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: CaF_2($K_{sp} = 3.4 \times 10^{-11}$) and SrF_2 ($K_{sp} = 2.9 \times 10^{-9}$). Compare their K_{sp} values. Let us assume that most of F^- ion concentration in the saturated solution is from SrF_2, as its K_{sp} is much higher than that of CaF_2. It means that first SrF_2 will establish its equilibrium (as if there is no CaF_2), then CaF_2 will dissolve in presence of ions furnished only by SrF_2.

Let the solubility of SrF_2 be x mol/L.

$$SrF_2\,(s) \rightleftharpoons Sr^{2+}\,(aq) + 2F^-(aq) \qquad K_{sp} = [Sr^{2+}]\,[F^-]^2 = (x)\,(2x)^2 = 4x^3$$

$$\Rightarrow \quad [Sr^{2+}] = x \text{ and } [F^-] = 2x \qquad \Rightarrow \quad x = \left(\frac{K_{sp}}{4}\right)^{1/3} = 9\times10^{-4}$$

Now the solubility of CaF_2 is determined in presence of 9×10^{-4} M F^- ions. It means neglect the contribution of F^- ions from CaF_2.

$$K_{sp} = [Ca^{2+}]\,[F^-]^2 \qquad \Rightarrow \qquad [Ca^{2+}] = \frac{K_{sp}}{[F^-]^2} = \frac{3.4\times10^{-11}}{(2\times9\times10^{-4})^2} = 1.0\times10^{-5}\ \text{M}$$

Hence the solubility of CaF_2 is 1.0×10^{-5} mol/L.

Note : Let us check our assumption. F^- ions from CaF_2 is twice the amount of Ca^{2+} ions i.e., 2.0×10^{-5} M, whereas, F^- ions from SrF_2 is $2 \times 9.0\times10^{-4}$ i.e. 1.8×10^{-3}M, which is much higher than 2.0×10^{-5} M.

Illustration - 23 *Calculate the simultaneous solubilities of AgSCN and AgBr.*

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

SOLUTION :

In this case, please note that the K_{sp} values of two salts are very similar. So the concentration of 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 AgSCN and AgBr be x and y respectively in mol/L.

$$\underset{}{AgSCN(s)} \rightleftharpoons \underset{x}{Ag^+(aq)} + \underset{x}{SCN^-(aq)}$$

$$AgBr(s) \rightleftharpoons \underset{y}{Ag^+(aq)} + \underset{y}{Br^-(aq)}$$

At equilibrium:

$$[Ag^+] = x + y\,; \quad [SCN^-] = x\,; \quad [Br^-] = y$$

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

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

Note that : $\quad [Ag^+] = [Br^-] + [SCN^-]$

[This is an Electrical charge neutrality equation]

$$[Ag^+] = \frac{K_{sp\,AgBr}}{[Ag^+]} + \frac{K_{sp\,AgSCN}}{[Ag^+]}$$

$$\Rightarrow \quad [Ag^+] = \sqrt{K_{sp\,AgBr} + K_{sp\,AgSCN}}$$

$$= x + y = 1.22\times10^{-6} \qquad \ldots\text{(i)}$$

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

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

$$x = 8.0\times10^{-7}\,; \quad y = 4.0\times10^{-7}$$

Illustration - 24 *Two weak monobasic organic acids HA and HB have dissociation constants as* 3.0×10^{-5} *and* 1.5×10^{-5} *respectively at 25°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 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

$$\begin{array}{lcccc} HA & \rightleftharpoons & H^+ & + & A^- \\ c & & & & \\ c-x & & x & & x \end{array}$$

$$\begin{array}{lcccc} HB & \rightleftharpoons & H^+ & + & B^- \\ c & & & & \\ c-y & & y & & y \end{array}$$

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

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

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

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

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

Divide the two expressions to get :

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

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

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

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

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

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

Illustration - 25 *Determine the solubility of AgCN in a buffer solution maintained at pH = 3.*
K_{sp} *(AgCN)* $= 2.0 \times 10^{-16}$; K_a*(HCN)* $= 6.0 \times 10^{-10}$

SOLUTION :

AgCN is a sparingly soluble salt in aqueous medium.

$$AgCN(s) \rightleftharpoons Ag^+(aq) + CN^-(aq)$$

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

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

$$\begin{array}{lccc} AgCN(s) & \rightleftharpoons & Ag^+ & + CN^- \\ & & x & x \end{array}$$

$$\begin{array}{lcccc} H^+ & + & CN^- & \longrightarrow & HCN \\ 10^{-3} & & x & & \\ 10^{-3}-x & & & & x \end{array}$$

$$\begin{array}{lcccc} HCN & \rightleftharpoons & H^+ & + & CN^- \\ x & & 10^{-3} & & \\ x-y & & 10^{-3}+y & & y \\ & & \approx 10^{-3} & & \end{array}$$

We have two equations now :

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

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

Solve the equations to get :

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

Note that in the solution :

$[Ag^+] = [CN^-] + [HCN]$

(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 ≈ x. You can check the same by comparing $[H^+]$ and K_a in the expression for x.

Illustration - 26 *How much AgBr could dissolve in 1.0 L of 0.4 M NH_3 ? Assume that $Ag(NH_3)_2^+$ is the only complex formed. Given: The dissociation constant for $Ag(NH_3)_2^+ \rightleftharpoons Ag^+ + 2NH_3$; $K_d = 6.0 \times 10^{-8}$ and $K_{sp}(AgBr) = 5.0 \times 10^{-13}$.*

SOLUTION :

Let solubility of AgBr be x M. Thus, $[Br^-] = x$ M but $[Ag^+] \neq x$ M since it will react with NH_3 to form a complex and thus, its concentration will be decided by the dissociation of the complex. So, let $[Ag^+] = y$M.

$$AgBr(s) \rightleftharpoons Ag^+(aq) + Br^-(aq)$$

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

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

$$Ag^+ \; + \; 2NH_3 \longrightarrow Ag(NH_3)_2^+$$

Ag^+	$2NH_3$	$Ag(NH_3)_2^+$
x	0.4	
	$0.4 - 2x$	x

$$Ag(NH_3)_2^+ \rightleftharpoons Ag^+ + 2NH_3 \; ; \; K_d = 6.0 \times 10^{-8}$$

$Ag(NH_3)_2^+$	Ag^+	$2NH_3$
x		$0.4 - 2x$
$x - y$	y	$0.4 - 2x + 2y$ (~ 0.4)

$$K_d = \frac{[Ag^+][NH_3]^2}{[Ag(NH_3)_2^+]} = \frac{y(0.4 - 2x + 2y)^2}{x - y} = 6 \times 10^{-8}$$

Assuming $x - y \approx x$ since K_d is low and $x << 0.4$, 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 *HN_3 (hydroazoic acid) is a weak acid dissociating as: $HN_3 \rightleftharpoons H^+ + N_3^-$. Find the concentration of Ag^+ ions, if excess of solid AgN_3 is added to a solution maintained at pH = 4. The ionisation constant K_a of HN_3 is 2.0×10^{-5}. The solubility of AgN_3 in pure water is found to be 5.4×10^{-3} M at 25°C.*

SOLUTION :

AgN_3 is a sparingly soluble salt, dissociating in water as : $\quad AgN_3 \rightleftharpoons Ag^+ + N_3^-$

$$K_{sp} = [Ag^+][N_3^-]$$

Since solubility of AgN_3 in water is 5.4×10^{-3}, $K_{sp} = (5.4 \times 10^{-3})^2 = 2.92 \times 10^{-5}$

Now we have to find the solubility of AgN_3 in solution having pH = 4.

Let solubility of AgN_3 be x M at pH = 4.

$\Rightarrow \quad [Ag^+] = x$ M, but $[N_3^-] \neq x$ M

($[N_3^-]$ *will be decided by dissociation of* HN_3).

Let $[N_3^-] = y$ M

First, assume that whole of N_3^- (x M) formed from AgN_3 reacts with H^+ ions to form HN_3.

$\Rightarrow \quad [HN_3] = x$ M

Now HN_3 dissociates as follows :

HN_3	$\rightleftharpoons$ H^+	N_3^-
x	10^{-4}	–
$x - y$	$10^{-4} + y \approx 10^{-4}$	y

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

Now we have a simultaneous equilibrium in aqueous solution involving dissociation of AgN_3 and HN_3.

$$K_{sp} \text{ of } AgN_3 = [Ag^+][N_3^-] = xy \qquad \ldots (i)$$

$$K_a \text{ of } HN_3 = \frac{[H^+][N_3^-]}{[HN_3]} = \frac{[H^+]\,y}{(x - y)} \qquad \ldots (ii)$$

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

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

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

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