

## SIMULTANEOUS EQUILIBRIUM

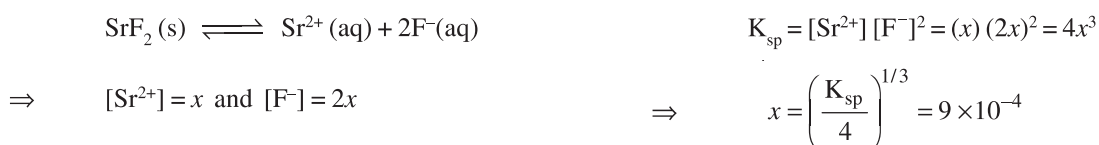
## Section - 7

When two salts having a common ion (either cation or anion) are together in water, then their respective solubilities are not independent of each other.

**Illustrating the concept :**

Consider a solution containing two salts:  $\text{CaF}_2$  ( $K_{sp} = 3.4 \times 10^{-11}$ ) and  $\text{SrF}_2$  ( $K_{sp} = 2.9 \times 10^{-9}$ ). Compare their  $K_{sp}$  values. Let us assume that most of  $\text{F}^-$  ion concentration in the saturated solution is from  $\text{SrF}_2$ , as its  $K_{sp}$  is much higher than that of  $\text{CaF}_2$ . It means that first  $\text{SrF}_2$  will establish its equilibrium (as if there is no  $\text{CaF}_2$ ), then  $\text{CaF}_2$  will dissolve in presence of ions furnished only by  $\text{SrF}_2$ .

Let the solubility of  $\text{SrF}_2$  be  $x$  mol/L.



Now the solubility of  $\text{CaF}_2$  is determined in presence of  $9 \times 10^{-4} \text{ M F}^-$  ions. It means neglect the contribution of  $\text{F}^-$  ions from  $\text{CaF}_2$ .

$$K_{sp} = [\text{Ca}^{2+}][\text{F}^-]^2 \Rightarrow [\text{Ca}^{2+}] = \frac{K_{sp}}{[\text{F}^-]^2} = \frac{3.4 \times 10^{-11}}{(2 \times 9 \times 10^{-4})^2} = 1.0 \times 10^{-5} \text{ M}$$

Hence the solubility of  $\text{CaF}_2$  is  $1.0 \times 10^{-5} \text{ mol/L}$ .

**Note :** Let us check our assumption.  $\text{F}^-$  ions from  $\text{CaF}_2$  is twice the amount of  $\text{Ca}^{2+}$  ions i.e.,  $2.0 \times 10^{-5} \text{ M}$ , whereas,  $\text{F}^-$  ions from  $\text{SrF}_2$  is  $2 \times 9.0 \times 10^{-4} \text{ i.e. } 1.8 \times 10^{-3} \text{ M}$ , which is much higher than  $2.0 \times 10^{-5} \text{ M}$ .

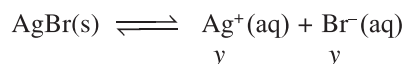
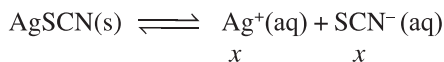
**Illustration - 23** Calculate the simultaneous solubilities of  $\text{AgSCN}$  and  $\text{AgBr}$ .

$$K_{sp}(\text{AgSCN}) = 1.0 \times 10^{-12} ; \quad K_{sp}(\text{AgBr}) = 5.0 \times 10^{-13}$$

**SOLUTION :**

In this case, please note that the  $K_{sp}$  values of two salts are very similar. So the concentration of  $\text{Ag}^+$  ions (the common ion) can not be calculated from a single salt alone and we have to consider the equilibrium of the two salts simultaneously.

Let the simultaneous solubilities of  $\text{AgSCN}$  and  $\text{AgBr}$  be  $x$  and  $y$  respectively in mol/L.



At equilibrium:

$$[\text{Ag}^+] = x + y ; \quad [\text{SCN}^-] = x ; \quad [\text{Br}^-] = y$$

$$[\text{Ag}^+][\text{Br}^-] = K_{sp} \text{ AgBr}$$

$$\text{and } [\text{Ag}^+][\text{SCN}^-] = K_{sp} \text{ AgSCN}$$

$$\text{Note that : } [\text{Ag}^+] = [\text{Br}^-] + [\text{SCN}^-]$$

[This is an Electrical charge neutrality equation]

$$[\text{Ag}^+] = \frac{K_{sp} \text{ AgBr}}{[\text{Br}^-]} + \frac{K_{sp} \text{ AgSCN}}{[\text{Ag}^+]}$$

$$\begin{aligned} \Rightarrow [\text{Ag}^+] &= \sqrt{K_{sp} \text{ AgBr} + K_{sp} \text{ AgSCN}} \\ &= x + y = 1.22 \times 10^{-6} \quad \dots \text{(i)} \end{aligned}$$

$$\text{Also, } \frac{[\text{Br}^-]}{[\text{SCN}^-]} = \frac{y}{x} = \frac{K_{sp} \text{ AgBr}}{K_{sp} \text{ AgSCN}} = 0.5 \quad \dots \text{(ii)}$$

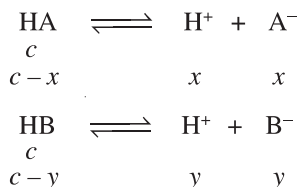
Using (i) and (ii), we get :

$$x = 8.0 \times 10^{-7} ; \quad y = 4.0 \times 10^{-7}$$

**Illustration - 24** Two weak monobasic organic acids HA and HB have dissociation constants as  $3.0 \times 10^{-5}$  and  $1.5 \times 10^{-5}$  respectively at  $25^\circ\text{C}$ . If 500 ml of 1 M solutions of each of these two acids are mixed to produce 1 litre of mixed acid solution, what is the pH of the resulting solution ?

**SOLUTION :**

Note that  $K_a$  of two acids is nearly same. In such cases, we have to consider  $\text{H}^+$  from both HA and HB simultaneously. The concentration of HA and HB in the mixture = 0.5 M [equal volumes are mixed] =  $c$  M



Now,  $[\text{H}^+]_{\text{final}} = [\text{H}^+]_{\text{from HA}} + [\text{H}^+]_{\text{from HB}}$

$$\Rightarrow K_{a\text{HA}} = \frac{(x+y)x}{c-x} \quad \text{and} \quad K_{a\text{HB}} = \frac{(x+y)y}{c-y}$$

As  $K_a$  of both acid  $\sim 10^{-5}$  and  $\text{H}^+$  from one acid acts as common ion for other's dissociation,  $x$  and  $y$  are very less as compared to  $c$ .

$$\Rightarrow c-x \approx c \quad \text{and} \quad c-y \approx c$$

$$\Rightarrow K_{a(\text{HA})} \approx \frac{(x+y)x}{c} \quad \text{and} \quad K_{a(\text{HB})} \approx \frac{(x+y)y}{c}$$

Divide the two expressions to get :

$$\frac{2}{1} = \frac{x}{y} \Rightarrow x = 2y$$

$$\text{Substitute for } y = \frac{1}{2}x \text{ in } K_{a(\text{HA})} = \frac{x^2 + xy}{c}$$

$$\Rightarrow 3.0 \times 10^{-5} = \frac{x^2 + 0.5x^2}{0.5} \Rightarrow x = \sqrt{10} \times 10^{-3} \text{ M}$$

$$\text{and } y = \frac{\sqrt{10}}{2} \times 10^{-3} \text{ M}$$

$$[\text{H}^+] = x + y = \frac{3\sqrt{10}}{2} \times 10^{-3} \text{ M}$$

$$\text{pH} = -\log_{10} \left( \frac{3\sqrt{10}}{2} \times 10^{-3} \right) \Rightarrow \text{pH} = 2.32$$

**Illustration - 25** Determine the solubility of AgCN in a buffer solution maintained at  $\text{pH} = 3$ .

$$K_{sp}(\text{AgCN}) = 2.0 \times 10^{-16} ; K_a(\text{HCN}) = 6.0 \times 10^{-10}$$

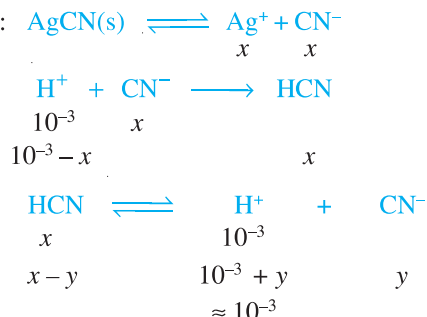
**SOLUTION :**

AgCN is a sparingly soluble salt in aqueous medium.



Let the solubility of AgCN be  $x$  M. Thus,  $[\text{Ag}^+] = x$  M and  $[\text{CN}^-] = x$  M from salt but it will not be equal to  $x$  finally.

The  $\text{CN}^-$  ions will react with  $\text{H}^+$  in the solution to form HCN (a weakly dissociated acid) and we have to assume that in solution,  $[\text{CN}^-] = y$  M finally which will be decided by the dissociation of HCN as explained below:



We have two equations now :

$$K_{sp}(\text{AgCN}) = [\text{Ag}^+][\text{CN}^-] = xy = 2 \times 10^{-16}$$

$$\text{and } K_a(\text{HCN}) = \frac{[\text{H}^+][\text{CN}^-]}{[\text{HCN}]} = \frac{10^{-3}y}{x-y} = 6 \times 10^{-10}$$

Solve the equations to get :

$$x = [\text{Ag}^+] = \sqrt{\frac{K_{sp}}{K_a} ([\text{H}^+] + K_a)} = 1.82 \times 10^{-5} \text{ M}$$

Note that in the solution :

$$[\text{Ag}^+] = [\text{CN}^-] + [\text{HCN}]$$

(Electrical charge neutrality equation)

**Note :** In this example, since the dissociation constant of acid is very low and pH of the solution is fairly high, we could have assumed that  $x - y \approx x$ . You can check the same by comparing  $[\text{H}^+]$  and  $K_a$  in the expression for  $x$ .

**Illustration - 26** How much AgBr could dissolve in 1.0 L of 0.4 M  $\text{NH}_3$ ? Assume that  $\text{Ag}(\text{NH}_3)_2^+$  is the only complex formed. Given: The dissociation constant for  $\text{Ag}(\text{NH}_3)_2^+ \rightleftharpoons \text{Ag}^+ + 2\text{NH}_3$ ;  $K_d = 6.0 \times 10^{-8}$  and  $K_{sp}(\text{AgBr}) = 5.0 \times 10^{-13}$ .

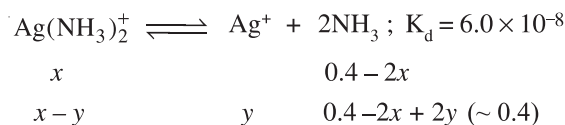
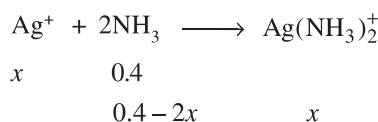
**SOLUTION :**

Let solubility of AgBr be  $x$  M. Thus,  $[\text{Br}^-] = x$  M but  $[\text{Ag}^+] \neq x$  M since it will react with  $\text{NH}_3$  to form a complex and thus, its concentration will be decided by the dissociation of the complex. So, let  $[\text{Ag}^+] = y$  M.



$$\Rightarrow K_{sp} = [\text{Ag}^+][\text{Br}^-] = yx = 5.0 \times 10^{-13}$$

Since the formation constant ( $K_f$ ) of the complex is very high, assume that whole of  $\text{Ag}^+$  formed is consumed.



$$K_d = \frac{[\text{Ag}^+][\text{NH}_3]^2}{[\text{Ag}(\text{NH}_3)_2^+]} = \frac{y(0.4 - 2x + 2y)^2}{x - y} = 6 \times 10^{-8}$$

Assuming  $x - y \approx x$  since  $K_d$  is low and  $x \ll 0.4$ , we get :

$$K_d = \frac{y(0.4)^2}{x}$$

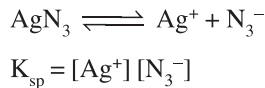
Solving for  $x$  :  $x = 1.15 \times 10^{-3}$  M

(Verify the approximation yourself).

**Illustration - 27**  $\text{HN}_3$  (hydroazotic acid) is a weak acid dissociating as:  $\text{HN}_3 \rightleftharpoons \text{H}^+ + \text{N}_3^-$ . Find the concentration of  $\text{Ag}^+$  ions, if excess of solid  $\text{AgN}_3$  is added to a solution maintained at  $\text{pH} = 4$ . The ionisation constant  $K_a$  of  $\text{HN}_3$  is  $2.0 \times 10^{-5}$ . The solubility of  $\text{AgN}_3$  in pure water is found to be  $5.4 \times 10^{-3}$  M at  $25^\circ\text{C}$ .

**SOLUTION :**

$\text{AgN}_3$  is a sparingly soluble salt, dissociating in water as :



$$K_{sp} = [\text{Ag}^+][\text{N}_3^-]$$

Since solubility of  $\text{AgN}_3$  in water is  $5.4 \times 10^{-3}$ ,  $K_{sp} = (5.4 \times 10^{-3})^2 = 2.92 \times 10^{-5}$

Now we have to find the solubility of  $\text{AgN}_3$  in solution having  $\text{pH} = 4$ .

Let solubility of  $\text{AgN}_3$  be  $x$  M at  $\text{pH} = 4$ .

$$\Rightarrow [\text{Ag}^+] = x \text{ M, but } [\text{N}_3^-] \neq x \text{ M}$$

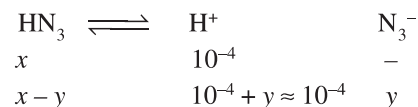
( $[\text{N}_3^-]$  will be decided by dissociation of  $\text{HN}_3$ ).

Let  $[\text{N}_3^-] = y$  M

First, assume that whole of  $\text{N}_3^-$  ( $x$  M) formed from  $\text{AgN}_3$  reacts with  $\text{H}^+$  ions to form  $\text{HN}_3$ .

$$\Rightarrow [\text{HN}_3] = x \text{ M}$$

Now  $\text{HN}_3$  dissociates as follows :



[As  $\text{pH}$  is maintained at 4 hence  $[\text{H}^+] = 10^{-4}$  M]

Now we have a simultaneous equilibrium in aqueous solution involving dissociation of  $\text{AgN}_3$  and  $\text{HN}_3$ .

$$K_{sp} \text{ of } \text{AgN}_3 = [\text{Ag}^+][\text{N}_3^-] = xy \quad \dots \text{(i)}$$

$$K_a \text{ of } \text{HN}_3 = \frac{[\text{H}^+][\text{N}_3^-]}{[\text{HN}_3]} = \frac{[\text{H}^+]y}{(x-y)} \quad \dots \text{(ii)}$$

Solving (i) and (ii) simultaneously, we have :

$$x = [\text{Ag}^+] = \sqrt{\frac{K_{sp}}{K_a} ([\text{H}^+] + K_a)}$$

Substitute the values of  $K_{sp}$ ,  $K_a$  and  $[\text{H}^+]$  to get  $x = 0.0132 \text{ mol/L}$

**Note :** In this example, since the dissociation constant of acid is quite high and  $\text{pH}$  of the solution is quite low, we can not assumed that  $x - y \approx x$ . You can check the same by comparing  $[\text{H}^+]$  and  $K_a$  in the expression for  $x$ .