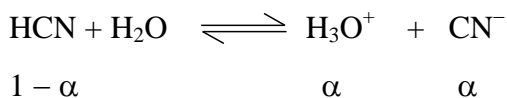
$$K_a = \frac{[\text{H}_3\text{O}^+][\text{HCOO}^-]}{[\text{HCOOH}]} = \frac{c\alpha \times c\alpha}{c(1-\alpha)} = \frac{c\alpha^2}{1-\alpha} = \frac{0.1 \times (0.045)^2}{1-0.045} = \frac{0.1 \times (0.045)^2}{0.955}$$

$$K_a = 2.12 \times 10^{-4}$$

### Illustration 6

Calculate the pH of a 1 M solution of HCN. ( $K_a$  for HCN =  $4.8 \times 10^{-10}$ )

#### Solution:



Let the degree of dissociation of HCN be  $\alpha$ . The equilibrium molar concentrations of HCN,  $\text{H}_3\text{O}^+$  and  $\text{CN}^-$  will be  $1-\alpha$ ,  $\alpha$  and  $\alpha$  respectively.

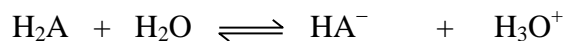
# IONIC EQUILIBRIUM

Let us first calculate  $\alpha$  using  $\alpha = \sqrt{\frac{K_a}{c}} = \sqrt{\frac{4.8 \times 10^{-10}}{1}} = 2.19 \times 10^{-5}$

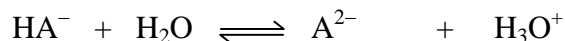
Since,  $\alpha$  is very much smaller than 0.1, so the assumption is valid.  $\therefore [\text{H}_3\text{O}^+] = \alpha = 2.19 \times 10^{-5}$   
 $\text{pH} = -\log 2.19 \times 10^{-5} = \mathbf{4.66}$

## 6.3 pH CALCULATION OF A SOLUTION OF A WEAK DIPROTIC ACID

Let us take a weak diprotic acid ( $\text{H}_2\text{A}$ ) in water whose concentration is  $c$  M. Diprotic acid is the one, which is capable of giving 2 protons in water. In an aqueous solution of a diprotic acid, following equilibria exist.



Conc. at equilib.  $c(1 - \alpha_1) \qquad c\alpha_1(1 - \alpha_2) \qquad (c\alpha_1 + c\alpha_1\alpha_2)$



Conc. at equilib.  $c\alpha_1(1 - \alpha_2) \qquad c\alpha_1\alpha_2 \qquad (c\alpha_1\alpha_2 + c\alpha_1)$

where  $\alpha_1$  is the degree of ionization (dissociation) of  $\text{H}_2\text{A}$  in presence of  $\text{HA}^-$  and  $\alpha_2$  is the degree of ionisation of  $\text{HA}^-$  in presence of  $\text{H}_2\text{A}$ .

For the first equilibrium,

$$(\text{K}_{\text{eq}})_1 [\text{H}_2\text{O}] = \frac{[\text{H}_3\text{O}^+][\text{HA}^-]}{[\text{H}_2\text{A}]} = \text{K}_{a_1}$$

$$\therefore \text{K}_{a_1} = \frac{(c\alpha_1 + c\alpha_1\alpha_2)[c\alpha_1(1 - \alpha_2)]}{c(1 - \alpha_1)} = \frac{[c\alpha_1(1 + \alpha_2)][\alpha_1(1 - \alpha_2)]}{1 - \alpha_1} \quad \dots(\text{i})$$

Similarly, for the second equilibrium,

$$[\text{K}_{\text{eq}}]_2 [\text{H}_2\text{O}] = \frac{[\text{H}_3\text{O}^+][\text{A}^{2-}]}{[\text{HA}^-]} = \text{K}_{a_2}$$

where  $\text{K}_{a_1}$  and  $\text{K}_{a_2}$  represents the first and second ionisation constants of  $\text{H}_2\text{A}$ .

$$\text{K}_{a_2} = \frac{(c\alpha_1 + c\alpha_1\alpha_2)(c\alpha_1\alpha_2)}{c\alpha_1(1 - \alpha_2)} = \frac{[c\alpha_1(1 + \alpha_2)]\alpha_2}{1 - \alpha_2} \quad \dots(\text{ii})$$

Knowing the values of  $\text{K}_{a_1}$ ,  $\text{K}_{a_2}$  and  $c$ , the values of  $\alpha_1$  and  $\alpha_2$  can be calculated using equations (i) and (ii).

After getting the values of  $\alpha_1$  and  $\alpha_2$ ,  $[\text{H}_3\text{O}^+]$  can be calculated as.

$$[\text{H}_3\text{O}^+]_{\text{T}} = c\alpha_1 + c\alpha_1\alpha_2$$

Finally, if the total  $[\text{H}_3\text{O}^+]$  from acid is less than  $10^{-6}$  M, the contribution of  $\text{H}_3\text{O}^+$  from water should be taken into account for calculating pH while if it is  $\geq 10^{-6}$  M, then  $[\text{H}_3\text{O}^+]$  contribution from water can be ignored.

Using this  $[\text{H}_3\text{O}^+]$ , pH of the solution can be calculated.

# IONIC EQUILIBRIUM

## Approximation:

For diprotic acids,  $K_{a_2} \ll K_{a_1}$  and  $\alpha_2$  would be even smaller than  $\alpha_1$ .

$$\therefore 1 - \alpha_2 \approx 1 \text{ and } 1 + \alpha_2 \approx 1$$

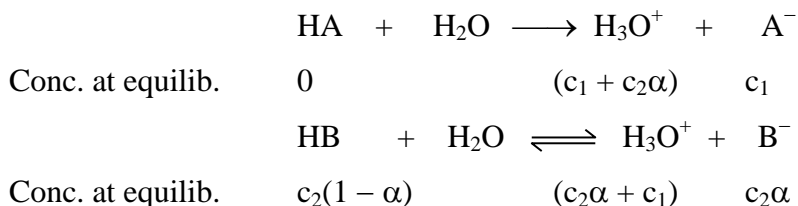
Thus, equation (i) can be reduced to  $K_{a_1} = \frac{c\alpha_1 \times \alpha_1}{1 - \alpha_1}$

This expression is similar to the expression for a weak monoprotic acid. Hence, even for a diprotic acid (or a polyprotic acid) the  $[H_3O^+]$  can be calculated from its first equilibrium constant expression alone provided

$$K_{a_2} \ll K_{a_1}.$$

## 6.4 pH CALCULATION OF SOLUTION OF A MIXTURE OF STRONG ACID AND WEAK ACID (BOTH MONOPROTIC) IN WATER

Let the strong acid and weak acid (both monoprotic) taken are HA and HB respectively and their respective concentrations are  $c_1$  and  $c_2$  M. In the presence of strong acid (HA), the degree of dissociation of weak acid (HB) would be suppressed due to common ion effect. Let the degree of dissociation of HB in presence of HA be  $\alpha$  and its ionisation constant be  $K_a$ . The various equilibria are



For the equilibrium of HB,

$$K_a = \frac{[H_3O^+][B^-]}{[HB]} = \frac{(c_1 + c_2\alpha) c_2\alpha}{c_2(1 - \alpha)}$$

$$\therefore K_a = \frac{(c_1 + c_2\alpha) \alpha}{1 - \alpha} \quad \dots(i)$$

Using the values of  $K_a$ ,  $c_1$  and  $c_2$ ,  $\alpha$  can be calculated from equation (i)

After obtaining the value of  $\alpha$ ,  $[H_3O^+]$  can be calculated as  $[H_3O^+]_T = c_1 + c_2\alpha$ .

Finally, if the total  $[H_3O^+]$  from acid is less than  $10^{-6}$  M, the contribution of  $H_3O^+$  from water should be taken into account for calculating pH while if it is  $\geq 10^{-6}$  M, then  $[H_3O^+]$  contribution from water can be ignored.

Using this  $[H_3O^+]$ , pH of the solution can be calculated.

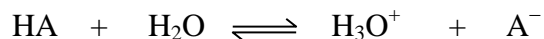
## Approximation:

Calculate  $\alpha' = \sqrt{\frac{K_a}{c_2}}$  (where  $\alpha'$  is the degree of dissociation of HB in absence of HA), if  $\alpha'$  is less than or equal to 0.1, we can ignore  $[H_3O^+]$  from weak acid (HB) and pH can be calculated using strong acid (HA) only.

## IONIC EQUILIBRIUM

### 6.5 pH CALCULATION OF SOLUTION OF A MIXTURE OF TWO WEAK MONOPROTIC ACIDS IN WATER

Let us have two weak monoprotic acids as HA and HB and their concentrations are  $c_1$  and  $c_2$  M respectively. Let their ionisation constants are  $K_{a_1}$  and  $K_{a_2}$  respectively. The degree of dissociation of each would be affected in presence of other due to common ion effect. Let  $\alpha_1$  be the degree of dissociation of HA in presence of HB and  $\alpha_2$  be the degree of dissociation of HB in presence of HA. In an aqueous solution of a mixture of HA and HB, following equilibria exist.



Conc. at equilib.  $c_1(1 - \alpha_1)$   $(c_1\alpha_1 + c_2\alpha_2)$   $c_1\alpha_1$



Conc. at equilib.  $c_2(1 - \alpha_2)$   $(c_2\alpha_2 + c_1\alpha_1)$   $c_2\alpha_2$

$$\therefore K_{a_1} = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} = \frac{(c_1\alpha_1 + c_2\alpha_2) c_1\alpha_1}{c_1(1 - \alpha_1)} = \frac{(c_1\alpha_1 + c_2\alpha_2) \alpha_1}{(1 - \alpha_1)} \quad \dots(i)$$

$$\text{and } K_{a_2} = \frac{[\text{H}_3\text{O}^+][\text{B}^-]}{[\text{HB}]} = \frac{(c_1\alpha_1 + c_2\alpha_2) c_2\alpha_2}{c_2(1 - \alpha_2)} = \frac{(c_1\alpha_1 + c_2\alpha_2) \alpha_2}{(1 - \alpha_2)} \quad \dots(ii)$$

Knowing the values of  $K_{a_1}$ ,  $K_{a_2}$ ,  $c_1$  and  $c_2$ ,  $\alpha_1$  and  $\alpha_2$  can be calculated using equation (i) and (ii). The  $[\text{H}_3\text{O}^+]$  can then be calculated as

$$[\text{H}_3\text{O}^+]_T = c_1\alpha_1 + c_2\alpha_2$$

Finally, if the total  $[\text{H}_3\text{O}^+]$  from acid is less than  $10^{-6}$  M, the contribution of  $\text{H}_3\text{O}^+$  from water should be taken into account for calculating pH while if it is  $\geq 10^{-6}$  M, then  $[\text{H}_3\text{O}^+]$  contribution from water can be ignored.

Using this  $[\text{H}_3\text{O}^+]$ , pH of the solution can be calculated.

#### Approximation:

If the ionisation constant of one acid (say HA) is very much greater than the ionisation constant of other weak acid (HB) i.e.,  $K_{a_1} \gg K_{a_2}$ , then the contribution to the total  $[\text{H}_3\text{O}^+]$  is made largely by HA and HB's contribution would be very small and can be ignored.

Thus,  $(c_1\alpha_1 + c_2\alpha_2) \approx c_1\alpha_1$

Therefore, equation (i) can be reduced to

$$K_{a_1} = \frac{c_1\alpha_1^2}{1 - \alpha_1}$$

This is an expression similar to the expression for a weak monoprotic acid. Hence, even for a diprotic acid (or a polyprotic acid) the  $[\text{H}_3\text{O}^+]$  can be calculated from its first equilibrium constant expression alone provided

$$K_{a_2} \ll K_{a_1}.$$

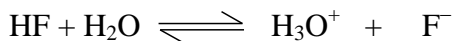


## IONIC EQUILIBRIUM

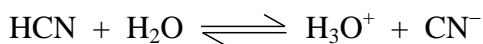
### Illustration 7

At 25°C, the dissociation constants of HCN and HF are  $4.0 \times 10^{-10}$  and  $6.7 \times 10^{-4}$ . Calculate the pH of a mixture of 0.1 M HF and 0.1 M HCN.

### Solution:



$$0.1 - x \quad (x+y) \quad x$$



$$0.1 - y \quad (x+y) \quad y$$

$$K_a(\text{HF}) = \frac{[\text{H}_3\text{O}^+][\text{F}^-]}{[\text{HF}]} = \frac{(x+y)x}{(0.1-x)}$$

$$K_a(\text{HCN}) = \frac{[\text{H}_3\text{O}^+][\text{CN}^-]}{[\text{HCN}]} = \frac{(x+y)y}{(0.1-y)}$$

Since,  $K_a(\text{HCN}) \ll K_a(\text{HF})$ , the  $[\text{H}_3\text{O}^+]$  from HCN can be ignored with respect to  $[\text{H}_3\text{O}^+]$  from HF.

$$\therefore [\text{H}_3\text{O}^+] \simeq x$$

$$\therefore K_a(\text{HF}) = \frac{x^2}{0.1 - x}$$

$x$  can also be ignored with respect to 0.1 since  $\alpha = \sqrt{\frac{6.7 \times 10^{-4}}{0.1}} = 0.081$ , is less than 0.1.

$$\therefore K_a(\text{HF}) = 6.7 \times 10^{-4} = \frac{x^2}{0.1}$$

$$\therefore x = 8.18 \times 10^{-3}$$

We can check the assumption (of ignoring  $\text{H}_3\text{O}^+$  from HCN) by putting this value of  $x$  in the expression of  $K_a(\text{HCN})$ .

$$K_a(\text{HCN}) = \frac{x \times y}{0.1 - y}$$

$y$  can also be ignored with respect to 0.1 as  $\alpha = \sqrt{\frac{4 \times 10^{-10}}{0.1}} = 6.32 \times 10^{-5}$ , is far less than 0.1.

$$\therefore K_a(\text{HCN}) = \frac{(8.18 \times 10^{-3}) \times y}{0.1} = 4 \times 10^{-10}$$

$$\therefore y = 4.89 \times 10^{-9}$$

# IONIC EQUILIBRIUM

We can see that  $y$  is very small as compared to  $x$ , so our assumption was correct.

$$\therefore \text{pH} = -\log [\text{H}_3\text{O}^+] = -\log 8.18 \times 10^{-3} = \mathbf{2.08}$$

## 6.6 pH CALCULATION OF BASES

The pH calculation of bases involves similar methods as we have done for acids. In these cases, instead of  $\text{H}_3\text{O}^+$ , we will first calculate  $\text{OH}^-$  (using  $K_b$ 's, concentrations etc) and then pOH. Now pH is calculated using  $\text{pH} + \text{pOH} = \text{p}K_w = 14$ .

For calculating pH of bases, remember that  $[\text{OH}^-]$  from water needs to be considered only if the  $[\text{OH}^-]$  from base is  $< 10^{-6} \text{ M}$  and if  $[\text{OH}^-]$  from base is  $\geq 10^{-6} \text{ M}$ , the  $[\text{OH}^-]$  from water can be ignored.

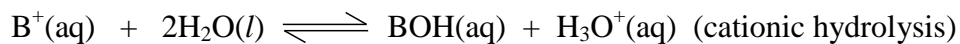
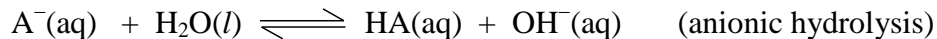
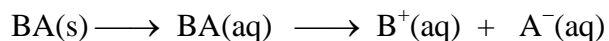
For weak bases, first calculate the value of  $\alpha$  from the expression  $\alpha = \sqrt{\frac{K_b}{c}}$ . If this value of  $\alpha$  comes out to be

less than or equal to 0.1, then the assumption is valid and  $[\text{OH}^-]$  is calculated using the expression,  $[\text{OH}^-] = \sqrt{K_b \times c}$  but if the  $\alpha$  value obtained from the given expression  $> 1$ , then the assumption is not valid and one has

to calculate  $\alpha$  using the expression,  $K_b = \frac{c\alpha^2}{1-\alpha}$  and then calculate  $[\text{OH}^-]$  using the expression,  $[\text{OH}^-] = c\alpha$ .

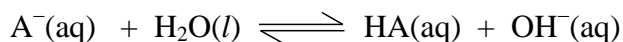
## 7. SALT HYDROLYSIS

When a salt is added to water, the solid salt first dissolves to form aqueous salt, which then dissociate into ions. The dissociation of the salt is always taken 100% unless and otherwise mentioned in the problem. The ions of the salt then may or may not react with water. The cations when react with water, always produces  $\text{H}_3\text{O}^+$  ions and anion on reaction with water always produces  $\text{OH}^-$  ions. Depending upon the extent of hydrolysis and the amount of  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$  in the solution, the solution behaves acidic or alkaline or neutral. Let the salt be represented as BA.



### 7.1 ANIONIC HYDROLYSIS

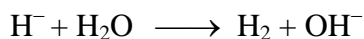
Anions can function as a base on reaction with water and hydrolyze as follows:



The extent of hydrolysis of a given anion depends on its basic strength.

#### (a) Complete hydrolysis

The anions, which are stronger base than  $\text{OH}^-$  and the conjugate acids of the anions are weaker acid than  $\text{H}_2\text{O}$ , they will show complete hydrolysis in aqueous medium. For example,



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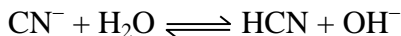
# IONIC EQUILIBRIUM

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## (b) Hydrolysis to a limited extent

The anions, which are weaker base than  $\text{OH}^-$  and the conjugate acids are stronger acid than  $\text{H}_2\text{O}$  but weaker acid than  $\text{H}_3\text{O}^+$  will hydrolyse to a limited extent in aqueous medium.

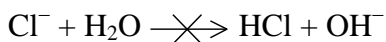
For example,



Other examples are  $\text{CH}_3\text{COO}^-$ ,  $\text{NO}_2^-$ ,  $\text{S}^{2-}$  etc.

## (c) No hydrolysis

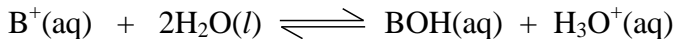
The anions that are weaker base than  $\text{OH}^-$  and the conjugate acids are stronger than both  $\text{H}_2\text{O}$  and  $\text{H}_3\text{O}^+$  do not hydrolyse at all.



Other examples include  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{ClO}_4^-$  etc.

## 7.2 CATIONIC HYDROLYSIS

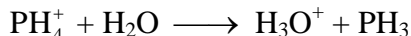
Cations can function as acid on reaction with water and hydrolyze as follows:



The extent of hydrolysis of a given cation depends on its acidic strength.

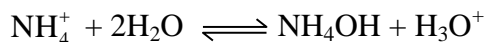
### (a) Complete hydrolysis

The cations, which are stronger acid than  $\text{H}_3\text{O}^+$  and their conjugate bases are very much weaker than  $\text{H}_2\text{O}$  will show complete hydrolysis. Example is  $\text{PH}_4^+$  ion.



### (b) Hydrolysis to a limited extent

The cations, which are weaker acid than  $\text{H}_3\text{O}^+$  ion and their conjugate bases are stronger than  $\text{H}_2\text{O}$  but weaker than  $\text{OH}^-$ , show hydrolysis to a limited extent. For example,



Other ions showing hydrolysis to limited extent are  $\text{C}_6\text{H}_5\text{NH}_3^+$ ,  $\text{CH}_3\text{NH}_3^+$  etc.

### (c) No hydrolysis

The cations, which are weaker acid than  $\text{H}_3\text{O}^+$  and their conjugate bases are stronger than both  $\text{H}_2\text{O}$  and  $\text{OH}^-$  do not hydrolyze at all. Example is alkali and alkaline earth metal ions.



There are four types of salt.

- (i) Salt of strong acid and weak base
- (ii) Salt of weak acid and strong base

## IONIC EQUILIBRIUM

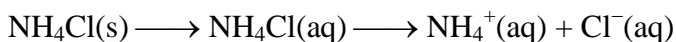
(iii) Salt of weak acid and weak base

(iv) Salt of strong acid and strong base

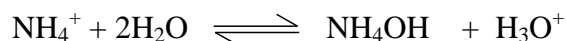
Salts of first three type undergoes hydrolysis and the salt of fourth type do not undergo any hydrolysis.

### 7.3 SALT OF A STRONG ACID AND WEAK BASE

Let us take a salt,  $\text{NH}_4\text{Cl}$ . It is a salt made from the reaction of strong acid,  $\text{HCl}$  and weak base,  $\text{NH}_4\text{OH}$ .



Out of  $\text{NH}_4^+$  and  $\text{Cl}^-$ , only  $\text{NH}_4^+$  ion hydrolyses and let its degree of hydrolysis be  $h$  and  $K_h$  be its hydrolysis constant. Let 'c' M be the concentration of the salt, so the concentration of  $\text{NH}_4^+$  would also be 'c' M.



Initial conc.	c	0	0
Conc. at equilb.	$c(1 - h)$	ch	ch

$$K_{\text{eq}} = \frac{[\text{NH}_4\text{OH}][\text{H}_3\text{O}^+]}{[\text{H}_2\text{O}]^2 [\text{NH}_4^+]}$$

$$K_{\text{eq}} [\text{H}_2\text{O}]^2 = \frac{[\text{NH}_4\text{OH}][\text{H}_3\text{O}^+]}{[\text{NH}_4^+]} = K_h \dots\dots(i)$$

Multiplying numerator and denominator of equation (i) by  $\text{OH}^-$  gives

$$\frac{[\text{NH}_4\text{OH}][\text{H}_3\text{O}^+][\text{OH}^-]}{[\text{NH}_4^+][\text{OH}^-]} = K_h$$

$$\therefore K_h = \frac{K_w}{K_b} \quad (\text{since } [\text{H}_3\text{O}^+][\text{OH}^-] = K_w \text{ and } \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_4\text{OH}]} = K_b)$$

$$K_h = \frac{K_w}{K_b} = \frac{ch \times ch}{c(1-h)} = \frac{ch^2}{1-h}$$

Assuming  $h$  to be smaller than 0.1, it can be ignored with respect to 1. So,  $1 - h \simeq 1$ .

$$K_h \approx ch^2$$

$$h = \sqrt{\frac{K_h}{c}} = \sqrt{\frac{K_w}{K_b \times c}}$$

$$\therefore [\text{H}_3\text{O}^+] = ch = c \times \sqrt{\frac{K_w}{K_b \times c}} = \sqrt{\frac{K_w \times c}{K_b}}$$

Taking log of both the sides

$$\log [\text{H}_3\text{O}^+] = \frac{1}{2} \log K_w + \frac{1}{2} \log c - \frac{1}{2} \log K_b$$

## IONIC EQUILIBRIUM

Multiplying both sides by  $-1$ ,

$$-\log [\text{H}_3\text{O}^+] = -\frac{1}{2} \log K_w - \frac{1}{2} \log c + \frac{1}{2} \log K_b$$

$$\therefore \text{pH} = \frac{1}{2} \text{p}K_w - \frac{1}{2} \text{p}K_b - \frac{1}{2} \log c = \frac{1}{2} (\text{p}K_w - \text{p}K_b - \log c)$$

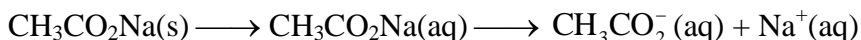
(since,  $-\log K_w = \text{p}K_w$  and  $\log K_b = -\text{p}K_b$ )

$$\therefore \text{pH} = 7 - \frac{1}{2} \text{p}K_b - \frac{1}{2} \log c$$

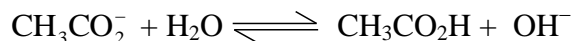
Since, two terms are to be subtracted from 7, so, the pH of such salt solutions would be less than 7 and will behave acidic in nature. 'c' in the above expression represents concentration of the ion undergoing hydrolysis and not the concentration of the salt.

### 7.4 SALT OF WEAK ACID AND A STRONG BASE

Let us take a salt,  $\text{CH}_3\text{CO}_2\text{Na}$ . It is a salt made from the reaction of weak acid,  $\text{CH}_3\text{CO}_2\text{H}$  and strong base,  $\text{NaOH}$ .



Out of  $\text{CH}_3\text{CO}_2^-$  and  $\text{Na}^+$ , only  $\text{CH}_3\text{CO}_2^-$  ion hydrolyses and let its degree of hydrolysis be  $h$  and  $K_h$  be its hydrolysis constant. Let 'c' M be the concentration of the salt, so the concentration of  $\text{CH}_3\text{CO}_2^-$  would also be 'c'M.



Initial conc.	c	0	0
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Conc. at equilib.	$c(1-h)$	ch	ch
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$$K_{\text{eq}} = \frac{[\text{CH}_3\text{CO}_2\text{H}][\text{OH}^-]}{[\text{H}_2\text{O}][\text{CH}_3\text{CO}_2^-]}$$

$$K_{\text{eq}} [\text{H}_2\text{O}] = \frac{[\text{CH}_3\text{CO}_2\text{H}][\text{OH}^-]}{[\text{CH}_3\text{CO}_2^-]} = K_h \quad \dots\dots(i)$$

Multiplying numerator and denominator of equation (i) by  $\text{H}_3\text{O}^+$  gives

$$\frac{[\text{CH}_3\text{CO}_2\text{H}][\text{OH}^-][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{CO}_2^-][\text{H}_3\text{O}^+]} = K_h$$

$$\therefore K_h = \frac{K_w}{K_a} \text{ (since } [\text{H}_3\text{O}^+][\text{OH}^-] = K_w \text{ and } \frac{[\text{CH}_3\text{CO}_2^-][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{CO}_2\text{H}]} = K_a \text{)}$$

$$K_h = \frac{K_w}{K_a} = \frac{ch \times ch}{c(1-h)} = \frac{ch^2}{1-h}$$

Assuming  $h$  to be smaller than 0.1, it can be ignored with respect to 1. So,  $1-h \simeq 1$ .

# IONIC EQUILIBRIUM

$$K_h \approx ch^2$$

$$h = \sqrt{\frac{K_h}{c}} = \sqrt{\frac{K_w}{K_a \times c}}$$

$$\therefore [\text{OH}^-] = ch = c \times \sqrt{\frac{K_w}{K_a \times c}} = \sqrt{\frac{K_w \times c}{K_a}}$$

$$\therefore [\text{H}_3\text{O}^+] = \frac{K_w}{[\text{OH}^-]} = K_w \times \sqrt{\frac{K_a}{K_w \times c}} = \sqrt{\frac{K_w \times K_a}{c}}$$

Taking log of both the sides

$$\log [\text{H}_3\text{O}^+] = \frac{1}{2} \log K_w + \frac{1}{2} \log K_a - \frac{1}{2} \log c$$

Multiplying both sides by  $-1$ ,

$$-\log [\text{H}_3\text{O}^+] = -\frac{1}{2} \log K_w - \frac{1}{2} \log K_a + \frac{1}{2} \log c$$

$$\therefore \text{pH} = \frac{1}{2} \text{p}K_w + \frac{1}{2} \text{p}K_a + \frac{1}{2} \log c = \frac{1}{2} (\text{p}K_w + \text{p}K_a + \log c)$$

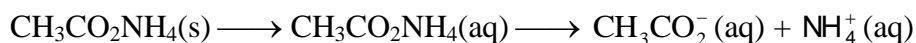
$$(\text{since, } -\log K_w = \text{p}K_w \text{ and } -\log K_a = \text{p}K_a)$$

$$\therefore \text{pH} = 7 + \frac{1}{2} \text{p}K_a + \frac{1}{2} \log c$$

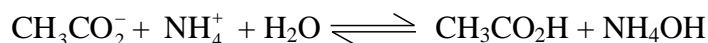
Since, two terms are to be added to 7, so, the pH of such salt solutions would be more than 7 and will behave alkaline in nature. 'c' in the above expression represents concentration of the ion undergoing hydrolysis and not the concentration of the salt.

## 7.5 SALT OF WEAK ACID AND WEAK BASE

Let us take a salt,  $\text{CH}_3\text{CO}_2\text{NH}_4$ . It is a salt made from the reaction of weak acid,  $\text{CH}_3\text{CO}_2\text{H}$  and weak base,  $\text{NH}_4\text{OH}$ .



Out of  $\text{CH}_3\text{CO}_2^-$  and  $\text{NH}_4^+$ , both the ions hydrolyses and let their degree of hydrolysis be h and  $K_h$  be the hydrolysis constant of salt. Let 'c' M be the concentration of the salt, so the concentration of  $\text{CH}_3\text{CO}_2^-$  and  $\text{NH}_4^+$  would also be 'c'M.



Initial conc.	c	c	0	0
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Conc. at equilb.	$c(1 - h)$	$c(1 - h)$	ch	ch
------------------	------------	------------	----	----

$$K_{\text{eq}} = \frac{[\text{CH}_3\text{CO}_2\text{H}][\text{NH}_4\text{OH}]}{[\text{H}_2\text{O}][\text{CH}_3\text{CO}_2^-][\text{NH}_4^+]}$$

## IONIC EQUILIBRIUM

$$K_{eq} [H_2O] = \frac{[CH_3CO_2H][NH_4OH]}{[CH_3CO_2^-][NH_4^+]} = K_h \quad \dots\dots(i)$$

Multiplying numerator and denominator of equation (i) by  $H_3O^+$  and  $OH^-$  gives

$$\frac{[CH_3CO_2H][NH_4OH][H_3O^+][OH^-]}{[CH_3CO_2^-][NH_4^+][H_3O^+][OH^-]} = K_h$$

$$\therefore K_h = \frac{K_w}{K_a \times K_b} \quad (\text{since } [H_3O^+][OH^-] = K_w, \quad \frac{[CH_3CO_2^-][H_3O^+]}{[CH_3CO_2H]} = K_a$$

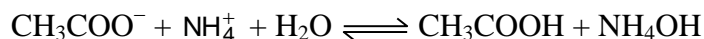
$$\text{and } \frac{[NH_4^+][OH^-]}{[NH_4OH]} = K_b)$$

Substituting the concentration terms,

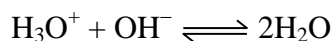
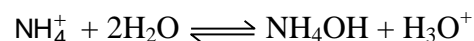
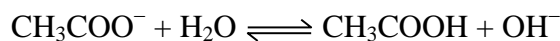
$$K_h = \frac{K_w}{K_a \times K_b} = \frac{ch \times ch}{c(1-h) \times c(1-h)} = \frac{h^2}{(1-h)^2}$$

$$\therefore \frac{h}{1-h} = \sqrt{\frac{K_w}{K_a \times K_b}}$$

Before moving further, let us clarify the assumption we have made here. In this case, we have assumed that both the ions (i.e., cation and anion) get hydrolysed to produce a weak acid and a weak base (hence, we can't straight away predict whether the solution is acidic, basic or neutral). Here, we have considered the degree of hydrolysis of both the ions to be same. Now we present an explanation as to why this is correct and then state reasons for the validity of this assumption. Actually the hydrolysis reaction given earlier,



is made up of the following three reactions,



If we add these three reactions, the net reaction is the one stated previously. This suggests that both  $CH_3COO^-$  and  $NH_4^+$  get hydrolysed independently and their hydrolysis depends on:

(i) their initial concentration and (ii) the value of  $K_h$ , which is  $\frac{K_w}{K_a}$  for  $CH_3COO^-$  and  $\frac{K_w}{K_b}$  for  $NH_4^+$ . Since both the ions were produced from the same salt, their initial concentrations are same. Therefore unless and until the value of  $\frac{K_w}{K_a}$  and  $\frac{K_w}{K_b}$  or  $K_a$  and  $K_b$  are same, the degree of hydrolysis of the two ions cannot be same.

## IONIC EQUILIBRIUM

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To explain why this assumption is valid, we need to now look at the third reaction, i.e., combination of  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$  ions. It is obvious that this reaction happens only because one reaction produced  $\text{H}_3\text{O}^+$  ion and the other produced  $\text{OH}^-$  ions. We can also note that this reaction causes both the hydrolysis reaction to occur more since their product ions are being consumed. Keep this thing in mind that the ***equilibrium, which has smaller value of equilibrium constant, is affected more by the common ion effect.*** For the same reason if for any reason a reaction is made to occur to a greater extent by the consumption of any one of the product ions, the reaction with the smaller value of equilibrium constant tends to get affected more.

Therefore, we conclude that the hydrolysis of both the ions occurs more in the presence of each other (due to the consumption of the product ions) than in each other's absence as well as the hydrolysis of the ion which occurs to lesser extent (due to smaller value of  $K_h$ ) is affected more than the one whose  $K_h$  is greater. Hence, we can conclude that the ***degree of hydrolysis of both the ions would be close to each other in magnitude when they are hydrolysed in the presence of each other.***

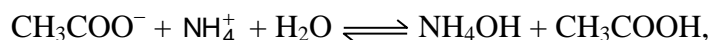
Now, in order to calculate the pH of this solution, we need to understand one more principle. Let us assume that we have an aqueous solution of  $\text{CH}_3\text{COOH}$ . Let us also assume that we do not know whether  $\text{CH}_3\text{COO}^-$  and  $\text{H}_3\text{O}^+$  are in the solution or not (even though  $\text{H}_3\text{O}^+$  would be there since the solution is aqueous). We can see that the reaction quotient,  $Q$  for the reaction,



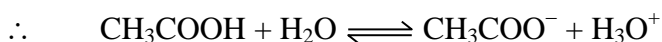
is zero (if we assume no  $\text{CH}_3\text{COO}^-$  or  $\text{H}_3\text{O}^+$ ).

Therefore,  $Q < K_a$ . The reaction would therefore move forward to reach equilibrium. The same is true when  $\text{CH}_3\text{COO}^-$  and  $\text{H}^+$  are present without  $\text{CH}_3\text{COOH}$ . Hence, we conclude, ***“Any equilibrium that can exist (i.e., when all reactants and / or all products are present) will exist (except when pure solids or pure liquids are not present)”.*** In case of pure solids or pure liquids, the above statement will not be true.

As can be seen in the hydrolysis reaction,



$\text{CH}_3\text{COOH}$  is present in the solution. This implies that the equilibrium between  $\text{CH}_3\text{COOH}$ ,  $\text{CH}_3\text{COO}^-$  and  $\text{H}_3\text{O}^+$  can exist and therefore would exist.



In fact, the equilibrium between  $\text{NH}_4\text{OH}$ ,  $\text{NH}_4^+$  and  $\text{OH}^-$  also exists.

Now, the pH of the solution can be calculated using acetic acid equilibrium as,



ch

c (1 - h)

$$K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{COOH}]} = \frac{c(1-h)[\text{H}_3\text{O}^+]}{ch}$$

$$\therefore [\text{H}_3\text{O}^+] = K_a \times \left( \frac{h}{1-h} \right)$$



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Substituting  $\frac{h}{1-h}$  as  $\sqrt{\frac{K_w}{K_a K_b}}$

$$[H_3O^+] = K_a \times \left( \frac{h}{1-h} \right) = K_a \times \sqrt{\frac{K_w}{K_a K_b}} = \sqrt{\frac{K_w K_a}{K_b}}$$

$$pH = -\log [H_3O^+] = -\log \sqrt{\frac{K_w \times K_a}{K_b}}$$

Taking log of both the sides, gives

$$\log [H_3O^+] = \frac{1}{2} \log K_w + \frac{1}{2} \log K_a - \frac{1}{2} \log K_b$$

Multiplying both sides by  $-1$ ,

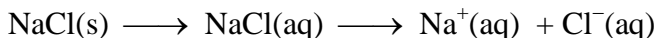
$$-\log [H_3O^+] = -\frac{1}{2} \log K_w - \frac{1}{2} \log K_a + \frac{1}{2} \log K_b$$

$$pH = \frac{1}{2} pK_w + \frac{1}{2} pK_a - \frac{1}{2} pK_b = \frac{1}{2} (pK_w + pK_a - pK_b)$$

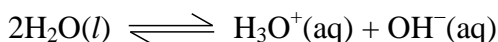
**Note:** If  $K_a > K_b$  the solution is acidic, if  $K_a < K_b$  the solution will be basic and if  $K_a = K_b$  the solution will be neutral.

### 7.6 SALT OF A STRONG ACID AND A STRONG BASE

Let us consider a salt, NaCl made by the reaction of strong acid, HCl and strong base, NaOH.



Neither of the two ions of the salt undergoes hydrolysis. So, the solution contains only the equilibrium of ionization of water.



Thus, the pH of such salts always remain constant and the solution behaves neutral at  $pH = 7$  at  $25^\circ C$

## 8. BUFFER SOLUTIONS

There are various ways of changing the pH of a solution. One could add an acid, base or just water to a solution and change its pH. The original solution could be that of an acid, base or a salt solution. The pH change would correspond to the amount of  $H^+$  or  $OH^-$  added. In case of addition of water, the concentration of  $H^+$  changes due to change in volume. However, there are certain type of solutions where the pH change is small compared to the addition of acid or base. Such solutions are called **Buffer Solutions**.

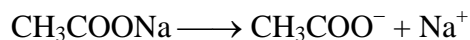
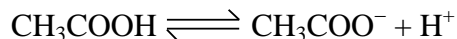
Buffer Solutions are those, which resist a change in pH upon addition of small amount of acid or base. This does not mean that the pH will not change, and all it means is that the pH change would be less than the change that would have occurred had it not been a buffer.

## IONIC EQUILIBRIUM

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There are various types of buffers: (i) Buffer of weak acid and its salt with a strong base; (ii) buffer of a weak base and its salt with a strong acid; (iii) the solution of the salt of a weak acid and a weak base.

To understand the working of a buffer, let us first take the example of a buffer made of a weak acid and its salt with a strong base. Let the acid be  $\text{CH}_3\text{COOH}$  and the salt be  $\text{CH}_3\text{COONa}$ . Let 20 mole of each be present originally in the solution. The reactions that would occur in the solution are:



We can assume that only the salt contributes  $\text{CH}_3\text{COO}^-$  ions and the  $\text{CH}_3\text{COO}^-$  ions from salt would decrease the dissociation of acetic acid (due to common ion effect). Therefore we can also assume that the entire acid remains undissociated. So we have 20 mole of  $\text{CH}_3\text{COO}^-$  and 20 mole of  $\text{CH}_3\text{COOH}$ .

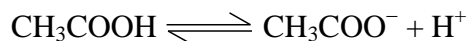
Now, if we add 10 mol of  $\text{H}^+$  to this solution, it would react with 10 mol of  $\text{CH}_3\text{COO}^-$  and convert it into 10 mol of  $\text{CH}_3\text{COOH}$ . This reaction goes to completion because the equilibrium constant for the reaction,  $\text{CH}_3\text{COO}^- + \text{H}^+ \longrightarrow \text{CH}_3\text{COOH}$  is very high ( $K_a^{-1}$ ). This means that all the  $\text{H}^+$  added from outside disappears. Then 10 mol of  $\text{CH}_3\text{COOH}$  formed would dissociate further. But the dissociation of  $\text{CH}_3\text{CO}_2\text{H}$  would be very little because it is a weak acid (weak acids dissociate to a very small extent) and moreover due to the common ion effect created by the 10 mol  $\text{CH}_3\text{COO}^-$  (left behind), the dissociation would be further diminished. Therefore, 10 mol of produced  $\text{CH}_3\text{COOH}$  dissociates to give a very small amount of  $\text{H}^+$ , which is very small compared to the amount initially added. Consequently, the pH changes by a small value.

If we had added 10 mol of  $\text{OH}^-$  instead of  $\text{H}^+$ , it would have reacted with 10 mol of  $\text{CH}_3\text{COOH}$  and converted it into 10 mol of  $\text{CH}_3\text{COO}^-$  &  $\text{H}_2\text{O}$ . This reaction also goes to completion because the equilibrium constant for the reaction,  $\text{CH}_3\text{COOH} + \text{OH}^- \longrightarrow \text{CH}_3\text{COO}^- + \text{H}_2\text{O}$  is very high ( $K_b^{-1}$ ). This means that all the  $\text{OH}^-$  added from outside disappears. Then 10 mol of  $\text{CH}_3\text{COO}^-$  formed would hydrolyze further. But its hydrolysis occurs to a very little extent because the equilibrium constant for hydrolysis is very small and moreover due to the common ion effect (may be we should call it common 'mass effect'!) created by the 10 mol  $\text{CH}_3\text{COOH}$  (left behind), the dissociation would be further diminished. Therefore, 10 mol of produced  $\text{CH}_3\text{COO}^-$  hydrolyses to give a very small amount of  $\text{OH}^-$ , which is very small compared to the amount initially added. Consequently, the pH changes by a small value.

It should be clearly understood that the reason a buffer is able to resist change in pH is because on adding  $\text{H}^+$ , the solution consumes it to produce a weak acid and on adding  $\text{OH}^-$ , the solution produces a weak base. And since the produced weak acid or weak base give lesser amounts of  $\text{H}^+$  or  $\text{OH}^-$  ions than from which they were produced, it eventually leads to a small pH change.

A similar explanation would work for the buffer made by a weak base and its salt with a strong acid. In the case of a solution of salt of weak acid and weak base, say for example  $\text{CH}_3\text{COONH}_4$ , the ions produced in solution are  $\text{CH}_3\text{COO}^-$  and  $\text{NH}_4^+$ . On adding  $\text{H}^+$ ,  $\text{CH}_3\text{COO}^-$  reacts with it to form  $\text{CH}_3\text{COOH}$  and on adding  $\text{OH}^-$ ,  $\text{NH}_4^+$  reacts with it to form  $\text{NH}_4\text{OH}$ . Therefore on adding  $\text{H}^+$ , the solution consumes it to produce a weak acid and on adding  $\text{OH}^-$  the solution produces a weak base.

We shall now calculate the pH of a buffer solution made up of a weak acid and its salt with a strong base. This can be as follow



## IONIC EQUILIBRIUM

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$$K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{CO}_2\text{H}]} = \frac{[\text{Salt}][\text{H}^+]}{[\text{Acid}]}$$

$$[\text{H}^+] = K_a \times \frac{[\text{Acid}]}{[\text{Salt}]}$$

Taking log of both sides,

$$\log [\text{H}^+] = \log K_a + \log \frac{[\text{Acid}]}{[\text{Salt}]}$$

Multiplying both sides by  $-1$ ,

$$-\log [\text{H}^+] = -\log K_a - \log \frac{[\text{Acid}]}{[\text{Salt}]}$$

$$\therefore \text{pH} = \text{p}K_a + \log \frac{[\text{Salt}]}{[\text{Acid}]}$$

This is known as the Henderson's equation of a buffer.

For a buffer made up of weak base and its salt with a strong acid the Henderson's equation looks like this:

$$\text{pOH} = \text{p}K_b + \log \frac{[\text{Salt}]}{[\text{Base}]}$$

### 8.1 BUFFER CAPACITY

It is defined as the amount of a strong acid or strong base required to change the pH of a buffer by one unit. Let there be a buffer solution of volume 1 L with 'b' mole of salt and 'a' mol of salt + acid. The pH of the buffer would be given by

$$\text{pH} = \text{p}K_a + \log \frac{b}{a-b}$$

On adding 'x' mol of a strong acid (monobasic), the pH changes to  $\text{pH}' = \text{p}K_a + \log \frac{b-x}{(a-b+x)}$ .

$$\therefore \Delta \text{pH} = \log \frac{b}{a-b} - \log \frac{b-x}{(a-b+x)}$$

$$\Delta \text{pH} = \log \left[ \frac{b}{a-b} \times \frac{(a-b+x)}{(b-x)} \right] = \frac{1}{2.303} \ln \left[ \frac{b}{a-b} \times \frac{(a-b+x)}{(b-x)} \right]$$

Differentiating with respect to x we get

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## IONIC EQUILIBRIUM

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$$\frac{d\Delta pH}{dx} = \frac{1}{\frac{b}{(a-b)} \times \left( \frac{a-b+x}{b-x} \right)} \times \frac{b}{a-b} \times \frac{[(b-x) \times 1 - (a-b+x) \times -1]}{(b-x)^2} \times \frac{1}{2.303}$$
$$= \frac{a}{(a-b+x)(b-x)2.303}$$

Taking the inverse

$\frac{dx}{d\Delta p} = \frac{(a-b+x)(b-x)2.303}{a}$ . This is defined as buffer capacity. It is the ratio of the small amount of acid or base added to the change in pH caused in the buffer.

### 8.2 MAXIMUM BUFFER CAPACITY

It can be proved that the maximum buffer capacity is achieved when the salt and acid or base concentration is equal.

Differentiating buffer capacity with respect to 'b', the amount of salt present in the and equating it to zero, gives

$$\frac{d}{db} \left( \frac{dx}{d\Delta p} \right) = \frac{2.303}{a} \times [-1 \times (b-x)] + [1 \times (a-b+x)] = 0$$

$a - 2b + 2x = 0$ ; since  $x$  is very small we ignore  $2x$  and we get

$$a - 2b = 0$$

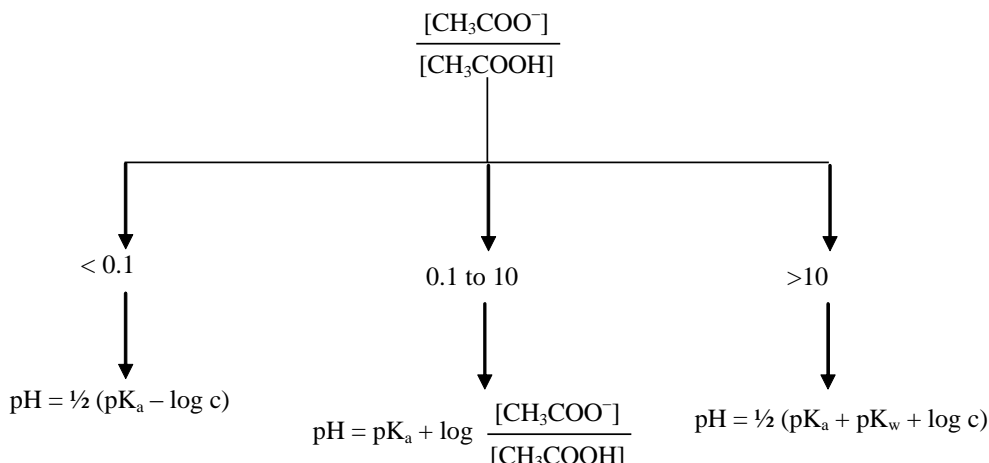
$$\therefore b = a/2$$

The buffer shows maximum buffer capacity when the amount of acid or base and the salt are same.

### 8.3 USE OF VARIOUS RELATIONS

Let us consider three situations. (i) a solution of  $\text{CH}_3\text{COOH}$  (ii) a solution of  $\text{CH}_3\text{COONa}$  and (iii) a solution of  $\text{CH}_3\text{COOH}$  and  $\text{CH}_3\text{COONa}$  (buffer). In all the three solutions, there will be some  $\text{CH}_3\text{COO}^-$  and  $\text{CH}_3\text{COOH}$ . But the relations used for calculating the pH differs. For (i), the relation used is :  $\text{pH} = \frac{1}{2} (\text{pK}_a - \log c)$ ; for (ii), the relation used is:  $\frac{1}{2} (\text{pK}_w + \text{pK}_a + \log c)$  and for (iii), the relation used is  $\text{pH} = \text{pK}_a + \log \frac{[\text{Salt}]}{[\text{Acid}]}$ . To understand as to when a particular relation is to be used, the following chart should be kept in mind.

# IONIC EQUILIBRIUM



Although it is difficult to give an exact limit up to which a buffer can be used, it is generally accepted that a buffer solution can be used for practical purposes when its [Salt]/[Acid] lies within the range of 0.1 to 10 (as shown above).

Therefore, it can be concluded that a particular weak acid (or base) can be employed for making useful buffer solution of pH (or pOH) lying within the range of  $(\text{pK}_a \pm 1)$  or  $(\text{pK}_b \pm 1)$ . For example, acetic acid ( $\text{pK}_a = 4.75$  at  $25^\circ\text{C}$ ) and sodium acetate mixture can be used for preparing buffer solutions whose pH values are roughly in the range of 3.75 to 5.75. Outside this range, the buffer capacity of acetic acid–sodium acetate solution is too small to be used for any practical purpose.

## Illustration 8

$\text{CH}_3\text{COOH}$  (50 ml, 0.1 M) is titrated against 0.1 M NaOH solution. Calculate the pH after the addition of 0 ml, 10 ml, 20 ml, 25 ml, 40 ml, 50 ml and 60 ml of NaOH.  $K_a$  of  $\text{CH}_3\text{COOH}$  is  $2 \times 10^{-5}$ .

### Solution:

(i) When 0 ml of NaOH is added, the pH calculation should be done due to acetic acid only.

$$\therefore [\text{H}^+] = \sqrt{K_a \times c} = \sqrt{2 \times 10^{-5} \times 0.1} = \sqrt{2 \times 10^{-6}}$$

$$\text{pH} = -\log \sqrt{2 \times 10^{-6}} = -\frac{1}{2} [\log 2 - 6] = 3 - 0.15 = \mathbf{2.85}$$

(ii) When 10 ml of NaOH is added, it reacts with  $\text{CH}_3\text{COOH}$  to produce salt,  $\text{CH}_3\text{CO}_2\text{Na}$  and water. Some  $\text{CH}_3\text{CO}_2\text{H}$  would be left behind and  $\text{CH}_3\text{CO}_2\text{Na}$  is produced. So, the solution is that of an acidic buffer.

$$\therefore \text{pH} = \text{pK}_a + \log \frac{[\text{Salt}]}{[\text{Acid}]} = 4.699 + \log \frac{10 \times 0.1}{(50 \times 0.1) - (10 \times 0.1)} = 4.699 + \log \frac{1}{4} = \mathbf{4.0969}$$

(iii) When 20 ml of NaOH is added,

$$\text{pH} = \text{pK}_a + \log \frac{20 \times 0.1}{(50 \times 0.1) - (20 \times 0.1)} = 4.699 + \log \frac{2}{3} = \mathbf{4.5229}$$

(iv) When 25 ml of NaOH is added,

## IONIC EQUILIBRIUM

$$\text{pH} = 4.699 + \log \frac{25 \times 0.1}{(50 \times 0.1) - (25 \times 0.1)} = 4.699$$

(v) When 40 ml of NaOH is added,

$$\text{pH} = 4.699 + \log \frac{40 \times 0.1}{(50 \times 0.1) - (40 \times 0.1)} = 4.699 + \log 4 = \mathbf{5.3011}$$

(v) When 50 ml of NaOH is added,

Here, if we use the buffer equation, pH would be  $= \infty$ .

The buffer equation cannot be used, as there is no acid. Therefore we will use the hydrolysis equation.

$$\therefore [\text{H}^+] = \sqrt{\frac{K_w K_a}{c}}$$

$$c = \frac{0.1}{2} \quad [\because \text{Total volume is 100 ml and millimoles of salt is } 50 \times 0.1]$$

$$[\text{H}^+] = \sqrt{\frac{10^{-14} \times 2 \times 10^{-5} \times 2}{0.1}}$$

$$\text{pH} = \mathbf{8.699}$$

(vii) When 60 ml of NaOH is added, the excess of  $\text{OH}^-$  ions from NaOH would suppress the hydrolysis of  $\text{CH}_3\text{COO}^-$  ion. So we can ignore the contribution of  $\text{OH}^-$  ion from the hydrolysis of  $\text{CH}_3\text{COO}^-$  ion and pH calculation should be done with  $\text{OH}^-$  from NaOH only.

$$\therefore [\text{OH}^-] = \frac{0.1 \times 10}{110} = \frac{1}{110}$$

$$\text{pOH} = 2.0414$$

$$\therefore \text{pH} = 14 - 2.0414 = \mathbf{11.9586}$$

### Illustration 9

A buffer solution contains 0.04 mole of  $\text{Na}_2\text{HPO}_4$  and 0.02 mole of  $\text{NaH}_2\text{PO}_4$  per litre.  
(a) Calculate pH if  $\text{pK}_a$  of  $\text{NaH}_2\text{PO}_4$  is 6.84. (b) If 1 ml of 1 N HCl is added to a litre of the buffer, calculate the change in pH.

### Solution:

In this mixture  $\text{NaH}_2\text{PO}_4$  is the acid and  $\text{Na}_2\text{HPO}_4$  is the salt.

$$\text{pH} = \text{pK}_a + \log \frac{[\text{Salt}]}{[\text{Acid}]} = 6.84 + \log \frac{0.04}{0.02} = 6.84 + \log 2 = 6.84 + 0.30 = \mathbf{7.14}.$$

(b) 1 ml of 1 N HCl contains 0.001 mole of  $\text{H}^+$ . It will convert 0.001 mole of  $\text{Na}_2\text{HPO}_4$  to 0.001 mole of  $\text{NaH}_2\text{PO}_4$ .

## IONIC EQUILIBRIUM

$$\text{pH} = \text{pK}_a + \log \frac{0.04 - 0.001}{0.02 + 0.001} = 6.84 + \log \frac{0.039}{0.021} = 7.109$$

The change in pH is **0.031**.

### Illustration 10

Calculate the pH of a solution made by adding 0.001 mole of NaOH to 100 ml of 0.5 M acetic acid and 0.5 M sodium acetate solution.

### Solution:

$$\text{Moles of acetic acid in 100 ml of solution} = \frac{0.5}{1000} \times 100 = 0.05$$

$$\text{Moles of sodium acetate in 100 ml of solution} = \frac{0.5}{1000} \times 100 = 0.05$$

When NaOH is added, acetic acid is converted into sodium acetate.

$$\text{Moles of acetic acid after addition of 0.001 mole of NaOH} = (0.05 - 0.001) = 0.049$$

$$\begin{aligned} \text{Moles of sodium acetate after addition of 0.001 mole of NaOH} &= (0.05 + 0.001) \\ &= 0.051 \end{aligned}$$

$$\begin{aligned} \text{pH} &= \text{pK}_a + \log \frac{[\text{Salt}]}{[\text{Acid}]} = -\log(1.8 \times 10^{-5}) + \log \frac{0.051 \times 10}{0.049 \times 10} \\ &= 4.7447 + 0.0174 = \mathbf{4.7621}. \end{aligned}$$

## 9. SOLUBILITY, MOLAR SOLUBILITY AND SOLUBILITY PRODUCT

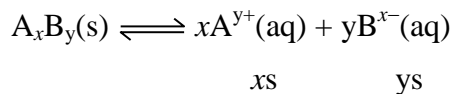
There are two ways to express a substance's solubility (a) solubility and (b) molar solubility.

(a) The number of grams of solute in one litre of a saturated solution (g/litre) is termed as solubility.

(b) The number of moles of solute in one litre of a saturated solution (moles /litre) is defined as molar solubility.

Both these definitions refer to the concentration of saturated solutions at some given temperature (usually 25°C).

Let us consider solubility of any general salt,  $A_xB_y$ . Let the solubility of this salt be 's' mol per litre.



For saturated solution (at equilibrium),

$$K_{eq} = \frac{[A^{y+}]^x \times [B^{x-}]^y}{[A_xB_y]}$$

# IONIC EQUILIBRIUM

$$K_{eq} [A_x B_y] = [A^{y+}]^x [B^{x-}]^y$$

$$K_{SP} = [A^{y+}]^x [B^{x-}]^y \quad (\text{since } A_x B_y \text{ is a pure solid})$$

where  $K_{sp}$  is called **solubility product**. The term on right hand side is called solubility product if the solution is saturated and ionic product if the solution is not saturated (i.e., not at equilibrium).

$$K_{SP} = (xS)^x \times (yS)^y$$

$$K_{sp} = x^x \times y^y \times s^{(x+y)}$$

It should be noted that if the ionic product is more than  $K_{SP}$ , the equilibrium will shift in backward direction and some amount of salt is thrown out of solution (precipitation) and finally an equilibrium is developed in such a way that the ionic product becomes equal to solubility product. If ionic product is less than  $K_{SP}$ , the solution is unsaturated and more of the salt can be dissolved. If ionic product is equal to  $K_{SP}$ , the solution is saturated and if ionic product is more than  $K_{SP}$ , the solution is called super saturated.

From the solubility product principle, we may infer that,

- When the ionic product of a salt in solution is equal to its solubility product, the solution is saturated and the undissociated salt remains in equilibrium with its ions in the solution.
- When the ionic product of a salt in solution is less than the solubility product, the solution is unsaturated and the solution contains only ions and no undissociated salt.
- When the ionic product is greater than the solubility product, the excess ions in solution combine and gets precipitated. So when the product of the concentrations of the constituent ions raised to appropriate powers exceeds the solubility product of the salt, the salt will be precipitated.

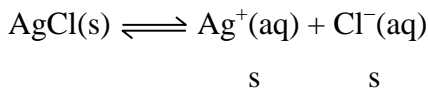
For example, in order to precipitate CuS,

$$[Cu^{2+}][S^{2-}] > K_{SP}(CuS)$$

## 10. DIFFERENT CASES OF CALCULATING SOLUBILITIES

### 10.1 SOLUBILITY OF A SALT OF STRONG ACID AND STRONG BASE IN PURE WATER

Let us consider a salt of this type as AgCl. Let the solubility of the salt be  $s$  moles per litre. Such salt do not hydrolyse.



$$K_{sp} = [Ag^+] \times [Cl^-]$$

$$K_{sp} = s \times s = s^2$$

$$s = \sqrt{K_{SP}}$$

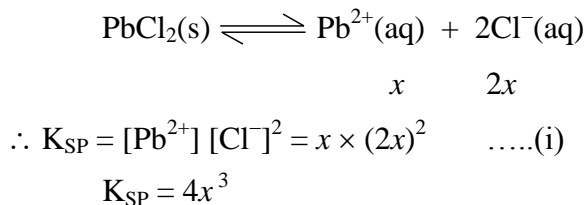
Knowing solubility product, solubility( $s$ ) of AgCl can be calculated.



## IONIC EQUILIBRIUM

### 10.2 SOLUBILITY OF A SALT OF STRONG ACID AND STRONG BASE IN PURE WATER HAVING STOICHIOMETRY 1 : 2.

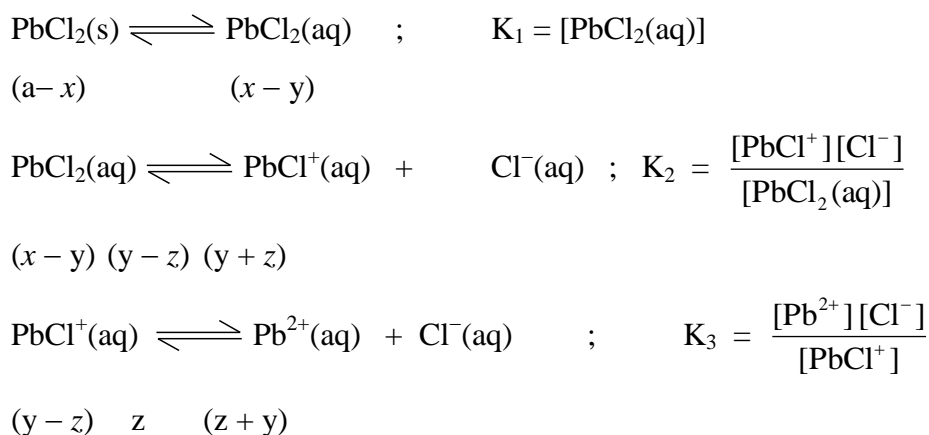
Let the salt of this type be  $\text{PbCl}_2$ . Let a moles of  $\text{PbCl}_2$  are added to a litre of water, of which  $x$  moles dissolves. This means the solubility of  $\text{PbCl}_2$  is  $x$  moles/litre. The equilibrium of  $\text{PbCl}_2$  would be represented as



Thus, relation between solubility and  $K_{\text{SP}}$  for all the salts is not same and depends on the stoichiometry of the salt.

Another point to be kept in mind is that in this case, we have assumed that  $\text{PbCl}_2(\text{aq})$  dissociates completely in two steps. Then only the concentration  $\text{Cl}^{-}$  will be double than that of  $\text{Pb}^{2+}$ , otherwise not. Let us see why?

The solubility equilibria of  $\text{PbCl}_2$  are



This can be seen that if the dissociation of  $\text{PbCl}_2(\text{aq})$  to  $\text{PbCl}^{+}$  &  $\text{Cl}^{-}$  and dissociation of  $\text{PbCl}^{+}$  to  $\text{Pb}^{2+}$  &  $\text{Cl}^{-}$  is taken as 100%, then only concentration of  $\text{Cl}^{-}$  would be double than that of  $\text{Pb}^{2+}$ .

Otherwise, the concentration of  $\text{Cl}^{-}$  would be less than double the concentration of  $\text{Pb}^{2+}$ . Let us take the product of  $K_1$ ,  $K_2$  and  $K_3$  to get  $K_{\text{SP}}$ .

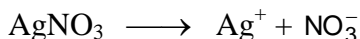
$$\begin{array}{l} K_1 \times K_2 \times K_3 = [\text{PbCl}_2(\text{aq})] \times \frac{[\text{PbCl}^{+}][\text{Cl}^{-}]}{[\text{PbCl}_2(\text{aq})]} \times \frac{[\text{Pb}^{2+}][\text{Cl}^{-}]}{[\text{PbCl}^{+}]} = [\text{Pb}^{2+}][\text{Cl}^{-}]^2 \\ \therefore K_{\text{SP}} = [\text{Pb}^{2+}][\text{Cl}^{-}]^2 = (z)(y+z)^2 \quad \dots\dots(\text{ii}) \end{array}$$

We can see that the equation (i) and (ii) are not same. They can only be same, when  $z = y = x$ . Such assumptions are always taken for these types of salts unless and otherwise degree of dissociation of all the involved species is given in the problem.

### 10.3 SOLUBILITY OF A SALT OF STRONG ACID AND STRONG BASE IN PRESENCE OF A COMMON ION (INCAPABLE OF FORMING COMPLEX)

## IONIC EQUILIBRIUM

Let us calculate the solubility of AgCl in 0.1 M AgNO<sub>3</sub> solution.



Let the solubility of AgCl in presence of 0.1 M AgNO<sub>3</sub> be  $s'$  moles per litre. Then

$$[\text{Ag}^+]_{\text{AgCl}} = s' \text{ M}$$

$$[\text{Ag}^+]_{\text{AgNO}_3} = 0.1 \text{ M}$$

$$[\text{Ag}^+]_{\text{Total}} = (0.1 + s') \text{ M}$$

$$K_{\text{sp}} = [\text{Ag}^+]_{\text{Total}} \times [\text{Cl}^-]$$

$$K_{\text{sp}} = (0.1 + s') \times (s')$$

$s'$  can be ignored with respect to 0.1 M,  $\therefore (0.1 + s') \approx 0.1$

$$\therefore s' = \frac{K_{\text{sp}}}{0.1}$$

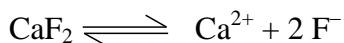
$s'$  can be calculated provided we know  $K_{\text{sp}}$  of AgCl. It can be noticed that  $s'$  would be less than  $s$ .

### Illustration 11

The solubility product of CaF<sub>2</sub> is  $3.9 \times 10^{-11}$  at 25°C. What is the solubility (in grams) of this salt in a litre of 0.1 N NaF solution?

### Solution:

Let the solubility of CaF<sub>2</sub> in the presence of 0.1 N NaF be  $x$ .



$$[\text{Ca}^{2+}] = x$$

$$[\text{F}^-] = 2x + 0.1$$

$$K_{\text{sp}} = [\text{Ca}^{2+}] [\text{F}^-]^2 = x(2x + 0.1)^2 = 4x^3 + 0.4x^2 + 0.01x$$

Since  $x$  is small,  $x^2$  and  $x^3$  terms would be very-very small and can be neglected.

$$\therefore 0.01x = 3.9 \times 10^{-11}$$

$$x = \frac{3.9 \times 10^{-11}}{0.01} = 3.9 \times 10^{-9}$$

The smallness of  $x$  justifies the earlier supposition that  $x^3$  and  $x^2$  is negligible.

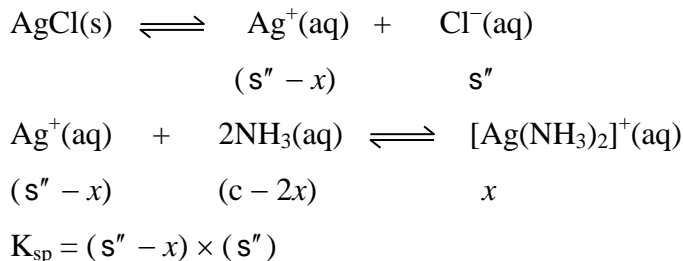
$$\text{Molecular weight of CaF}_2 = (40 + 38) = 78$$

$$\text{Mass of CaF}_2 \text{ per litre} = 3.9 \times 10^{-9} \times 78 = 3.042 \times 10^{-7} \text{ g litre}^{-1}.$$

## 10.4 SOLUBILITY OF A SALT OF STRONG ACID AND STRONG BASE IN A SOLVENT CAPABLE OF FORMING COMPLEX

## IONIC EQUILIBRIUM

Let us consider the solubility of AgCl in  $c$  M  $\text{NH}_3$  (as solvent). Let the solubility of AgCl in ammonia be  $s''$  mole  $\text{L}^{-1}$  and  $x$  mole  $\text{L}^{-1}$  is the amount of salt forming complex.



$$K_f = \frac{x}{(s'' - x) \times (c - 2x)^2}$$

where  $K_f$  is equilibrium constant for the formation of complex ion/species and is called formation constant.

$K_f$  values of complex formation are very high, so almost entire amount of  $\text{Ag}^+$  would be converted to complex. This means that the value of  $x$  approaches  $s''$ . Thus  $(s'' - x)$  would be very small. Let this small value be  $y$ . Also the value of  $x$  is small, so  $2x$  can be ignored with respect to  $c$ .

$$\therefore (c - 2x) \approx c$$

$$\therefore K_{\text{SP}} = y \times s''$$

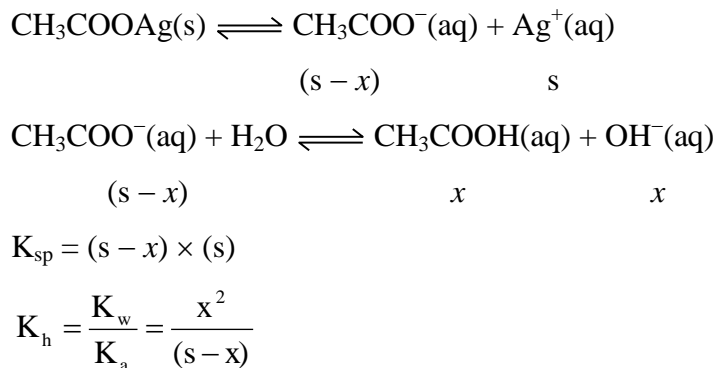
$$K_f = \frac{s''}{y \times (c)^2} = \frac{s''^2}{K_{\text{SP}} \times (c)^2}$$

$$\therefore s'' = c \times \sqrt{K_{\text{SP}} \times K_f}$$

Knowing the values of  $K_{\text{sp}}$ ,  $K_f$  and  $c$ , we can calculate the value of  $s''$  and  $x$ . It can notice that  $s''$  would be greater than  $s$ . Thus complex formation increases the solubility of a salt.

### 10.5 SOLUBILITY OF A SALT OF WEAK ACID AND STRONG BASE IN PURE WATER

Let the salt of this type be  $\text{CH}_3\text{COOAg}$  and its solubility be  $s$  moles per litre. Such salts undergo hydrolysis. Out of  $\text{CH}_3\text{COO}^-$  and  $\text{Ag}^+$  ions,  $\text{CH}_3\text{COO}^-$  ion will get hydrolysed. Let the amount of  $\text{CH}_3\text{COO}^-$  ion getting hydrolysed be  $x$  moles per litre.

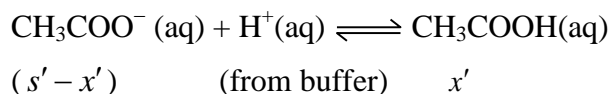
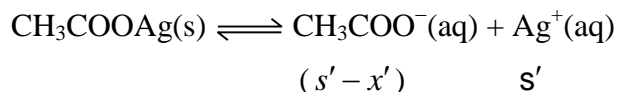


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Solving these two equations, we get the values of  $s$  and  $x$ .

### 10.6 SOLUBILITY OF A SALT OF WEAK ACID AND STRONG BASE IN ACIDIC BUFFER

Let the solubility of  $\text{CH}_3\text{COOAg}$  be  $s'$  mole per litre in acidic buffer. Now, in presence of free  $\text{H}^+$  (from acidic buffer), the anion of weak acid will form weak acid at equilibrium, but the  $[\text{H}^+]$  in a buffer will remain constant.



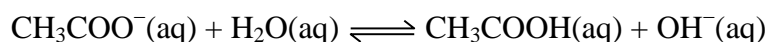
$$\therefore K_{sp} = (s' - x') \times (s')$$

$$\frac{1}{K_a} = \frac{x'}{(s' - x') \times [\text{H}^+]_{\text{buffer}}}$$

Knowing the values of  $K_{sp}$ ,  $K_a$  and the concentration of  $\text{H}^+$  ions in the buffer, we can calculate  $s'$  and  $x'$ . The value of  $s'$  would be greater than  $s$ , this implies that the solubility of a salt of weak acid and strong base is more in acidic buffer than in pure water.

### 10.7 SOLUBILITY OF A SALT OF WEAK ACID AND STRONG BASE IN BASIC BUFFER

Now let the solubility of  $\text{CH}_3\text{COOAg}$  be  $s''$  mole/L in basic buffer.



In basic buffer, due to the presence of free  $\text{OH}^-$ , the second equilibrium will lie in the reverse direction, so very little amount of  $\text{CH}_3\text{COO}^-$  will get hydrolysed, which can be neglected.

$$\therefore [\text{CH}_3\text{COO}^-] \approx s'' \text{ M}$$

$$[\text{Ag}^+] \approx s'' \text{ M}$$

$$K_{sp} = [\text{CH}_3\text{COO}^-] \times [\text{Ag}^+] = s''^2$$

$$s'' = \sqrt{K_{sp}}$$

The value of  $s''$  would be smaller than  $s$ , which implies that the solubility of  $\text{CH}_3\text{COOAg}$  will be less in basic buffer than in pure water.

### 10.8 SOLUBILITY OF A SALT OF WEAK BASE AND STRONG ACID

The solubility of a salt of weak base and strong acid (anilinium chloride) may also be calculated in the same fashion under different conditions as we have done in the case of  $\text{CH}_3\text{COOAg}$ .

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**In pure water:** Hydrolysis of ion of weak base will take place to produce weak base and  $H^+$ .

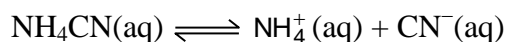
**In acidic buffer:** Hydrolysis will be suppressed due to the presence of  $H^+$  of buffer and can be neglected.

**In basic buffer:** The ion of weak base will combine with  $OH^-$  of buffer to give weak base.

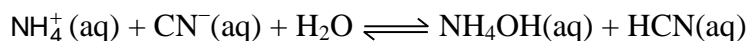
It can be concluded that such salts have highest solubility in basic buffer, then in pure water and least in acidic buffer.

### 10.9 SOLUBILITY OF A SALT OF WEAK ACID AND WEAK BASE IN PURE WATER

Let us consider a salt of weak acid and weak base,  $NH_4CN$ . Let its solubility be  $s$  mol/L and  $x$  mol/L is the amount of salt getting hydrolysed.



$$s - x \quad s - x$$



$$s - x \quad s - x \quad x \quad x$$

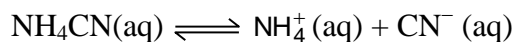
$$K_{sp} = (s - x)^2$$

$$K_h = \frac{K_w}{K_a \times K_b} = \frac{x^2}{(s - x)^2}$$

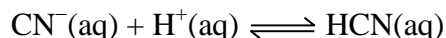
Solving these two equations, we can calculate  $s$  and  $x$ .

### 10.10 SOLUBILITY OF A SALT OF WEAK ACID AND WEAK BASE IN ACIDIC BUFFER

Under acidic conditions, the hydrolysis of ion of weak base is suppressed and the ion of weak acid will combine with  $H^+$  to give weak acid. Let the solubility of the salt be  $s'$  mol/L and  $x'$  mol/L be the amount of weak acid being formed.



$$s' \quad (s' - x')$$



$$(s' - x') \quad (\text{from buffer}) \quad x'$$

$$K_{sp} = (s') \times (s' - x')$$

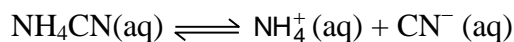
$$\frac{1}{K_a} = \frac{x'}{(s' - x') \times [H^+]_{\text{buffer}}}$$

Knowing  $[H^+]$  in buffer,  $K_a$  and  $K_{sp}$  values, we can calculate the solubility of  $NH_4CN$  in acidic buffer. The solubility of  $NH_4CN$  in acidic buffer would be higher than in pure water.

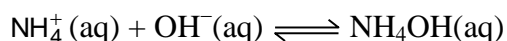
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### 10.11 SOLUBILITY OF A SALT OF WEAK ACID AND WEAK BASE IN A BASIC BUFFER

Under basic conditions, the hydrolysis of ion of weak acid is suppressed and the ion of weak base will combine with  $\text{OH}^-$  to give weak base. Let the solubility of the salt be  $s''$  mol/L and  $x''$  mol/L be the amount of weak base formed by the reaction of ion of weak base with  $\text{OH}^-$  (from buffer).



$$(s'' - x'') \quad s''$$



$$(s'' - x'') \quad (\text{from buffer}) \quad x''$$

$$\therefore K_{\text{sp}} = s'' \times (s'' - x'')$$

$$\frac{1}{K_{\text{b}}} = \frac{x''}{(s'' - x'') \times [\text{OH}^-]_{\text{buffer}}}$$

Knowing  $[\text{OH}^-]$  in buffer,  $K_{\text{b}}$  and  $K_{\text{sp}}$  values, we can calculate the solubility of  $\text{NH}_4\text{CN}$  in basic buffer. The solubility of  $\text{NH}_4\text{CN}$  in basic buffer would be higher than in pure water.

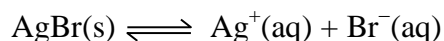
### 10.12 SIMULTANEOUS SOLUBILITY OF TWO OR MORE SPARINGLY SOLUBLE SALTS

Simultaneous solubility means the solubility of a sparingly soluble salt in presence of another sparingly soluble salt having a common ion. Let us assume the simultaneous solubilities of  $\text{AgCl}$  and  $\text{AgBr}$  in a solution are  $x$  and  $y$  mol/L.



$$(x + y) \quad x$$

$$K_{\text{sp}} = [\text{Ag}^+]_{\text{total}} \times [\text{Cl}^-]$$



$$(x + y) \quad y$$

$$K_{\text{sp}} = [\text{Ag}^+]_{\text{total}} \times [\text{Br}^-]$$

$$K_{\text{sp}} \text{ of AgCl} = (x + y) \times x$$

$$K_{\text{sp}} \text{ of AgBr} = (x + y) \times y$$

From the above two expressions, we can calculate the simultaneous solubilities of  $\text{AgCl}$  and  $\text{AgBr}$ .

## 11. SELECTIVE PRECIPITATION

Let us have a solution containing more than one ion capable of forming a precipitate with another ion, which is added to the system. The added ion will selectively form precipitate with any one of the ions present in the solution. This process of selectively or preferentially precipitating an ion from a solution of more than one ion is

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called selective precipitation. The selective precipitation of ions from a solution in the form of a salt, (which is partially soluble) can be done by adding precipitating agent drop by drop.

If the stoichiometry of the precipitated salts is same, then the salt with minimum solubility product (and hence also the minimum solubility) will precipitate first, followed by the salt of next higher solubility and so on. For example, in a solution containing  $\text{Cl}^-$ ,  $\text{Br}^-$  and  $\text{I}^-$  ions, when  $\text{Ag}^+$  ions are added, then out of the three, the least soluble silver salt is precipitated first. If the addition of  $\text{Ag}^+$  ions is continued further, eventually a stage will be reached when the next lesser soluble salt starts precipitating along with the least soluble salt and so on.

If the stoichiometry of the precipitated salts is not the same, then from the solubility product data alone, we will not be straight away able to predict, which ion will precipitate first. Let us take a solution containing 0.1 M each of  $\text{Cl}^-$  and  $\text{CrO}_4^{2-}$  ion and the precipitating ion used is  $\text{Ag}^+$ . We are given the solubility products of  $\text{AgCl}$  and  $\text{Ag}_2\text{CrO}_4$  as  $1 \times 10^{-10} \text{ M}^2$  and  $1 \times 10^{-13} \text{ M}^3$  respectively.

We know that the precipitation takes place only if the ionic product exceeds solubility product. Though the solubility product of  $\text{Ag}_2\text{CrO}_4$  is less than that of  $\text{AgCl}$ , yet it is  $\text{AgCl}$  (lesser soluble) that precipitates first when  $\text{Ag}^+$  ions are added to the solution. Thus order to predict which ion precipitates first, we will first calculate the concentration of  $\text{Ag}^+$  required to make each of their ionic products equal to solubility products.



$$K_{\text{sp}}(\text{AgCl}) = [\text{Ag}^+] \times [\text{Cl}^-]$$

Minimum concentration of  $\text{Ag}^+$  required to precipitate 0.1 M  $\text{Cl}^-$  as  $\text{AgCl}$  would be

$$[\text{Ag}^+] = \frac{K_{\text{sp}}(\text{AgCl})}{[\text{Cl}^-]} = \frac{1 \times 10^{-10}}{0.1} = 1 \times 10^{-9} \text{ M}$$



$$K_{\text{sp}}(\text{Ag}_2\text{CrO}_4) = [\text{Ag}^+]^2 \times [\text{CrO}_4^{2-}]$$

Minimum concentration of  $\text{Ag}^+$  required to precipitate 0.1 M  $\text{CrO}_4^{2-}$  as  $\text{Ag}_2\text{CrO}_4$  would be

$$[\text{Ag}^+] = \sqrt{\frac{K_{\text{sp}}(\text{Ag}_2\text{CrO}_4)}{[\text{CrO}_4^{2-}]}} = \sqrt{\frac{1 \times 10^{-13}}{0.1}} = 1 \times 10^{-6} \text{ M}$$

When  $\text{AgNO}_3$  is added to the solution, the minimum of the two concentrations of  $\text{Ag}^+$  needed to start the precipitation will be reached first and thus the corresponding ion ( $\text{Cl}^-$  in this case) will be precipitated in preference to the other.

When the concentration of  $\text{Ag}^+$  becomes equal to  $1 \times 10^{-9} \text{ M}$ ,  $\text{AgCl}$  starts precipitating. During the course of precipitation, concentration of  $\text{Cl}^-$  decreases and the corresponding concentration of  $\text{Ag}^+$  to start the precipitation increase. A stage will reach when the concentration of  $\text{Ag}^+$  becomes equal to  $1 \times 10^{-6} \text{ M}$ , which is required to precipitate  $\text{CrO}_4^{2-}$  ion. The addition of more of  $\text{AgNO}_3$  causes the precipitation of both the ions together but at this stage, practically whole of  $\text{Cl}^-$  ions have been precipitated.

We can even calculate the % of  $\text{Cl}^-$  ion precipitated by the time  $\text{CrO}_4^{2-}$  ion starts precipitating. Let the concentration of  $\text{Cl}^-$  left, at the time when concentration of  $\text{Ag}^+$  ion reaches  $1 \times 10^{-6} \text{ M}$  (required to precipitate  $\text{CrO}_4^{2-}$  ion) be represented as  $[\text{Cl}^-]_{\text{left}}$ .

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$$\therefore K_{SP}(\text{AgCl}) = [\text{Ag}^+] [\text{Cl}^-]_{\text{left}}$$

$$[\text{Cl}^-]_{\text{left}} = \frac{1 \times 10^{-10}}{1 \times 10^{-6}} = 1 \times 10^{-4} \text{ M}$$

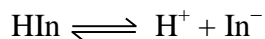
$$\% \text{ of } \text{Cl}^- \text{ left unprecipitated} = \frac{1 \times 10^{-4}}{0.1} \times 100 = 0.1\%$$

$$\therefore \% \text{ of } \text{Cl}^- \text{ precipitated (by the time } \text{CrO}_4^{2-} \text{ ion starts precipitating)} = 100 - 0.1 = \mathbf{99.9\%}$$

## 12. INDICATORS

Indicators are the substances, which indicates the end-point of a titration by changing their colour. They are in general, either weak organic acids or weak organic bases having characteristically different colours in the ionised and unionised forms. For example, methyl orange is a weak base (having red colour in ionised form and yellow colour in the unionised form) and phenolphthalein is a weak acid (having pink colour in the ionized form while its unionised form is colourless).

Let us consider the equilibrium between the ionised and unionised form of an acid indictor (HIn).



$$\therefore K_{\text{HIn}} = \frac{[\text{H}^+] [\text{In}^-]}{[\text{HIn}]} \quad [K_{\text{HIn}} = \text{Indicator constant or dissociation constant of indicator}]$$

$$\text{or} \quad [\text{H}^+] = K_{\text{HIn}} \times \frac{[\text{HIn}]}{[\text{In}^-]}$$

Taking negative logarithm of both sides

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

$$\therefore \text{pH} = \text{p}K_{\text{HIn}} + \log \frac{[\text{In}^-]}{[\text{HIn}]}$$

$$\text{pH} = \text{p}K_{\text{HIn}} + \log \frac{[\text{Ionised form}]}{[\text{Unionised form}]}$$

In general, the intensity of a coloured solution depends on the concentration of the colour imparting species. If the solution contains two coloured species, then the colour of the solution depends on the relative concentration of the colour imparting species. When the solution contains two coloured species as HIn and  $\text{In}^-$ , then it is seen that the solution acquires a distinct colour of  $\text{In}^-$  only when the concentration of  $\text{In}^-$  is approximately at least 10 times greater than the concentration of HIn and vice versa.



## IONIC EQUILIBRIUM

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Let us consider two cases.

### Case I :

In order for the solution to show colour due to  $\text{In}^-$ , the minimum ratio of  $\frac{[\text{In}^-]}{[\text{HIn}]}$  should be 10.

$$\therefore \text{pH} = \text{pK}_{\text{HIn}} + \log(10) = \text{pK}_{\text{HIn}} + 1$$

At this stage, the percentage of the indicator in  $\text{In}^-$  form would be given by

$$\frac{[\text{In}^-]}{[\text{In}^-] + [\text{HIn}]} \times 100 = \frac{10}{10 + 1} \times 100 \approx 91$$

Thus, nearly 91% of the indicator has been present in the ionised form ( $\text{In}^-$ ). In fact  $\text{pH} = \text{pK}_{\text{HIn}} + 1$  is the minimum pH up to which the solution has a distinct colour characteristic of  $\text{In}^-$ . At pH greater than this value, some more indicator will be present in the ionised form. Thus at  $\text{pH} \geq \text{pK}_{\text{HIn}} + 1$ , the solution has a colour characteristic of  $\text{In}^-$ .

### Case II :

In order for the solution to show colour due to  $\text{HIn}$ , the minimum ratio of  $\frac{[\text{In}^-]}{[\text{HIn}]}$  should be 1/10.

$$\therefore \text{pH} = \text{pK}_{\text{HIn}} + \log \frac{1}{10} = \text{pK}_{\text{HIn}} - 1$$

At this stage, the percentage of the indicator in  $\text{In}^-$  form would be given by

$$\frac{[\text{In}^-]}{[\text{In}^-] + [\text{HIn}]} \times 100 = \frac{1}{10 + 1} \times 100 \approx 9.1$$

Thus, nearly 9.1% of the indicator has been present in the ionised form ( $\text{In}^-$ ) and  $\approx 91\%$  of the indicator is present in the unionized form ( $\text{HIn}$ ). In fact  $\text{pH} = \text{pK}_{\text{HIn}} - 1$  is the maximum pH up to which the solution has a distinct colour characteristic of  $\text{HIn}$ . At pH smaller than this value, some more indicator will be present in the unionised form. Thus at  $\text{pH} \leq \text{pK}_{\text{HIn}} - 1$ , the solution has a colour characteristic of  $\text{HIn}$ .

Therefore, in between the pH range  $\text{pK}_{\text{HIn}} - 1$  to  $\text{pK}_{\text{HIn}} + 1$ , transition of colour takes place for any acid–base indicator.  $\text{pK}_{\text{HIn}} \pm 1$  is called the range of indicator.

## 13. Solved Examples

### Example 1:

An indicator is a weak acid and the pH range of its colour is 3.1 to 4.5. If the neutral point of the indicator lies in the center of the hydrogen ion concentrations corresponding to the given pH range, calculate the ionization constant of the indicator.

### Solution:

The hydrogen ion concentrations of the given pH range are

For pH 3.1,

$$\text{pH} = -\log [\text{H}^+] = 3.1$$

$$[\text{H}^+] = 7.94 \times 10^{-4} \text{ M}$$

For pH 4.5,

$$\text{pH} = 4.5 = -\log [\text{H}^+]$$

$$\therefore [\text{H}^+] = 3.16 \times 10^{-5} \text{ M}$$

The average of these two hydrogen ion concentrations is

$$\frac{(7.9 \times 10^{-4}) + (3.16 \times 10^{-5})}{2} = 4.128 \times 10^{-4} \text{ M}$$

At this concentration of  $\text{H}^+$ , we will get neutral point of the indicator, at which  $[\text{In}^-] = [\text{HIn}]$ .

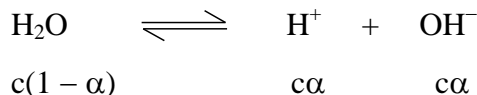
$$\therefore \text{pH} = \text{pK}_{\text{HIn}} \quad \text{or } [\text{H}^+] = K_{\text{HIn}} = 4.128 \times 10^{-4}$$

### Example 2:

At  $25^\circ\text{C}$ , the degree of ionization of water was found to be  $1.8 \times 10^{-9}$ . Calculate the ionization constant and ionic product of water at this temperature.

### Solution:

If  $x$  is the degree of ionization of water, then



$$c = [\text{H}_2\text{O}] = \frac{1000}{18} = 55.56 \text{ M}$$

$$K_{\text{eq}} = \frac{[\text{H}^+][\text{OH}^-]}{[\text{H}_2\text{O}]} = \frac{(c\alpha)^2}{c(1-\alpha)} \approx c\alpha^2 \quad (\text{since } \alpha \text{ is very much less than } 1)$$

$$K_{\text{eq}} = 55.56 \times (1.8 \times 10^{-9})^2 = 1.8 \times 10^{-16} \text{ M}$$

$$K_w = [\text{H}^+][\text{OH}^-] = (c\alpha)^2 = (55.56 \times 1.8 \times 10^{-9})^2 = 1.0 \times 10^{-14} \text{ M}^2$$

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### Example 3:

At 25°C, will a precipitate of  $\text{Mg}(\text{OH})_2$  form in a  $1 \times 10^{-4} \text{ M}$  solution of  $\text{Mg}(\text{NO}_3)_2$  if pH of the solution is adjusted to 9.0. [ $K_{\text{SP}} (\text{Mg}(\text{OH})_2 = 8.9 \times 10^{-12} \text{ M}^3$ ]. At which minimum pH will the precipitation start?

### Solution:

If pH = 9.0,  $[\text{H}^+] = 1 \times 10^{-9} \text{ M}$ , then

$$[\text{OH}^-] = \frac{K_w}{[\text{H}^+]} = \frac{1 \times 10^{-14}}{1 \times 10^{-9}} = 1 \times 10^{-5} \text{ M}$$

The ionic product of  $\text{Mg}(\text{OH})_2$  in the solution would be

$$[\text{Mg}^{2+}] [\text{OH}^-]^2 = (1 \times 10^{-4}) (1 \times 10^{-5})^2 = 1 \times 10^{-14} \text{ M}^3$$

Since, the value of ionic product is smaller than  $K_{\text{SP}} (8.9 \times 10^{-12})$ , so no precipitate of  $\text{Mg}(\text{OH})_2$  will be formed.

The minimum concentration of  $\text{OH}^-$  needed to precipitate  $\text{Mg}^{2+}$  from the solution is

$$[\text{OH}^-] = \sqrt{\frac{K_{\text{SP}}}{[\text{Mg}^{2+}]}} = \sqrt{\frac{8.9 \times 10^{-12}}{1 \times 10^{-4}}} = 2.98 \times 10^{-4} \text{ M}$$

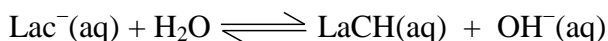
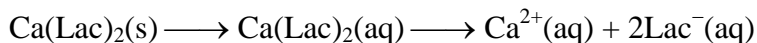
$\therefore$  Maximum pOH = 3.54

and minimum pH =  $14 - 3.54 = 10.46$

### Example 4:

Calcium lactate is a salt of a weak organic acid and is represented as  $\text{Ca}(\text{Lac})_2$ . A saturated solution of  $\text{Ca}(\text{Lac})_2$  contains 0.13 mol of this salt in 0.5 litre solution. The pOH of this solution is 5.6. Assuming complete dissociation of the salt, calculate  $K_a$  for lactic acid.

### Solution:



Since it is salt of strong base and weak acid, its pH is calculated as

$$\text{pH} = \frac{1}{2} [\text{p}K_w + \text{p}K_a + \log c]$$

$$\text{pH} = 14 - \text{pOH} = 14 - 5.6 = 8.4$$

$$8.4 = \frac{1}{2} [14 + \text{p}K_a + \log 0.52] (\because c = 2 \times 0.13/0.5)$$

$$\text{p}K_a = (2 \times 8.4) - 14 - \log 0.52 = 3.08$$

$$\therefore K_a = 8.31 \times 10^{-4}$$

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### Example 5:

(a) Calculate the pH of a 0.01 M solution of benzoic acid, the  $K_a$  being  $7.3 \times 10^{-5}$ .

(b) 0.2 M solution of  $\text{Ba}(\text{OH})_2$  is found to be 90% ionised at  $25^\circ\text{C}$ . Find the pH of the solution at that temperature.

### Solution:

(a) First calculate  $\alpha$  using the expression,  $\alpha = \sqrt{\frac{K_a}{c}} = \sqrt{\frac{7.3 \times 10^{-5}}{0.01}} = 0.085$

$$\text{pH} = \frac{1}{2} (\text{p}K_a - \log c) = \frac{1}{2} (4.13 - 0.01) = 2.06$$

$$(b) [\text{OH}^-] = 0.2 \times 0.9 \times 2 = 0.36$$

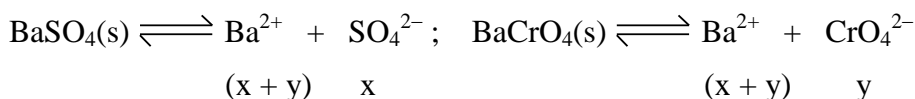
$$\text{pOH} = 0.44; \text{pH} = 13.56$$

### Example 6:

The solubility of  $\text{BaSO}_4$  and  $\text{BaCrO}_4$  at  $25^\circ\text{C}$  are  $1 \times 10^{-10}$  and  $2.4 \times 10^{-10}$  respectively. Calculate the simultaneous solubilities of  $\text{BaSO}_4$  and  $\text{BaCrO}_4$ .

### Solution:

Let the solubility of  $\text{BaSO}_4$  be  $x$  and that of  $\text{BaCrO}_4$  be  $y$  mole litre $^{-1}$  in the presence of each other.



$$[\text{Ba}^{2+}] [\text{SO}_4^{2-}] = 1 \times 10^{-10} = (x+y)x \quad \dots\dots(i)$$

$$[\text{Ba}^{2+}] [\text{CrO}_4^{2-}] = 2.4 \times 10^{-10} = (x+y)y \quad \dots\dots(ii)$$

Dividing (ii) by (i) we get

$$\frac{y}{x} = 2.4; \therefore y = 2.4x$$

Substituting the value of  $y$  in (i), we get

$$3.4x \times x = 1 \times 10^{-10}$$

$$x = 5.42 \times 10^{-6} \text{ M}$$

$$\therefore y = 2.4 \times 5.42 \times 10^{-6} = 1.3 \times 10^{-5} \text{ M}$$

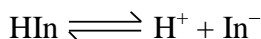
### Example 7:

A certain acid–base indicator is red in acid and blue in basic solution. At  $\text{pH} = 5$ , 75% of the indicator is present in the solution in its blue form. Calculate dissociation constant ( $K_a$ ) for the indicator and pH range over which the indicator changes from 90% red–10% blue to 90% blue–10% red.

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### Solution:

Since  $K_a$  is asked, the indicator must be an acid. Let the acid be represented by HIn.



In acid solution, the indicator will be predominantly present in the form of HIn (due to common ion effect). Since in acid solution the colour is red, this would be due to HIn. In basic solution, the indicator will be predominantly in the form of  $\text{In}^-$ . Since the indicator is blue in basic solution, so  $\text{In}^-$  must be blue in colour.

At pH = 5, the indicator is 75% blue. This also means it is 25% red.

$$\therefore K_a = \frac{10^{-5} \times 0.75}{0.25} = 3 \times 10^{-5}$$

$$\text{pH when it is 90\% red \& 10\% blue: } [\text{H}^+] = \frac{K_a \times [\text{HIn}]}{[\text{In}^-]} = \frac{3 \times 10^{-5} \times 0.9}{0.1} = 2.7 \times 10^{-4}$$

$$\therefore \text{pH} = 3.56$$

$$\text{pH when it is 90\% blue and 10\% red: } [\text{H}^+] = \frac{K_a \times [\text{HIn}]}{[\text{In}^-]} = \frac{3 \times 10^{-5} \times 0.1}{0.9} = 3.3 \times 10^{-6}$$

$$\text{pH} = 5.48$$

### Example 8:

What is the pH of a 1.0 M solution of acetic acid? To what volume must 1 litre of the solution be diluted so that the pH of the resulting solution will be twice the original value?

Given:  $K_a = 1.8 \times 10^{-5}$ .

### Solution:

Let us first calculate  $\alpha$  using  $\alpha = \sqrt{\frac{K_a}{c}}$

$$\alpha = \sqrt{\frac{1.8 \times 10^{-5}}{1}} = 4.24 \times 10^{-3}$$

Since,  $\alpha$  is very much smaller than 0.1, so the assumption is valid.  $\therefore [\text{H}^+] = \alpha = 2.19 \times 10^{-3}$

$$\therefore [\text{H}^+] = \sqrt{K_a \times c} = \sqrt{1.8 \times 10^{-5} \times 1} = 4.24 \times 10^{-3}$$

$$\text{pH} = -\log(4.24 \times 10^{-3}) = 3 - \log 4.24 = 3 - 0.6273 = 2.37$$

Now pH on dilution =  $2 \times 2.37 = 4.74$

$$[\text{H}^+] = 1.8 \times 10^{-5} = c\alpha$$

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$$K_a = \frac{c\alpha^2}{1-\alpha} = \frac{c\alpha \times \alpha}{1-\alpha} = \frac{1.8 \times 10^{-5} \times \alpha}{1-\alpha} = 1.8 \times 10^{-5}$$

$$\frac{\alpha}{1-\alpha} = 1; \therefore \alpha = 0.5$$

$$[H^+] = \alpha c$$

$$c = \frac{[H^+]}{\alpha} = \frac{1.8 \times 10^{-5}}{0.5} = 3.6 \times 10^{-5} \text{ M}$$

Let the volume to which 1 ℓ of 1 M acetic acid is diluted be V, then

$$1 \times 1 = 3.6 \times 10^{-5} \times V$$

$$V = \frac{1 \times 1}{3.6 \times 10^{-5}} = \frac{10^5}{3.6} = 0.277 \times 10^5 = 2.77 \times 10^4 \text{ litres.}$$

You can notice that  $\alpha$  increases on dilution and it become considerable and cannot be ignored with respect to 1.

### Example 9:

20 ml of 0.2 M NaOH is added to 50 ml of 0.2 M acetic acid. What is the pH of the resulting solution? Calculate the additional volume of 0.2 M NaOH required making the solution of pH 4.74. The ionization constant of acetic acid is  $1.8 \times 10^{-5}$ .

### Solution:

20 ml of 0.2 M NaOH would react with 20 ml of 0.2 M acetic acid.

$$[\text{Acid}] = 30 \text{ ml of } 0.2 \text{ M present in } 70 \text{ ml} = \frac{30 \times 0.2}{70} = \frac{6}{70} \text{ mole}$$

$$[\text{Salt}] = 20 \text{ ml of } 0.2 \text{ M present in } 70 \text{ ml} = \frac{20 \times 0.2}{70} = \frac{4}{70} \text{ mole}$$

$$\text{p}K_a = -\log 1.8 \times 10^{-5} = 4.74$$

$$\text{pH} = \text{p}K_a + \log \frac{[\text{Salt}]}{[\text{Acid}]} = 4.74 + \log \frac{4}{70} \times \frac{70}{6}$$

$$\text{pH} = 4.74 + \log 0.66 = 4.74 - 0.18 = 4.56$$

To make a solution of pH = 4.74,  $[\text{Acid}] = [\text{Salt}]$

So 25 ml of 0.2 M NaOH must be added to 50 ml of 0.2 M acetic acid.

Additional volume of NaOH to be added =  $25 - 20 = 5 \text{ ml}$ .

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### Example 10:

A weak base, BOH is titrated with a strong acid HA. When 10 ml of HA is added, the pH of the solution is 10.2 and when 25 ml is added, the pH of the solution is 9.1. Calculate the volume of acid that would be required to reach equivalence point.

### Solution:

Let the molarity of HA be ' $M_2$ ' and the molarity and volume of weak base (BOH) are ' $M_1$ ' and ' $V_1$ ' respectively.

In first case,

	BOH	+	HA	→	BA	+	H <sub>2</sub> O
mmole before reaction	$M_1 V_1$		$10M_2$		0		0
mmole after reaction	$(M_1 V_1 - 10M_2)$		0		$10M_2$		$10M_2$

Since the solution (after addition of 10 ml of HA) contains weak base (BOH) and salt of its conjugate base (BA), the solution behaves like a basic buffer.

$$\therefore \text{pOH} = \text{pK}_b + \log \frac{[\text{Salt}]}{[\text{Base}]}$$

$$14 - 10.2 = \text{pK}_b + \log \frac{10M_2}{(M_1 V_1 - 10M_2)}$$

Dividing numerator and denominator of log term by  $M_2$  gives

$$\therefore 3.8 = \text{pK}_b + \log \frac{\frac{10M_2}{M_2}}{\left( \frac{M_1 V_1}{M_2} - \frac{10M_2}{M_2} \right)}$$

$$3.8 = \text{pK}_b + \log \frac{10}{V_2 - 10} \quad \dots\dots(i)$$

where  $V_2$  is the volume of acid required to get equivalence point (At equivalence point,  $M_1 V_1 = M_2 V_2$ )

In second case,

	BOH	+	HA	→	BA	+	H <sub>2</sub> O
mmole before reaction	$M_1 V_1$		$25M_2$		0		0
mmole after reaction	$(M_1 V_1 - 25M_2)$		0		$25M_2$		$25M_2$

$$14 - 9.1 = 4.9 = \text{pK}_b + \log \frac{25M_2}{(M_1 V_1 - 25M_2)}$$

Dividing numerator and denominator of log term by  $M_2$

## IONIC EQUILIBRIUM

$$4.9 = pK_b + \log \frac{25}{V_2 - 25} \quad \dots\dots(ii)$$

Subtracting equation (i) from (ii)

$$4.9 - 3.8 = 1.1 = \left( \log \frac{25}{V_2 - 25} \right) - \left( \log \frac{10}{V_2 - 10} \right)$$

$$\text{Taking antilog, } 12.58 = \frac{5V_2 - 50}{2V_2 - 50}$$

$$\therefore V_2 = 28.72 \text{ ml}$$

### Example 11:

The solubility product of calcium oxalate is  $2 \times 10^{-9}$  at  $25^\circ\text{C}$ . Calculate the solubility of calcium oxalate at this temperature. What will be its solubility in a 0.1 M solution of ammonium oxalate? Assume that ammonium oxalate is completely ionized in solution. Name the effect, which operates on addition of ammonium oxalate to calcium oxalate

### Solution:

The solubility product,  $K_{SP}$  of calcium oxalate is given by

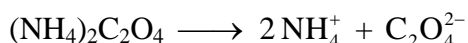
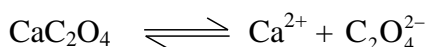
$$K_{SP} = [\text{Ca}^{2+}] [\text{C}_2\text{O}_4^{2-}] = 2 \times 10^{-9}$$

Let 's' be the solubility of calcium oxalate in mole litre<sup>-1</sup>.

$$s^2 = 2 \times 10^{-9}$$

$$s = \sqrt{2 \times 10^{-9}} = 4.472 \times 10^{-5} \text{ mole/l.}$$

Let the solubility of  $\text{CaC}_2\text{O}_4$  be  $s'$  in the presence of 0.1 M ammonium oxalate solution.



0.1 M

Since  $\text{CaC}_2\text{O}_4$  is sparingly soluble, the concentration of  $\text{C}_2\text{O}_4^{2-}$  derived from  $\text{CaC}_2\text{O}_4$  is negligible in comparison to 0.1.

$$K_{SP} = [\text{Ca}^{2+}] [\text{C}_2\text{O}_4^{2-}] = s' \times 0.1 = 2 \times 10^{-9}$$

$$s' = \frac{2 \times 10^{-9}}{0.1} = 2 \times 10^{-8} \text{ mole/l}$$

In the presence of ammonium oxalate, the solubility of  $\text{CaC}_2\text{O}_4$  drops from  $4.472 \times 10^{-5}$  to  $2 \times 10^{-8}$  mole/l. This effect is called common-ion effect.



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### Example 12:

What is the solubility of PbS (a) ignoring the hydrolysis of ions and (b) including the hydrolysis of ions (assume pH of the solution to be equal to 7)?

Given that  $K_{sp}(\text{PbS}) = 7.0 \times 10^{-29} \text{ M}^2$ ,  $K_{b_2}(\text{Pb}(\text{OH}^+)) = 1.5 \times 10^{-8} \text{ M}$ ,  $K_{a_1}(\text{H}_2\text{S}) = 1.1 \times 10^{-7} \text{ M}$

$K_{a_2}(\text{HS}^-) = 1.0 \times 10^{-14} \text{ M}$ .

### Solution:

Solubility ignoring hydrolysis

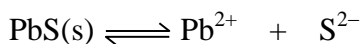
Let  $x'$  be the solubility of PbS ignoring hydrolysis, then

$$K_{sp}(\text{PbS}) = [\text{Pb}^{2+}][\text{S}^{2-}] = 7.0 \times 10^{-29} \text{ M}^2$$

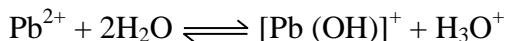
$$\text{Hence, } x'^2 = 7.0 \times 10^{-29} \text{ M}^2 \quad \text{or} \quad x' = 8.4 \times 10^{-15} \text{ M}$$

Solubility including hydrolysis

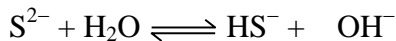
Let the solubility of PbS considering hydrolysis  $x$  moles/litre.



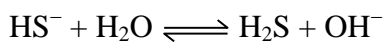
$$(x - y) \quad (x - z)$$



$$(x - y) \quad y \quad y$$



$$(x - z) \quad (z - a) \quad (z + a)$$



$$(z - a) \quad a \quad (z + a)$$

$$K_{sp}(\text{PbS}) = (x - y)(x - z) = 7 \times 10^{-29} \quad \dots\dots(i)$$

$$K_h(\text{Pb}^{2+}) = \frac{y^2}{(x - y)} = \frac{K_w}{K_{b_1}[(\text{Pb}(\text{OH})^+)]} = \frac{1 \times 10^{-14}}{1.5 \times 10^{-8}} = 6.7 \times 10^{-7} \text{ M} \quad \dots\dots(ii)$$

$$K_h(\text{S}^{2-}) = \frac{(z - a)(z + a)}{(x - z)} = \frac{K_w}{K_{a_2}} = \frac{1 \times 10^{-14}}{1 \times 10^{-14}} = 1 \text{ M} \quad \dots\dots(iii)$$

$$K_h(\text{HS}^-) = \frac{a(a + z)}{(z - a)} = \frac{K_w}{K_{a_1}} = \frac{1 \times 10^{-14}}{1.1 \times 10^{-7}} = 9.1 \times 10^{-8} \text{ M} \quad \dots\dots(iv)$$

Solving for  $x$ , we get

$$x = 1.0146 \times 10^{-10} \text{ M}$$

## IONIC EQUILIBRIUM

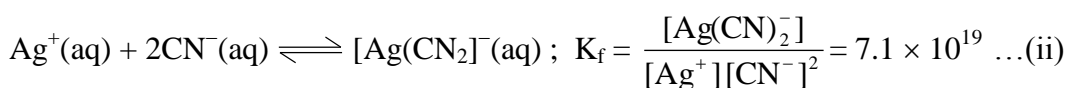
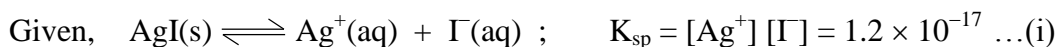
Thus, the solubility of PbS including hydrolysis is  $1.0146 \times 10^{-10}$  M. Comparing this value with that obtained after ignoring hydrolysis indicates that the solubility of PbS has been increased

$$\text{by a factor} = \frac{1.0146 \times 10^{-10}}{8.4 \times 10^{-15}} = 12078$$

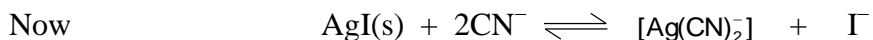
### Example 13:

Determine the number of mole of AgI which may be dissolved in 1.0 litre of 1.0 M  $\text{CN}^-$  solution. Given:  $K_{sp}$  for AgI and  $K_c$  for  $\text{Ag}(\text{CN})_2^-$  are  $1.2 \times 10^{-17} \text{ M}^2$  and  $7.1 \times 10^{19} \text{ M}^{-2}$  respectively.

### Solution:



Let 'x' mole of AgI be dissolved in  $\text{CN}^-$  solution, then



Mole before reaction                      1                      0                      0

Mole at equilibrium                      (1 - 2x)                      x                      x

By equations (i) and (ii),  $K_{eq} = K_{sp} \times K_f$

$$K_{eq} = \frac{[\text{Ag}(\text{CN})_2^-][\text{I}^-]}{[\text{CN}^-]^2} = 1.2 \times 10^{-17} \times 7.1 \times 10^{19}$$

$$K_{eq} = 8.52 \times 10^2 \quad \dots(iii)$$

$$\therefore K_{eq} = 8.52 \times 10^2 = \frac{x^2}{(1-2x)^2}$$

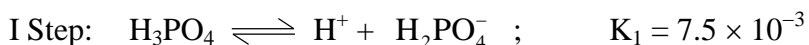
$$\text{or} \quad \frac{x}{1-2x} = 29.2$$

$$\therefore x = 0.49 \text{ mole.}$$

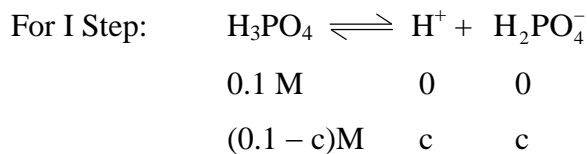
### Example 14:

Calculate the concentrations of all the species present in 0.1 M  $\text{H}_3\text{PO}_4$  solution. Given:  $K_1 = 7.5 \times 10^{-3}$ ,  $K_2 = 6.2 \times 10^{-8}$  and  $K_3 = 3.6 \times 10^{-13}$ .

### Solution:



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$$K_1 = \frac{[\text{H}^+][\text{H}_2\text{PO}_4^-]}{[\text{H}_3\text{PO}_4]} = \frac{c^2}{(0.1 - c)}$$

$$7.5 \times 10^{-3} = \frac{c^2}{(0.1 - c)}$$

Solving the quadratic equation,

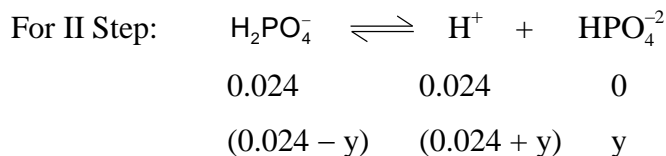
$$c = 0.024$$

$$\therefore [\text{H}^+] = 0.024 \text{ M}$$

$$\therefore [\text{H}_2\text{PO}_4^-] = 0.024 \text{ M}$$

$$[\text{H}_3\text{PO}_4] = 0.1 - 0.024 = 0.076 \text{ M}$$

The value of  $K_1$  is much larger than  $K_2$  and  $K_3$ . Also dissociation of II and III steps occurs in presence of  $\text{H}^+$  furnished in I step and thus, dissociation of II and III steps is further suppressed due to common ion effect.



The dissociation of  $\text{H}_2\text{PO}_4^-$  occurs in presence of  $[\text{H}^+]$  furnished in step I.

Thus, 
$$K_2 = \frac{[\text{H}^+][\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]}$$

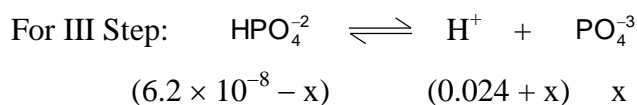
or 
$$6.2 \times 10^{-8} = \frac{(0.024 + y)y}{(0.024 - y)}$$

y is small  $\therefore 0.024 - y \approx 0.024$  and neglecting  $y^2$ .

$$6.2 \times 10^{-8} = \frac{0.024y}{0.024}$$

$$y = 6.2 \times 10^{-8}$$

or  $[\text{HPO}_4^{2-}] = K_2 = 6.2 \times 10^{-8} \text{ M}$



## IONIC EQUILIBRIUM

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$$K_3 = \frac{[H^+][PO_4^{-3}]}{[HPO_4^{-2}]} = \frac{(0.024 + x) \cdot x}{(6.2 \times 10^{-8} - x)}$$

Again neglecting  $x^2$  and assuming,  $6.2 \times 10^{-8} - x = 6.2 \times 10^{-8}$

$$\therefore 3.6 \times 10^{-13} = \frac{0.024x}{6.2 \times 10^{-8}}$$

$$\therefore [PO_4^{3-}] = x = \frac{3.6 \times 10^{-13} \times 6.2 \times 10^{-8}}{0.024} = 9.3 \times 10^{-19} \text{ M.}$$

### Example 15:

The pH of blood stream is maintained by a proper balance of  $H_2CO_3$  and  $NaHCO_3$  concentrations. What volume of 5 M  $NaHCO_3$  solution, should be mixed with 10 ml sample of blood, which is 2 M in  $H_2CO_3$  in order to maintain a pH of 7.4.  $K_a$  for  $H_2CO_3$  in blood is  $7.8 \times 10^{-7}$ ?

### Solution:

Let the volume of 5 M  $NaHCO_3$  solution added be x ml.

Number of millimoles of  $NaHCO_3 = 5x$

Number of millimoles of  $H_2CO_3 = 10 \times 2 = 20$

For the acidic buffer,  $pH = pK_a + \log \frac{[NaHCO_3]}{[H_2CO_3]}$

$$7.4 = -\log(7.8 \times 10^{-7}) + \log \frac{5x}{20}$$

On solving,  $x = 78.37 \text{ ml}$

$\therefore$  Volume of  $NaHCO_3$  solution required = 78.37 ml.