

# Ionic Equilibrium

## Solved Examples

### JEE Main/Boards

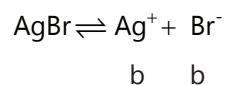
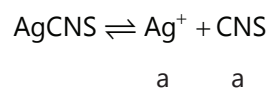
**Example 1:** Calculate simultaneous solubility of AgCNS and AgBr in a solution of water  $K_{sp}$  of AgCNS =  $1 \times 10^{-12}$ ,  $K_{sp}$  of AgBr =  $5 \times 10^{-13}$ .

**Sol:** For solution containing common ion, solubility and solubility product are related by following expression.

$$K_{sp} = S(S+c)$$

By taking the ratios of solubility product of two solutions, solubility can be determined.

Let the solubility of AgCNS and AgBr in water be  $a$  and  $b$  respectively.



$[\text{Ag}^+] = a + b$ ,  $[\text{CNS}^-] = a$  and

$$[\text{Br}^-] = b$$

$$K_{sp} \text{AgCNS} = [\text{Ag}^+][\text{CNS}^-] = a(a + b)$$

$$1 \times 10^{-12} = a(a + b) \quad \dots \text{(i)}$$

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

$$5 \times 10^{-13} = b(a + b) \quad \dots \text{(ii)}$$

Dividing eq. (i) by (ii),

$$\frac{1 \times 10^{-12}}{5 \times 10^{-13}} = \frac{a}{b}$$

$$2 = \frac{a}{b} \text{ or } a = 2b$$

Putting the value of  $a$  in eq. (i).

$$6b^2 = 1 \times 10^{-12}$$

$$b^2 = \frac{1}{6} \times 10^{-12}$$

$$b = 4.08 \times 10^{-7} \text{ mol L}^{-2}$$

$$a = 2 \times 4.08 \times 10^{-7} = 8.16 \times 10^{-7} \text{ mol L}^{-1}$$

**Example 2:**  $\text{MgSO}_4$  gives a precipitate with  $\text{NH}_4\text{OH}$  but not with  $\text{NH}_4\text{Cl}$  and  $\text{NH}_4\text{OH}$ . Why?

**Sol:** No doubt  $\text{NH}_4\text{OH}$  is weak base but it provides appreciable  $\text{OH}^-$  ion to exceed the product of ionic concentration of  $\text{Mg}^{2+}$  and  $\text{OH}^-$  than their  $K_{sp}$  and thus  $\text{MgSO}_4$  is precipitated out as  $\text{Mg}(\text{OH})_2$ . On the other hand the dissociation of  $\text{NH}_4\text{OH}$  is suppressed in presence of  $\text{NH}_4\text{Cl}$  and thus  $[\text{OH}^-]$  diminishes to the extent that  $[\text{Mg}^{2+}][\text{OH}^-]^2 < K_{sp}$ . Thus,  $\text{MgSO}_4$  is not precipitated.

**Example 3:** An aqueous solution contains 0.1 M of  $\text{Ba}^{2+}$  and 0.1 M  $\text{Ca}^{2+}$ . Calculate the maximum concentration of  $\text{Na}_2\text{SO}_4$  at which one of them is completely precipitated almost completely. What % of that ion is precipitated?

$$K_{sp} \text{ of } \text{BaSO}_4 = 1.5 \times 10^{-9};$$

$$K_{sp} \text{ of } \text{CaSO}_4 = 2 \times 10^{-4}.$$

**Sol:**  $[\text{SO}_4^{2-}]$  needed for precipitation of  $[\text{Ba}^{2+}]$  as  $\text{BaSO}_4$

$$= \frac{K_{sp}}{[\text{Ba}^{2+}]} = \frac{1.5 \times 10^{-9}}{0.1} = 1.5 \times 10^{-8}$$

$[\text{SO}_4^{2-}]$  needed for precipitation of  $[\text{Ca}^{2+}]$  as  $\text{CaSO}_4$

$$= \frac{2 \times 10^{-4}}{0.1} = 2 \times 10^{-3}.$$

Thus,  $[\text{SO}_4^{2-}]$  required for precipitation of  $\text{BaSO}_4$  is less and thus  $\text{BaSO}_4$  will precipitate first. The precipitation of  $\text{BaSO}_4$  will start when  $[\text{Na}_2\text{SO}_4]$  is  $1.5 \times 10^{-8}$  and will be maximum when  $[\text{Na}_2\text{SO}_4]$  is  $2 \times 10^{-3}$ .

Thus, maximum  $[\text{Na}_2\text{SO}_4]$  required for precipitation of  $\text{Ba}^{2+} = 2 \times 10^{-3}$  M. At this conc, of  $\text{SO}_4^{2-}$ ,  $[\text{Ba}^{2+}]$  left in solution is

$$[\text{Ba}^{2+}]_{\text{left}} = \frac{K_{sp}}{[\text{SO}_4^{2-}]} = \frac{1.5 \times 10^{-9}}{2 \times 10^{-3}} = 7.5 \times 10^{-7}$$

$$\therefore \% \text{ of } \text{Ba}^{2+} \text{ left} = \frac{7.5 \times 10^{-7} \times 100}{0.1} = 7.5 \times 10^{-4}\%$$

$\therefore$  % of  $\text{Ba}^{2+}$  precipitated

$$= 100 - 7.5 \times 10^{-4} = 99.9992\%$$

**Example 4:** Will a precipitate of  $\text{Mg}(\text{OH})_2$  be formed in a 0.001 M solution of  $\text{Mg}(\text{NO}_3)_2$ , if the pH of solution is adjusted to 9?

$$K_{sp} \text{ of } \text{Mg}(\text{OH})_2 = 8.9 \times 10^{-12}.$$

**Sol:** If  $K_{sp}$  of  $\text{Mg}(\text{OH})_2 > K_{sp}$  of  $\text{Mg}(\text{OH})_2$  in solution, precipitation will not occur.

If  $K_{sp}$  of  $\text{Mg}(\text{OH})_2 < K_{sp}$  of  $\text{Mg}(\text{OH})_2$  in solution, precipitation will occur.

$$\text{Given. pH} = 9; \therefore [\text{H}^+] = 10^{-9}$$

$$\text{or } [\text{OH}^-] = 10^{-5}$$

$$0.001 \text{ M } \text{Mg}(\text{NO}_3)_2 \text{ is present in a solution of } [\text{OH}^-] = 10^{-5}$$

Then product of ionic concentration for  $\text{Mg}(\text{OH})_2$

$$= [\text{Mg}^{2+}][\text{OH}^-]^2$$

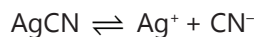
$$= [0.001][10^{-5}]^2$$

$$= 10^{-3} < K_{sp}, \text{ i. e., } 8.9 \times 10^{-12}$$

Therefore,  $\text{Mg}(\text{OH})_2$  will not precipitate out.

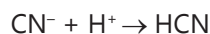
**Example 5:** Calculate the solubility of  $\text{AgCN}$  in a buffer solution of pH = 3. Given  $K_{sp}$  of  $\text{AgCN} = 1.2 \times 10^{-16}$  and  $K_a$  for  $\text{HCN} = 4.8 \times 10^{-10}$ .

**Sol:** Solution Let solubility of  $\text{AgCN}$  be a mol litre<sup>-1</sup>



a a (After reaction)

However, the  $\text{CN}^-$  formed will react with  $\text{H}^+$  to form  $\text{HCN}$



a  $10^{-3}$  (Before reaction)

0  $10^{-3}$  a (After reaction)

(buffer)

$$\therefore [\text{Ag}^+] = a \text{ and } [\text{HCN}] = a$$

Since  $\text{HCN}$  is weak acid and has low degree of dissociation. Also its dissociation is suppressed in presence of  $[\text{H}^+]$ . Thus

Now  $\text{HCN} \rightleftharpoons \text{H}^+ + \text{CN}^-$

$$\therefore \frac{[\text{CN}^-][\text{H}^+]}{[\text{HCN}]} = K_a$$

$$\text{or } [\text{CN}^-] = \frac{K_a[\text{HCN}]}{[\text{H}^+]} = \frac{a \times (4.8 \times 10^{-10})}{10^{-3}}$$

Now for  $\text{AgCN}(s) = \text{aq.} \rightleftharpoons \text{Ag}^+ + \text{CN}^-$

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

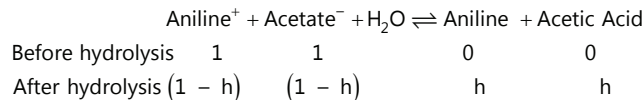
$$1.2 \times 10^{-16} = \frac{a \times a \times 4.8 \times 10^{-10}}{10^{-3}}$$

$$\therefore a^2 = \frac{1.2 \times 10^{-16} \times 10^{-3}}{4.8 \times 10^{-10}}$$

$$\therefore a = 1.58 \times 10^{-5} \text{ mol litre}^{-1}$$

**Example 6:** The dissociation constant for aniline, acetic acid and water at 25 C are  $3.83 \times 10^{-10}$ ,  $1.75 \times 10^{-5}$  and  $1.008 \times 10^{-14}$  respectively. Calculate degree of hydrolysis of aniline acetate in a deci normal solution. Also report its pH.

**Sol:**



Let concentration of salt be  $c$  mol litre<sup>-1</sup>

$$\therefore K_H = \frac{[\text{Aniline}][\text{Acetic acid}]}{[\text{Aniline}^+][\text{Acetate}^{-1}]} = \frac{ch \cdot ch}{c(1-h)c(1-h)}$$

$$K_H = \frac{h^2}{(1-h)^2} \quad \text{or} \quad \frac{h}{1-h} = \sqrt{K_H} = \sqrt{\frac{K_w}{K_a \times K_b}}$$

$$= \sqrt{\frac{1.008 \times 10^{-14}}{1.75 \times 10^{-5} \times 3.83 \times 10^{-10}}}$$

$$\therefore h = 54.95\%$$

$$\text{Also, pH} = \frac{1}{2} [\log K_b - \log K_w - \log K_a]$$

$$= \frac{1}{2} \log [3.83 \times 10^{-10}] - \log [1.008 \times 10^{-14}]$$

$$[-\log [1.75 \times 10^{-5}]] = 4.6683$$

If  $K_H = h^2$  is assumed (assuming  $1 - h \approx 1$ ), the value of  $h$  comes greater than 1 which is not possible and thus  $1 - h$  should not be neglected.

**Example 7:** A solution has 0.05M Mg<sup>2+</sup> and 0.05M NH<sub>3</sub>. Calculate the concentration of NH<sub>4</sub>Cl required to prevent the formation of Mg(OH)<sub>2</sub> in solution.

$$K_{sp} \text{ of Mg(OH)}_2 = 9.0 \times 10^{-12} \text{ and}$$

$$K_b \text{ of NH}_3 = 1.8 \times 10^{-5}$$

**Sol:** Suppose  $V$  mL of solution containing 0.1 M Mg<sup>2+</sup> and 0.8 M NH<sub>4</sub>Cl. Now  $V$  mL of NH<sub>3</sub> of a M is added to it in order to have just precipitation of Mg(OH)<sub>2</sub>, then

$$[\text{Mg}^{2+}][\text{OH}^-]^2 = K_{sp} \text{Mg(OH)}_2$$

$$\text{or} \left[ \frac{0.1 \times V}{2V} \right] [\text{OH}^-]^2 = 1.4 \times 10^{-5}$$

$$\left[ \therefore [\text{Mg}^{2+}] = \frac{\text{Milli moles}}{\text{Total Volume}} \right]$$

$$\therefore [\text{OH}^-] = 1.67 \times 10^{-5} \text{M}$$

The solution must therefore, contain [OH<sup>-</sup>] equal to =  $1.67 \times 10^{-5} \text{M}$ . Which are obtained by buffer solution of NH<sub>3</sub> and NH<sub>4</sub>Cl

$$\therefore -\log \text{OH} = -\log K_b + \log \frac{[\text{Salt}]}{[\text{Base}]}$$

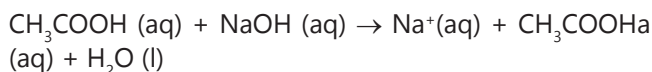
$$\text{or} -\log [1.67 \times 10^{-5}]$$

$$= -\log [1.8 \times 10^{-5}] + \log \frac{(0.8 \times V) / 2V}{(a \times V) / 2V}$$

$$\therefore a = 0.7421 \text{ M}$$

$$\therefore [\text{NH}_3] \text{ in solution} = \frac{0.7421 \times V}{2V} = 0.3710 \text{ M.}$$

**Example 8:** Calculate the molarity of an acetic acid solution if 34.57 mL of this solution are needed to neutralize 25.19 mL of 0.1025 M sodium hydroxide



**Sol: Strategy:**

1. Figure out how many moles of the titrant (in this case, the base) were needed.

$$25.19 \text{ mL} \times \frac{1 \text{ L}}{1000 \text{ mL}} = 0.02519 \text{ L}$$

$$0.02519 \text{ L} \times \frac{0.1025 \text{ mol}}{1 \text{ L}} = 0.002582 \text{ mol NaOH}$$

2. Use the balanced chemical equation to calculate the moles of analyte (in this case, the acid) present. 0.002582 mol

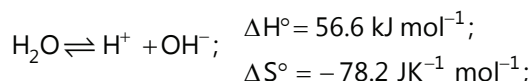
$$\text{NaOH} \times \frac{1 \text{ mol CH}_3\text{COOH}}{1 \text{ mol NaOH}} = 0.002582 \text{ mol CH}_3\text{COOH}$$

3. Use the volume of analyte to find the concentration of the analyte.

$$34.57 \text{ mL} \times \frac{1 \text{ L}}{1000 \text{ mL}} = 0.03457 \text{ L}$$

$$\frac{0.002582 \text{ mol CH}_3\text{COOH}}{0.03457 \text{ L}} = 0.07469 \text{ M CH}_3\text{COOH}$$

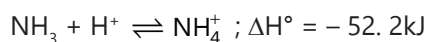
**Example 9:** Calculate the dissociation constant of NH<sub>4</sub>OH at 25°C, if  $\Delta H^\circ$  and  $\Delta S^\circ$  for the given changes are as follows:



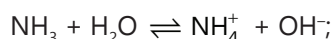
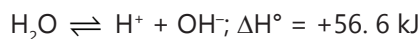
**Sol:** First calculate free energy from the given value of enthalpy and entropy by using the following expression,

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

Value of free energy change can be used to estimate the value of equilibrium constant can be calculated as  $\Delta G^\circ = -2.303 RT \log K_b$

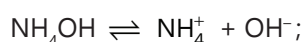


Adding,



$$\Delta H^\circ = +4.4 \text{ kJ mol}^{-1}$$

Similarly,  $\Delta S^\circ$  for the change =  $-76.53 \text{ Jk}^{-1} \text{ mol}^{-1}$  or for the change



$$\Delta H^\circ = 4.4 \text{ kJ mol}^{-1} \text{ and } \Delta S^\circ = -76.53 \text{ Jk}^{-1} \text{ mol}^{-1}$$

Now, we have  $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

$$\therefore \Delta G^\circ = 4.4 - (-76.53 \times 10^{-3}) \times 298 = 27.21 \text{ kJ mol}^{-1}$$

Also,  $\Delta G^\circ = -2.303 RT \log K_b$

$$27.21 = -2.303 \times 8.314 \times 10^{-3} \times 298 \times \log K_b$$

$$\therefore K_b = 1.7 \times 10^{-5}$$

## JEE Advanced/Boards

**Example 1:** Prove that the degree of dissociation of a weak monoprotic acid is given by  $\alpha = \frac{1}{1 + 10^{(\text{p}K_a - \text{pH})}}$

where  $K_a$  is the dissociation constant of the acid.

**Sol:** Suppose we start with  $C \text{ mol L}^{-1}$  of the monoprotic acid HA. Then



Initial molar conc.  $C$

Molar conc.  $C - C\alpha$   $C\alpha$   $C\alpha$

After dissociation =  $C(1 - \alpha)$

$$\text{Thus, } K_a = \frac{C\alpha \cdot C\alpha}{C(1 - \alpha)} = \frac{C\alpha^2}{1 - \alpha}$$

$$\text{Or } C = \frac{K_a(1 - \alpha)}{\alpha^2} \quad \dots \text{ (i)}$$

$$\text{Also, } [\text{H}^+] = C\alpha \quad \dots \text{ (ii)}$$

Substituting the value of  $C$  from eqs. (i), we get

$$[\text{H}^+] = \frac{K_a(1 - \alpha)}{\alpha^2} \times \alpha = \frac{K_a(1 - \alpha)}{\alpha}$$

$$\therefore -\log[\text{H}^+] = [\log K_a + \log(1 - \alpha) - \log \alpha]$$

$$\text{Or } \text{pH} = \text{p}K_a - \log(1 - \alpha) - \log \alpha$$

$$\text{Or } \log \frac{1 - \alpha}{\alpha} = \text{p}K_a - \text{pH}$$

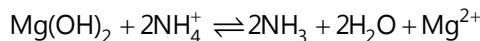
$$\text{Or } \frac{1 - \alpha}{\alpha} = 10^{\text{p}K_a - \text{pH}}$$

$$\text{Or } \frac{1}{\alpha} - 1 = 10^{\text{p}K_a - \text{pH}}$$

$$\text{Or } \frac{1}{\alpha} = 1 + 10^{\text{p}K_a - \text{pH}}$$

$$\text{Or } \alpha = \frac{1}{1 + 10^{\text{p}K_a - \text{pH}}}$$

**Example 2:** The solubility of  $\text{Mg}(\text{OH})_2$  is increases by the addition of  $\text{NH}_4^+$  ion. Calculate  $K_c$  for,



$$K_{\text{spMg}(\text{OH})_2} = 6 \times 10^{-12}, K_{\text{bNH}_3} = 1.8 \times 10^{-5}$$

**Sol:** The given reaction is:



$$\begin{aligned} \therefore K_c &= \frac{[\text{NH}_3]^2[\text{Mg}^{2+}]}{[\text{NH}_4^+]^2} \\ &= \frac{[\text{NH}_4\text{OH}]^2[\text{Mg}^{2+}]}{[\text{NH}_4^+]^2} \quad \dots \text{ (i)} \end{aligned}$$

For  $\text{NH}_4\text{OH}$ , a weak base

$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_4\text{OH}]} \quad \dots \text{ (ii)}$$

By Eqs. (i) and (ii)

$$K_c \times (K_b)^2 = [\text{Mg}^{2+}][\text{OH}^-]^2$$

$$= K_{\text{spMg}(\text{OH})_2}$$

$$\therefore K_c = \frac{K_{\text{sp}}}{(K_b)^2} = \frac{6 \times 10^{-12}}{(1.8 \times 10^{-5})^2} = 1.85 \times 10^{-2}$$

**Example 3:** 0.1 M  $\text{CH}_3\text{COOH}$  solution is titrated against 0.05 M  $\text{NaOH}$  solution. Calculate pH at  $\frac{1}{4}$  th and th stages of neutralization of acid. The pH for 0.1 M  $\text{CH}_3\text{COOH}$  is 3.

**Sol:** Given pH for 0.1 M  $\text{CH}_3\text{COOH} = 3$

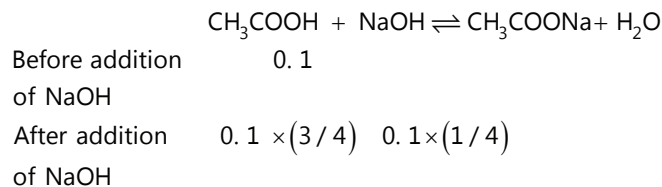
$$\therefore [\text{H}^+] = 10^{-3}$$

$$\text{Or } c\alpha = 10^{-3}$$

$$\text{Or } \alpha = \frac{10^{-3}}{0.1} = 10^{-2}$$

$$k_a = c\alpha^2 = (0.1) \times (10^{-2})^2 = 10^{-5}$$

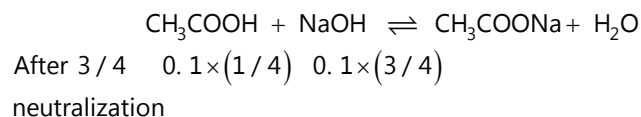
**Case I:** At 1/4th neutralization of acid



$$\therefore \text{pH} = -\log K_a + \log \frac{[\text{conjugate base}]}{[\text{Acid}]}$$

$$\text{Or pH} = -\log 10^{-5} + \log \frac{(0.1/4)}{(0.3/4)} \Rightarrow \text{pH} = 4.5228$$

**Case II:**



$$\therefore \text{pH} = -\log[10^{-5}] + \log \frac{0.3/4}{0.1/4} \Rightarrow \text{pH} = 5.4771$$

**Example 4:** 500 mL of 0.2 M aqueous solution of acetic acid is mixed with 500 mL of 0.2 M HCl at 25°C.

(i) Calculate the degree of dissociation of acetic acid in the resulting solution and pH of the solution.

(ii) If 6 g of NaOH is added to the above solution, determine the final pH.

[Assume there is no change in volume in mixing;  $K_a$  of acetic acid is  $1.75 \times 10^{-5} \text{ mol L}^{-1}$ ]

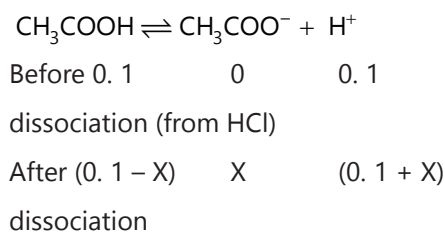
**Sol:** (i) Meq. of  $\text{CH}_3\text{COOH} = 500 \times 0.2 = 100$

Meq. of HCl =  $500 \times 0.2 = 100$

$$\therefore [\text{HCl}] = \frac{100}{1000} = 0.1;$$

$$[\text{CH}_3\text{COOH}] = \frac{100}{1000} = 0.1$$

**For  $\text{CH}_3\text{COOH}$ :**



$$\therefore K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]} = \frac{X(0.1 + X)}{(0.1 - X)}$$

Due to common ion effect dissociation of  $\text{CH}_3\text{COOH}$  is very small in presence of HCl.

Therefore,  $(0.1 + X) = 0.1$  and  $(0.1 - X) = 0.1$

$$\therefore K_a = \frac{X \cdot 0.1}{0.1}$$

$$\therefore X = K_a = 1.75 \times 10^{-5}$$

Thus, degree of dissociation

$$\alpha = \frac{X}{0.1} = \frac{1.75 \times 10^{-5}}{0.1} = 1.75 \times 10^{-4}$$

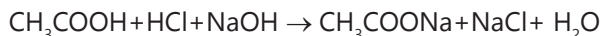
$$= 0.000175 = 0.0175\%$$

Also,  $[\text{H}^+] = 0.1 + X = 0.1$  ( $X \ll 0.1$ )

$$\therefore \text{pH} = -\log[\text{H}^+] = -\log[0.1] = 1$$

(ii) Eq. of NaOH or mole of NaOH added =  $6/40 = 0.15$

Therefore, new equilibrium will have,



$$\begin{array}{ccccccc} 0.1 & 0.1 & 0.15 & 0 & 0 & 0 \\ 0.05 & 0 & 0 & 0.05 & 0 & 0 \end{array}$$

Thus, the solution will act as acidic buffer having

$$[\text{CH}_3\text{COOH}] = \frac{0.05}{1000}$$

$$\text{and } [\text{CH}_3\text{COONa}] = \frac{0.05}{1000}$$

$$\text{Thus, pH} = -\log K_a + \log \frac{[\text{Salt}]}{[\text{Acid}]}$$

$$= -\log [1.75 \times 10^{-5}] + \log \frac{[0.05/1000]}{[0.05/1000]} = 4.757$$

**Example 5:** The average concentration of  $\text{SO}_2$  in the atmosphere over a city on a certain day is 10 ppm, when the average temperature is 298 K. Given that the solubility of  $\text{SO}_2$  in water at 298 K is  $1.3653 \text{ mol litre}^{-1}$  and the  $\text{p}K_a$  of  $\text{H}_2\text{SO}_4$  is 1.92. Estimate the pH of rain on that day.

**Sol:** Use Henry's law to find out  $[\text{SO}_2]$  dissolved in water. Concentration of  $\text{SO}_2$  in air is 10 ppm or 10 mole in  $10^6$  mole air or  $10^{-5}$  mole  $\text{SO}_2$  per mol of air. The concentration of  $\text{SO}_2$  in air being substantial and since, rain water is falling from enormously great height so, each drop of rain water will get saturated with  $\text{SO}_2$  before it reaches earth.

Now the given concentration or solubility of  $\text{SO}_2$  at 298 K is 1.3653 M.

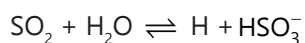
This value of solubility corresponds when  $P_{\text{SO}_2} = 1 \text{ atm}$

Thus, according to Henry's law

$[\text{SO}_2]$  dissolved in water  $\propto P_{\text{SO}_2}$  in gas phase

$[\text{SO}_2]$  dissolved in water  $\propto P_{\text{SO}_2}$  in air

$\therefore [\text{SO}_2]$  dissolved in water =  $1.3653 \times 10^{-5} \text{ M}$



1                      0      0

(1 -  $\alpha$ )              a      a

$$\therefore K_a = 10^{-1.92} = \frac{c\alpha \cdot c\alpha}{c(1-\alpha)} = \frac{c\alpha^2}{1-\alpha} \quad (\alpha \text{ is small})$$

$$\text{or } 0.012 = \frac{1.3653 \times 10^{-5} \times \alpha^2}{1-\alpha}$$

( $\because pK_b = 1.92, \therefore K_b = 0.012$ )

$$\therefore 1.3653 \times 10^{-5} \alpha^2 + 0.012 \alpha - 0.012 = 0$$

$$\therefore \alpha = 1$$

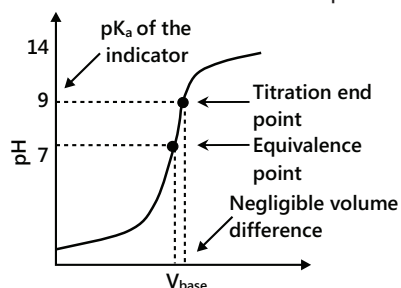
(Solving quadratic equation)

$$\therefore [\text{H}^+] = c\alpha = 1.3653 \times 1 = 1.3653$$

$$\therefore \text{pH} = 4.8648$$

**Example 6:** Why is it acceptable to use an indicator whose  $pK_a$  is not exactly the pH at the equivalence point?

**Sol:** As we can see in the following titration curve, even if the  $pK_a$  of the indicator is several units away from the pH at the equivalence point, there is only a negligible change in volume of titrant added due to the steep slope of the titration curve near the equivalence point.

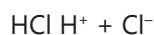


**Example 7:** What is the pH of the following solutions?

(a)  $10^{-3} \text{ M HCl}$               (b)  $0.0001 \text{ M NaOH}$

(c)  $0.0001 \text{ M H}_2\text{SO}_4$

**Sol:** (a) HCl is a strong electrolyte and is completely ionised.



$$\text{So, } [\text{H}^+] = 10^{-3} \text{ M}$$

$$\text{pH} = -\log[\text{H}^+] = -\log(10^{-3}) = 3$$

(b) NaOH is a strong electrolyte and is completely ionized.



$$\text{So, } [\text{H}^+] = 0.0001 \text{ M} = 10^{-4} \text{ M}$$

$$\text{pOH} = -\log(10^{-4}) = 4$$

$$\text{As } \text{pH} + \text{pOH} = 14$$

$$\text{So, } \text{pH} + 4 = 14$$

$$\text{or } \text{pH} = 10$$

**Alternative method:**

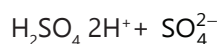
$$[\text{OH}^-] = 10^{-4} \text{ M}$$

We know that,  $[\text{H}^+][\text{OH}^-] = 1.0 \times 10^{-14}$

$$\text{So, } [\text{H}^+] = \frac{1.0 \times 10^{-14}}{10^{-4}} = 10^{-10} \text{ M}$$

$$\text{pH} = -\log[\text{H}^+] = -\log(10^{-10}) = 10$$

(c)  $\text{H}_2\text{SO}_4$  is a strong electrolyte and is ionized completely.



One molecule of  $\text{H}_2\text{SO}_4$  furnishes  $2\text{H}^+$  ions.

$$\text{So, } [\text{H}^+] = 2 \times 10^{-4} \text{ M}$$

$$\text{pH} = -\log[\text{H}^+] = -\log(2 \times 10^{-4}) = 3.70$$

**Example 8:** If very small amount of phenolphthalein is added to  $0.15 \text{ mol litre}^{-1}$  solution of sodium benzoate what fraction of the indicator will exist in the coloured form? State any assumption that you make.

$$K_a (\text{Benzoic acid}) = 6.2 \times 10^{-5}$$

$$K_w (\text{H}_2\text{O}) = 1 \times 10^{-14}$$

$$K_{\text{in}} (\text{Phenolphthalein}) = 3.16 \times 10^{-10}$$

**Sol:** Use the following expression to find out pH of salt hydrolysis and pH of indicator.

Formula for pH of salt hydrolysis:

$$\text{pH} = \frac{1}{2} [pK_w + pK_a + \log C]$$

Formula for pH of indicator:

$$\text{pH} = pK_{\text{in}} + \log_{10} \frac{[\text{In}^-]}{[\text{HIn}]}$$

Substitute the values in the above equation,

For pH of salt hydrolysis:

$$= \frac{1}{2} [14 - \log_{10} 6.2 \times 10^{-5} + \log 0.15] = 8.6918$$

For pH of indicator:

$$8.6918 = -\log_{10} (3.16 \times 10^{-10}) + \log_{10} \frac{[\text{In}^-]}{[\text{HIn}]}$$

$$0.16 = [\text{In}^-]/[\text{HIn}] = \text{Fraction of indicator in coloured form}$$

## JEE Main/Boards

### Exercise 1

**Q.1** The degree of dissociation of acetic acid in a 0.1 N solution is  $1.32 \times 10^{-2}$ . At what concentration of nitrous acid, its degree of dissociation will be same as that of acetic acid?

$$K_a(\text{HNO}_2) = 4 \times 10^{-4}$$

**Q.2** How many times is the  $\text{H}^+$  concentration in the blood ( $\text{pH} = 7.36$ ) greater than in the spinal fluid ( $\text{pH} = 7.53$ )?

**Q.3** A 0.400 M formic acid solution freezes at  $-0.758^\circ\text{C}$ . Calculate the  $K_a$  of the acid at that temperature. (Assume molarity equal to molality).  $K_f(\text{H}_2\text{O}) = 1.86^\circ\text{mol}^{-1}\text{kg}$ .

**Q.4** A sample of  $\text{AgCl}$  was treated with 5 mL of 1.5 M  $\text{Na}_2\text{CO}_3$  solution to give  $\text{Ag}_2\text{CO}_3$  the remaining solution contained 0.0026 g/litre  $\text{Cl}^-$  ion. Calculate the solubility of  $\text{AgCl}$ .

**Q.5** 100 mL of solution  $S_1$  contains 0.17 mg of  $\text{AgNO}_3$ . Another 200 mL solution  $S_2$  contains 0.117 mg of  $\text{NaCl}$ . On mixing these two solutions predict whether the precipitate of  $\text{AgCl}$  will appear or not  $K_{\text{sp}}(\text{AgCl}) = 10^{-10}\text{M}^2$

**Q.6** 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 centre of the hydrogen ion concentrations corresponding to given pH range, calculate the ionization constant of the indicator.

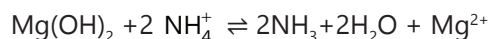
**Q.7** Calculate the hydrolysis constant of  $\text{NH}_4\text{Cl}$ ; determine the degree of hydrolysis of this salt in 0.01 M solution and the pH of the solution.  $K_b(\text{NH}_4\text{OH}) = 1.8 \times 10^{-5}$

**Q.8** Calculate the pH of 0.1 M acetic acid solution if its dissociation constant is  $1.8 \times 10^{-5}$ . If 1 litre of this solution is mixed with 0.05 mole of  $\text{HCl}$ , what will be the pH of the mixture

**Q.9** It is found that 0.1 M solution of three sodium salts  $\text{NaX}$ ,  $\text{NaY}$  and  $\text{NaZ}$  have pHs 7.0, 9.0 and 11.0, respectively. Arrange the acids  $\text{HX}$ ,  $\text{HY}$  and  $\text{HZ}$  in order of increasing strength. Where possible, calculate the ionisation constants of the acids.

**Q.10** Given a solution that is 0.5 M  $\text{CH}_3\text{COOH}$ . To what volume at  $25^\circ\text{C}$  must one  $\text{dm}^3$  of this solution be diluted in order to (a) double the pH; (b) double the hydroxide-ion concentration. Given that  $K_a = 1.8 \times 10^{-5}\text{M}$ .

**Q.11** The solubility of  $\text{Mg}(\text{OH})_2$  is increased by addition of  $\text{NH}_4^+$  ion.



If  $K_{\text{sp}}$  of  $\text{Mg}(\text{OH})_2 = 1 \times 10^{-11}$ ,  $K_b$  for  $\text{NH}_4\text{OH} = 1.8 \times 10^{-5}$  then calculate  $K_c$  for the reaction.

**Q.12** An unknown volume and unknown concentration of weak acid  $\text{HX}$  is titrated with  $\text{NaOH}$  of unknown concentration. After addition of 10.0  $\text{cm}^3$  of  $\text{NaOH}$  solution, pH of solution is 5.8 and after the addition of 20.0  $\text{cm}^3$  of  $\text{NaOH}$  solution, the pH is 6.4. Calculate the pH of aqueous solution of 0.1 M  $\text{NaX}$ .

**Q.13** A solution containing zinc and manganese ions each at a concentration of 0.01  $\text{mol dm}^3$  is saturated with  $\text{H}_2\text{S}$ . Calculate

- (i) pH at which the  $\text{MnS}$  will form a precipitate
- (ii) Conc. of  $\text{Zn}^{+2}$  ions remaining.

Given:  $[\text{H}_2\text{S}] = 0.1\text{ mol/lit}$ ,

$$K_{\text{sp}}(\text{ZnS}) = 1 \times 10^{-22}\text{mol}^2\text{lit}^{-2},$$

$$K_{\text{sp}}(\text{MnS}) = 5.6 \times 10^{-16}\text{mol}^2\text{lit}^{-2}.$$

$K_1$  and  $K_2$  for  $\text{H}_2\text{S}$  are  $1 \times 10^{-7}$  and  $1.1 \times 10^{-14}$

**Q.14** For the indicator thymol blue, the value of pH is 2.0, when half of the indicator is present in an unionized form. Calculate the percentage of the indicator in the unionized form in a solution of  $4.0 \times 10^{-3}\text{ mol/dm}^3$  hydrogen ion concentration.

**Q.15** The first ionization constant of  $\text{H}_2\text{S}$  is  $9.1 \times 10^{-8}$ . Calculate the concentration of  $\text{HS}^-$  ion in its 0.1 M solution. How will this concentration be affected if the solution is 0.1 M in  $\text{HCl}$  also? If the second dissociation constant of  $\text{H}_2\text{S}$  is  $1.2 \times 10^{-13}$ . Calculate the concentration of  $\text{S}^{2-}$  under both conditions.

**Q.16** The ionization constant of acetic acid is  $1.74 \times 10^{-5}$ . Calculate the degree of dissociation of acetic acid in its 0.05 M solution. Calculate the concentration of acetate ion in the solution and its pH.



**Q.17** It has been found that the pH of a 0.01 M solution of an organic acid is 4.15. Calculate the concentration of the anion, the ionization constant of the acid and its  $pK^a$

**Q.18** Assuming complete dissociation, calculate the pH of the following solutions:

- (i) 0.003 M HCl                      (ii) 0.005 M NaOH  
(iii) 0.002 M HBr                    (iv) 0.002 M KOH

**Q.19** Calculate the pH of the following solutions:

- (i) 2 g of TIOH dissolved in water to give 500 ml of solution.  
(ii) 0.3 g of  $\text{Ca}(\text{OH})_2$  dissolved in water to give 2 litre of solution  
(iii) 0.3 g of NaOH dissolved in water to give 200 mL of solution.  
(iv) 1 mL of 13.6 M HCl is diluted with water to give 1 litre of solution

**Q.20** If the solubility product of silver oxalate is  $1 \times 10^{-11}$ , what will be the weight of  $\text{Ag}_2\text{C}_2\text{O}_4$  in 2.5 litres of a saturated solution?

**Q.21** Determine hydrolysis constant, degree of hydrolysis and the pH of 0.01 M solution of ammonium cyanide.  $K_a(\text{HCN}) = 7.2 \times 10^{-10}$ .  $K_b(\text{NH}_3) = 1.8 \times 10^{-5}$

**Q.22** Assuming that the buffer in blood is  $\text{CO}_3^{2-} - \text{HCO}_3^-$ , calculate the ratio of conjugate base to acid necessary to maintain blood at its proper pH, 7.4.  $K_1(\text{H}_2\text{CO}_3) = 4.5 \times 10^{-7}$ .

**Q.23** How many moles of sodium hydroxide can be added to 1.0 L of a solution 0.10 M in  $\text{NH}_3$  and 0.10 M in  $\text{NH}_4\text{Cl}$  without changing the pOH by more than 1 unit. Assume no change in volume.  $K_b = 1.8 \times 10^{-5}$

## Exercise 2

### Single Correct Choice Type

**Q.1** The conjugate acid of  $\text{NH}_2^-$  is

- (A)  $\text{NH}_3$                       (B)  $\text{NH}_2\text{OH}$                       (C)  $\text{NH}_4^+$                       (D)  $\text{N}_2\text{H}_4$

**Q.2** Out of the following, amphiprotic species are

- I.  $\text{HPO}_3^{2-}$                       II.  $\text{OH}^-$                       III.  $\text{H}_2\text{PO}_4^-$                       IV.  $\text{HCO}_3^-$   
(A) I, III, IV                      (B) I and III                      (C) III and IV                      (D) All

**Q.3** pH of an aqueous solution of NaCl at  $85^\circ\text{C}$  should be

- (A) 7                      (B)  $> 7$                       (C)  $< 7$                       (D) 0

**Q.4** 1 cc of 0.1 N HCl is added to 99 cc solution of NaCl. The pH of the resulting solution will be

- (A) 7                      (B) 3                      (C) 4                      (D) 1

**Q.5** 10 ml of  $\frac{M}{200}$   $\text{H}_2\text{SO}_4$  is mixed with 40 ml of  $\frac{M}{200}$   $\text{H}_2\text{SO}_4$ . The pH of the resulting solution is

- (A) 1                      (B) 2  
(C) 2.3                      (D) None of these

**Q.6** If  $pK_b$  for fluoride ion at  $25^\circ\text{C}$  is 10.83, the ionisation constant of hydrofluoric acid in water at this temperature is:

- (A)  $1.74 \times 10^{-5}$                       (B)  $3.52 \times 10^{-3}$   
(C)  $6.75 \times 10^{-4}$                       (D)  $5.38 \times 10^{-2}$

**Q.7** The pH of an aqueous solution of 1.0 M solution of a weak monoprotic acid which is 1% ionised is

- (A) 1                      (B) 2                      (C) 3                      (D) 11

**Q.8** If  $K_1$  and  $K_2$  be first and second ionization constant of  $\text{H}_3\text{PO}_4$  and  $K_1 > K_2$  which is incorrect.

- (A)  $[\text{H}^+] = [\text{H}_2\text{PO}_4^-]$                       (B)  $[\text{H}^+] = K_1[\text{H}_3\text{PO}_4]$   
(C)  $K_2 = [\text{HPO}_4^-]$                       (D)  $[\text{H}^+] = 3[\text{PO}_4^{3-}]$

**Q.9** Which of the following solution will have pH close to 1.0?

- (A) 100 ml of M/100 HCl + 100 ml of M/10  
(B) 55 ml of M/10 HCl + 45 ml of M/10 NaOH  
(C) 10 ml of M/10 HCl + 90 ml of m/10 NaOH  
(D) 75ml of M/5 HCl + 25ml of M/5 NaOH

**Q.10** What is the percentage hydrolysis of NaCN in N/80 solution when the dissociation constant for HCN is  $1.3 \times 10^{-9}$  and  $K_w = 1.0 \times 10^{-14}$

- (A) 2.48                      (B) 5.26                      (C) 8.2                      (D) 9.6

**Q.11** The compound whose 0.1 M solution is basic is

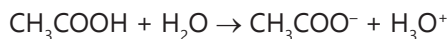
- (A) Ammonium acetate                      (B) Ammonium chloride  
(C) Ammonium sulphate                      (D) Sodium acetate



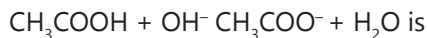
**Q.12** The  $\approx$  pH of the neutralisation point of 0.1 N ammonium hydroxide with 0.1 N HCl is

- (A) 1 (B) 6 (C) 7 (D) 9

**Q.13** If equilibrium constant of



is  $1.8 \times 10^{-5}$ , equilibrium constant for



- (A)  $1.8 \times 10^{-9}$  (B)  $1.8 \times 10^{-9}$   
(C)  $5.55 \times 10^{-9}$  (D)  $5.55 \times 10^{10}$

**Q.14** The  $\text{p}K_a$  of a weak acid, HA, is 4.80. The  $\text{p}K_b$  of a weak base, BOH, is 4.78. The pH of an aqueous solution of the corresponding salt, BA, will be:

- (A) 8.58 (B) 4.79 (C) 7.01 (D) 9.22

**Q.15** The range of most suitable indicator which should be used for titration of  $\text{X}^- \text{Na}^+$  (0.1 M, 10 ml) with 0.1 M HCl should be (Given:  $K_b(\text{X}^-) = 10^{-6}$ )

- (A) 2-3 (B) 3-5 (C) 6-8 (D) 8-10

**Q.16** The solubility of  $\text{A}_2\text{X}_3$  is  $y$  mol  $\text{dm}^{-3}$ . Its solubility product is

- (A)  $6y^2$  (B)  $64y^4$  (C)  $36y^5$  (D)  $108y^5$

**Q.17** If  $K_{sp}$  for  $\text{HgSO}_4$  is  $6.4 \times 10^{-5}$ , then solubility of this substance in mole per  $\text{m}^3$  is

- (A)  $8 \times 10^{-3}$  (B)  $6.4 \times 10^{-5}$   
(C)  $8 \times 10^{-6}$  (D) None of these

**Q.18** The solubility of a sparingly soluble salt  $\text{AB}_2$  in water is  $1.0 \times 10^{-5}$  mol  $\text{L}^{-1}$ . Its solubility product is:

- (A)  $10^{-15}$  (B)  $10^{-10}$  (C)  $4 \times 10^{-15}$  (D)  $4 \times 10^{-10}$

**Q.19** Which of the following is most soluble in water?

- (A)  $\text{MnS}$  ( $K_{sp} = 8 \times 10^{-37}$ ) (B)  $\text{ZnS}$  ( $K_{sp} = 7 \times 10^{-16}$ )  
(C)  $\text{Bi}_2\text{S}_3$  ( $K_{sp} = 1 \times 10^{-72}$ ) (D)  $\text{Ag}_3(\text{PO}_4)$  ( $K_{sp} = 1.8 \times 10^{-18}$ )

**Q.20** When equal volumes of the following solutions are mixed, precipitation of  $\text{AgCl}$  ( $K_{sp} = 1.8 \times 10^{-10}$ ) will occur only with:

- (A)  $10^{-4}\text{M}$  ( $\text{Ag}^+$ ) and  $10^{-4}\text{M}$  ( $\text{Cl}^-$ )  
(B)  $10^{-5}\text{M}$  ( $\text{Ag}^+$ ) and  $10^{-5}\text{M}$  ( $\text{Cl}^-$ )  
(C)  $10^{-6}\text{M}$  ( $\text{Ag}^+$ ) and  $10^{-6}\text{M}$  ( $\text{Cl}^-$ )  
(D)  $10^{-10}\text{M}$  ( $\text{Ag}^+$ ) and  $10^{-10}\text{M}$  ( $\text{Cl}^-$ )

**Q.21** The precipitate of  $\text{CaF}_2$  ( $K_{sp} = 1.7 \times 10^{-10}$ ) is obtained when equal volumes of the following are mixed

- (A)  $10^{-4}\text{M}$   $\text{Ca}^{3+}$  +  $10^{-4}\text{M}$   $\text{F}^-$   
(B)  $10^{-2}\text{M}$   $\text{Ca}^{2+}$  +  $10^{-3}\text{M}$   $\text{F}^-$   
(C)  $10^{-5}\text{M}$   $\text{Ca}^{2+}$  +  $10^{-3}\text{M}$   $\text{F}^-$   
(D)  $10^{-3}\text{M}$   $\text{Ca}^{2+}$  +  $10^{-5}\text{M}$   $\text{F}^-$

**Q.22** 50 litre of a solution containing  $10^{-5}$  mole of  $\text{Ag}^+$  is mixed with 50 litre of a  $2 \times 10^{-7}\text{M}$  HBr solution.  $[\text{Ag}^+]$  in resultant solution is: [Given:  $K_{sp}(\text{AgBr}) = 5 \times 10^{-13}$ ]

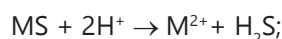
- (A)  $10^{-5}\text{M}$  (B)  $10^{-6}\text{M}$   
(C)  $10^{-7}\text{M}$  (D) None of these

**Q.23** pH of a saturated solution of silver salt of monobasic acid HA is found to be 9.

Find the  $K_{sp}$  of sparingly soluble salt  $\text{AgA}(s)$ . Given:  $K_a(\text{HA}) = 10^{-10}$

- (A)  $1.1 \times 10^{-11}$  (B)  $1.1 \times 10^{-10}$   
(C)  $10^{-12}$  (D) None of these

**Q.24** The solubility of metal sulphides in saturated solution of  $\text{H}_2\text{S}$  ( $[\text{H}_2\text{S}] = 0.1\text{M}$ ) can be represented by



$$K_{eq} = \frac{[\text{M}^{2+}][\text{H}_2\text{S}]}{[\text{H}^+]^2}$$

The value of  $k_{eq}$  is given for few metal sulphide. If conc. of each metal ion in solution is 0.01 M, which metal sulphides are selectively ppt at total  $[\text{H}^+] = 1\text{M}$  in saturated  $\text{H}_2\text{S}$  solution.

$$K_{eq} = \frac{[\text{M}^{2+}][\text{H}_2\text{S}]}{[\text{H}^+]^2}$$

Mns	ZnS	CoS	PbS
$3 \times 10^{10}$	$3 \times 10^{-2}$	3	$3 \times 10^{-7}$

- (A)  $\text{MnS}$ ,  $\text{ZnS}$ ,  $\text{CoS}$  (B)  $\text{PbS}$ ,  $\text{ZnS}$ ,  $\text{CoS}$   
(C)  $\text{PbS}$ ,  $\text{ZnS}$  (D)  $\text{PbS}$

**Q.25** Solid  $\text{Ba}(\text{NO}_3)_2$  is gradually dissolved in a  $1.0 \times 10^{-4}\text{M}$   $\text{Na}_2\text{CO}_3$  solution. At what concentration of  $\text{Ba}^{2+}$  will a precipitate begin to form? ( $K_{sp}$  for  $\text{BaCO}_3 = 5.1 \times 10^{-9}$ )

- (A)  $4.1 \times 10^{-5}\text{M}$  (B)  $5.1 \times 10^{-5}\text{M}$   
(C)  $8.1 \times 10^{-8}\text{M}$  (D)  $8.1 \times 10^{-7}\text{M}$

**Q.26**  $K_{sp}$  of  $MX_4$  and solubility of  $MX_4$  is  $S$  mol/litre is related by:

- (A)  $S = [K_{sp}/256]^{1/5}$       (B)  $S = [128/K_{sp}]^{1/4}$   
 (C)  $S = [256K_{sp}]^{1/5}$       (D)  $S = [K_{sp}/128]^{1/4}$

### Previous Years' Questions

**Q.1** A 0.004 M solution of  $Na_2SO_4$  is isotonic with a 0.010 M solution of glucose at same temperature. The apparent degree of association of  $Na_2SO_4$  is **(2004)**

- (A) 25%      (B) 50%      (C) 75%      (D) 85%

**Q.2**  $K_{sp}$  for  $Cr(OH)_3$  is  $2.7 \times 10^{-31}$ . What is its solubility in moles/litre. **(2004)**

- (A)  $1 \times 10^{-8}$       (B)  $8 \times 10^{-8}$   
 (C)  $1.1 \times 10^{-8}$       (D)  $0.18 \times 10^{-8}$

**Q.3**  $pK_a$  of acetic acid is 4.74. The concentration of  $CH_3COONa$  is 0.01 M. The pH of  $CH_3COONa$  is **(2004)**

- (A) 8.37      (B) 4.37      (C) 4.74      (D) 0.474

**Q.4** A weak acid HX has the dissociation constant  $1 \times 10^{-5}$  M. It forms a salt NaX on reaction with alkali. The degree of hydrolysis of 0.1 M solution of NaX is **(2004)**

- (A) 0.0001%      (B) 0.01%      (C) 0.1%      (D) 0.15%

**Q.5** In the given reaction, the oxide of sodium is



- (A) Acidic      (B) Basic      (C) Amphoteric      (D) Neutral

**Q.6** The dissociation of water at  $25^\circ C$  is  $1.9 \times 10^{-7}\%$  and the density of water is  $1.0 \text{ g/cm}^3$ . The ionisation constant of water is **(1995)**

- (A)  $3.42 \times 10^{-6}$       (B)  $3.42 \times 10^{-8}$   
 (C)  $1.00 \times 10^{-14}$       (D)  $2.00 \times 10^{-16}$

**Q.7** Which of the following statement (s) is (are) correct **(1998)**

- (A) The pH of  $1.0 \times 10^{-8} M$  solution of HCl is 8  
 (B) The conjugate base of  $H_2PO_4^-$  is  $HPO_4^{2-}$   
 (C) Autoprotolysis constant of water increases with temperature

(D) When a solution of a weak monoprotic acid is treated against a strong base, at half-neutralization point  $pH = \left(\frac{1}{2}\right) pK_a$

**Q.8** A buffer solution can be prepared from a mixture of **(1999)**

- (A) Sodium acetate and acetic acid in water  
 (B) Sodium acetate and hydrochloric acid in water  
 (C) Ammonia and ammonium chloride in water  
 (D) Ammonia and sodium hydroxide in water

Each of the questions given below consists of two statements, an assertion (Assertion) and reason (Reason). Select the number corresponding to the appropriate alternative as follows

(A) If both assertion and reason are true and reason is the correct explanation of assertion.

(B) If both assertion and reason are true and reason is not the correct explanation of assertion.

(C) If assertion is true but reason is false.

(D) If assertion is false but reason is true.

**Q.9 Assertion:**  $BaCO_3$  is more soluble in  $HNO_3$  than in plain water. **(2006)**

**Reason:** Carbonate is a weak base and reacts with the  $H^+$  from the strong acid, causing the barium salt to dissociate.

**Q.10 Assertion:**  $CHCl_3$  is more acidic than  $CHF_3$  **(2003)**

**Reason:** The conjugate base of  $CHCl_3$  is more stable than  $CHF_3$ .

**Q.11** The  $pK_a$  of a weak acid HA is 4.80. The  $pK_a$  of a weak base, BOH, is 4.78. The pH of an aqueous solution of the corresponding salt, BA will be **(2008)**

- (A) 9.58      (B) 4.79      (C) 7.01      (D) 9.22

**Q.12** The equilibrium constants  $K_{p1}$  and  $K_{p2}$  for the reaction  $X \rightleftharpoons 2Y$  and  $Z \rightleftharpoons P + Q$ , respectively are in the ratio of 1:9 the degree of dissociation of X and Z be equal then ration of total pressure at these equilibria is **(2008)**

- (A) 3 : 36      (B) 1 : 1      (C) 1 : 3      (D) 1 : 9

**Q.13** Solubility product of silver bromide is  $5.0 \times 10^{-13}$ . The quantity of potassium bromide (molar mass taken as  $120 \text{ g mol}^{-1}$ ) to be added to 1 litre of 0.05 M solution of silver nitrate to start the precipitation of AgBr is **(2010)**

- (A)  $1.2 \times 10^{-10} \text{ g}$  (B)  $1.2 \times 10^{-9} \text{ g}$   
(C)  $6.2 \times 10^{-5} \text{ g}$  (D)  $5.0 \times 10^{-8} \text{ g}$

**Q.14** In aqueous solution the ionization constants for carbonic acid are  $K_1 = 4.2 \times 10^{-7}$  and  $K_2 = 4.8 \times 10^{-11}$ . Select the correct statement for a saturated 0.034 M solution of the carbonic acid. **(2010)**

- (A) The concentration of  $\text{CO}_3^{2-}$  is 0.034 M.  
(B) The concentration of  $\text{CO}_3^{2-}$  is greater than that of  $\text{HCO}_3^-$   
(C) The concentration of  $\text{H}^+$  and  $\text{HCO}_3^-$  are approximately equal.  
(D) The concentration of  $\text{H}^+$  is double that of  $\text{HCO}_3^-$

**Q.15** At  $25^\circ\text{C}$ , the solubility product of  $\text{Mg}(\text{OH})_2$  is  $1.0 \times 10^{-11}$ . At which precipitating in the form of  $\text{Mg}(\text{OH})_2$  from a solution 0.001 M  $\text{Mg}^{2+}$  **(2010)**

- (A) 9 (B) 10 (C) 11 (D) 8

**Q.16** The strongest acid amongst the following compounds is: **(2011)**

- (A) HCOOH (B)  $\text{CH}_3\text{CH}_2\text{CH}(\text{Cl})\text{CO}_2\text{H}$   
(C)  $\text{ClCH}_2\text{CH}_2\text{CH}_2\text{COOH}$  (D)  $\text{CH}_3\text{COOH}$

**Q.17** A vessel at 1000 K contains  $\text{CO}_2$  with a Pressure of 0.5 atm. Some of the  $\text{CO}_2$  is converted into CO on the addition of graphite. If the total pressure at equilibrium is 0.8 atm the value of K is **(2011)**

- (A) 3 atm (B) 0.3 atm (C) 0.18 atm (D) 1.8 atm

**Q.18** The pH of a 0.1 molar solution of the acid HQ is 3. The value of the ionization constant,  $K_a$  of this acid is: **(2012)**

- (A)  $3 \times 10^{-1}$  (B)  $1 \times 10^{-3}$  (C)  $1 \times 10^{-5}$  (D)  $1 \times 10^{-7}$

**Q.19** How many litres of water must be added to 1 litre an aqueous solution of HCl with a pH of 1 to create an aqueous solution with pH of 2? **(2013)**

- (A) 0.1 L (B) 0.9 L (C) 2.0 L (D) 9.0 L

**Q.20** The equilibrium constant at 298 K for the reaction  $\text{A} + \text{B} \rightleftharpoons \text{C} + \text{D}$  is 100. If the initial concentration of all the four species were 1 M each, then equilibrium concentration of D (in  $\text{mol L}^{-1}$ ) will be: **(2016)**

- (A) 0.818 (B) 1.818 (C) 1.182 (D) 0.182

## JEE Advanced/Boards

### Exercise 1

**Q.1** Calculate the number of  $\text{H}^+$  present in one ml of solution whose pH is 13.

**Q.2** Calculate change in concentration of  $\text{H}^+$  ion in one litre of water, when temperature changes from 298 K to 310 K.

Given  $K_w(298) = 11^{-14}$  (310) =  $2.56 \times 10^{-14}$ .

**Q.3** (i)  $K_w$  for  $\text{H}_2\text{O}$  is  $9.62 \times 10^{-14}$  at  $60^\circ\text{C}$ .

What is pH of water at  $60^\circ\text{C}$ .

(ii) What is the nature of solution at  $60^\circ\text{C}$  whose

- (a) pH = 6.7 (b) pH = 6.35

**Q.4** The value of  $K_w$  at the physiological temperature ( $37^\circ\text{C}$ ) is  $2.56 \times 10^{-14}$ . What is the pH at the neutral point of water at this temperature?

**Q.5** Calculate pH of following solutions:

(a) 0.1 M  $\text{H}_2\text{SO}_4$  (50 ml) + 0.4 M HCl 50 (ml)

(b) 0.1 M HA + 0.1 M HB

$[K_a(\text{HA}) = 2 \times 10^{-5}; K_a(\text{HB}) = 4 \times 10^{-5}]$

**Q.6** What are the concentration of  $\text{H}^+$ ,  $\text{H}_2\text{C}_2\text{O}_4$ ,  $\text{H}_2\text{C}_2\text{O}_4^-$  and  $\text{C}_2\text{O}_4^{2-}$  in a 0.1 M solution of oxalic acid?

$[K_1 = 10^{-2} \text{ M and } K_2 = 10^{-5} \text{ M}]$

**Q.7** What are the concentrations of  $\text{H}^+$ ,  $\text{HSO}_4^-$ ,  $\text{SO}_4^{2-}$  and  $\text{H}_2\text{SO}_4$  in a 0.20 M solution of sulphuric acid?

Given:  $\text{H}_2\text{SO}_4 \rightarrow \text{H}^+ + \text{HSO}_4^-$ ; strong  $\text{HSO}_4^- \rightarrow \text{H}^+ + \text{SO}_4^{2-}$ ;  $K_2 = 1.3 \times 10^{-2} \text{ M}$

**Q.8** Calculate the pH of a solution which results from the mixing of 50.0 ml of 0.3 M HCl with 50.0 ml of 0.4 M  $\text{NH}_3$ .

$$[\text{p}K_a[\text{NH}_4^+]=9.26]$$

**Q.9** Calculate the pH of a solution made by mixing 50.0 ml of 0.2 M  $\text{NH}_4\text{Cl}$  & 75.0 ml of 0.1 M NaOH.

$$[\text{p}K_a[\text{NaOH}]=0.2]$$

**Q.10** What indicator should be used for the titration of 0.10 M  $\text{K}_2\text{H}_2\text{BO}_3$  with 0.10 M HCl?  $K_a(\text{H}_3\text{BO}_3) = 7.2 \times 10^{-10}$

**Q.11** An acid indicator has a  $K_a$  of  $3 \times 10^{-5}$ . The acid form of the indicator is red and the basic form is blue. By how much must the pH change in order to change the indicator form 75% red to 75% blue?

**Q.12** What is the  $\text{OH}^-$  concentration of a 0.08 M solution of  $\text{CH}_3\text{COONa}$ .  $[K_a(\text{CH}_3\text{COOH}) = 1.8 \times 10^{-5}]$

**Q.13** Calculate the pH of a 2.0 M solution of  $\text{NH}_4\text{Cl}$ .  $[K_b(\text{NH}_3)=1.8 \times 10^{-5}]$

**Q.14** Calculate  $\text{OH}^-$  concentration at the equivalent point when a solution of 0.1 M acetic acid is titrated with a solution of 0.1 M NaOH.  $[K_a$  for the acid =  $1.9 \times 10^{-5}]$

**Q.15** Calculate the hydronium ion concentration and pH at the equivalence point in the reaction of 22.0 mL of 0.10 M acetic acid,  $\text{CH}_3\text{COOH}$ , with 22.0 mL of 0.10 M NaOH.  $[K_a = 1.8 \times 10^{-5}]$

**Q.16** The values of  $K_{sp}$  for the slightly soluble salts MX and  $\text{QX}_2$  are each equal to  $4.0 \times 10^{-18}$ . Which salt is more soluble? Explain your answer.

**Q.17** Calculate the Simultaneous solubility of AgSCN and AgBr.  $K_{sp}(\text{AgSCN}) = 1.1 \times 10^{-12}$ ,  $K_{sp}(\text{AgBr}) = 5 \times 10^{-13}$ .

**Q.18** A solution contains HCl,  $\text{Cl}_2\text{HCCOOH}$  &  $\text{CH}_3\text{COOH}$  at concentrations 0.09 M in HCl, 0.09 M in  $\text{Cl}_2\text{HCCOOH}$  & 0.1 M in  $\text{CH}_3\text{COOH}$ . pH for the solution is 1. Ionization constant of  $\text{CH}_3\text{COOH} = 10^{-5}$ . What is the magnitude of K for dichloroacetic acid?

**Q.19** Determine the  $[\text{S}^{2-}]$  in a saturated (0.1 M)  $\text{H}_2\text{S}$  solution to which enough HCl has been added to produce a  $[\text{H}^+]$  of  $2 \times 10^{-4}$ .  $K_1 = 10^{-7}$ ,  $K_2 = 10^{-14}$ .

**Q.20** 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  $K_a = 1.8 \times 10^{-5}$ .

**Q.21** It is desired to prepare 100 ml of a buffer of pH 5.00. Acetic, benzoic and formic acids and their salts are available for use. Which acid should be used for maximum effectiveness against increase in pH? What acid-salt ratio should be used?  $\text{p}K_a$  values of these acids are: acetic 4.74; benzoic 4.18 and formic 3.68.

**Q.22** When a 40 mL of a 0.1 M weak base is titrated with 0.16 M HCl, the pH of the solution at the end point is 5.23. What will be the pH if 15 mL of 0.12 M NaOH is added to the resulting solution.

**Q.23** A buffer solution was prepared by dissolving 0.05 mol formic acid & 0.06 mol sodium formate in enough water to make 1.0 L of solution.  $K_a$  for formic acid is  $1.80 \times 10^{-4}$ .

(a) Calculate the pH of the solution.

(b) If this solution were diluted to 10 times its volume, what would be the pH?

(c) If the solution in (b) were diluted to 10 times its volume, what would be the pH?

## Exercise 2

### Single Correct Choice Type

**Q.1** A solution with pH 2.0 is more acidic than the one with pH 6.0 by a factor of:

- (A) 3      (B) 4      (C) 3000      (D) 10000

**Q.2** The first and second dissociation constants of an acid  $\text{H}_2\text{A}$  are  $1.0 \times 10^{-5}$  and  $5.0 \times 10^{-10}$  respectively. The overall dissociation constant of the acid will be:

- (A)  $5.0 \times 10^{-5}$       (B)  $5.0 \times 10^{15}$   
(C)  $5.0 \times 10^{-15}$       (D)  $0.2 \times 10^5$

**Q.3** An aqueous solution contains 0.01 M  $\text{RNH}_2$  ( $K_b = 2 \times 10^{-6}$ ) &  $10^{-4}$  M NaOH.

The concentration of  $\text{OH}^-$  is nearly:

- (A)  $2.414 \times 10^{-4}$       (B)  $10^{-4}$  M  
(C)  $1.414 \times 10^{-4}$       (D)  $2 \times 10^{-4}$

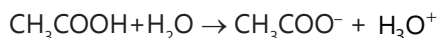
**Q.4** The degree of hydrolysis of a salt of weak acid and weak base in its 0.1 M solution is found to be 50%. If the molarity of the solution is 0.2 M, the percentage hydrolysis of the salt should be

- (A) 100% (B) 50% (C) 25% (D) None of these

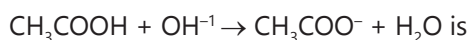
**Q.5** The pH of the neutralisation point of 0.1N ammonium hydroxide with 0.1N HCl is

- (A) 1 (B) 6 (C) 7 (D) 9

**Q.6** If equilibrium constant of



is  $1.8 \times 10^{-5}$ , equilibrium constant for



- (A)  $1.8 \times 10^{-9}$  (B)  $1.8 \times 10^9$   
(C)  $5.55 \times 10^{-9}$  (D)  $5.55 \times 10^{10}$

**Q.7** The  $\text{pK}_a$  of a weak acid, HA, is 4.80. The  $\text{pK}_b$  of a weak base, BOH, is 4.78. The pH of an aqueous solution of the corresponding salt, BA, will be:

- (A) 8.58 (B) 4.79 (C) 7.01 (D) 9.22

**Q.8** How many gm of solid NaOH must be added to 100 ml of a buffer solution which is 0.1 M each w.r.t. Acid HA and salt  $\text{Na}^+ \text{A}^-$  to make the pH of solution 5.5. Given  $\text{pK}_a(\text{HA}) = 5$ . (Use  $\text{antilog}(0.5) = 3.16$ )

- (A)  $2.08 \times 10^{-1}$  (B)  $3.05 \times 10^{-3}$   
(C)  $2.01 \times 10^{-2}$  (D) None of these

**Q.9** If 40 ml of 0.2 M KOH is added to 160 ml of 0.1 M HCOOH [ $K_a = 2 \times 10^{-4}$ ], the pOH of the resulting solution is

- (A) 3.4 (B) 3.7 (C) 7 (D) 10.3

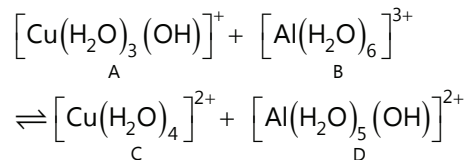
**Q.10** 1 M NaCl and 1M HCl are present in an aqueous solution. The solution is

- (A) Not a buffer solution and with  $\text{pH} < 7$   
(B) Not a buffer solution with  $\text{pH} > 7$   
(C) A buffer solution with  $\text{pH} < 7$   
(D) A buffer solution with  $\text{pH} > 7$

**Q.11** The  $\text{pK}_a$  of a weak acid (HA) is 4.5. The pOH of an aqueous buffered solution of HA in which 50% of the acid is ionized is:

- (A) 4.5 (B) 2.5 (C) 9.5 (D) 7.0

**Q.12** In the following reaction:



(A) C is the conjugate base of A, and D is the conjugate acid of B

(B) A is a base and B the acid

(C) C is the conjugate acid of A, and D is the conjugate base of B

(D) None of the above

**Q.13** Which does not react with NaOH or which is not acid salt?

- (A)  $\text{NaH}_2\text{PO}_2$  (B)  $\text{Na}_2\text{HPO}_3$  (C)  $\text{Na}_2\text{HPO}_4$  (D)  $\text{NaHCO}_3$

**Q.14** pH of the following solution is affected by dilution:

- (A) 0.01 M  $\text{CH}_3\text{COONa}$   
(B) 0.01 M  $\text{NaHCO}_3$   
(C) Buffer of 0.01 M  $\text{CH}_3\text{COONa}$  and 0.01 M  $\text{CH}_3\text{COOH}$   
(D) 0.01 M  $\text{CH}_3\text{COONH}_4$

**Q.15** Which of the following mixtures does not constitute a buffer?

- (A)  $\text{CH}_3\text{COOH} + \text{CH}_3\text{COONa}$  (B)  $\text{Na}_2\text{CO}_3 + \text{NaHCO}_3$   
(C)  $\text{NaCl} + \text{HCl}$  (D)  $\text{NH}_4\text{Cl} + (\text{NH}_4)_2\text{SO}_4$

**Q.16** Which of the following mixtures constitute a buffer?

- (A)  $\text{Na}_2\text{CO}_3 + \text{HCl}$  (B)  $\text{NaOH} + \text{CH}_3\text{COOH}$   
(C)  $\text{NH}_3 + \text{CH}_3\text{COONH}_4$  (D)  $\text{NaOH} + \text{BaCl}_2$

### Multiple Correct Choice Type

**Q.17** In which of the following pairs of solutions is there no effect on the pH upon dilution?

- (A) 0.1 M  $\text{NH}_3$  and 0.1 M  $(\text{NH}_4)_2\text{SO}_4$   
(B) 0.1 M  $\text{NaH}_2\text{PO}_4$  and 0.1 M  $\text{Na}_2\text{HPO}_4$   
(C) 0.1 M HCl and 0.01 M NaOH  
(D) 0.1 M KCl and 0.1 M HCl

**Q.18** Which of the following statement(s) is/are correct?

- (A) The pH of  $1.0 \times 10^{-8}$  M solution of HCl is 8  
 (B) The conjugate base of  $\text{H}_2\text{PO}_4^-$  is  $\text{HPO}_4^{2-}$   
 (C) Autoprotolysis constant of water increases with temperature  
 (D) When a solution of a weak monoprotic acid is titrated again a strong base, at half neutralization point  $\text{pH} = (1/2) \text{pKa}$ .

**Q.19** A 2.5 gm impure sample containing weak monoacidic base (Mol. wt. = 45) is dissolved in 100 ml water and titrated with 0.5 M HCl when  $\left(\frac{1}{5}\right)^{\text{th}}$  of the base was neutralised the pH was found to be 9 and at equivalent point pH of solution is 4.5. Given: All data at  $25^\circ\text{C}$  &  $\log 2 = 0.3$ .

Select correct statement(s).

- (A)  $K_b$  of base is less than  $10^{-6}$   
 (B) Concentration of salt (C) at equivalent point is 0.25 M  
 (C) Volume of HCl is used at equivalent point is 100 ml  
 (D) Weight percentage of base in given sample is 80%.

**Q.20** Select incorrect statement(s).

- (A) Phenolphthalein is suitable indicator for the titration of HCl (aq) with  $\text{NH}_4\text{OH}$  (aq).  
 (B) An acid-base indicator in a buffer solution of  $\text{pH} = \text{pK}_{\text{in}} + 1$  is ionized to the extent of 90%.  
 (C) In the titration of a monoacidic weak base with a strong acid, the pH at the equivalent point is always calculated by

$$\text{pH} = \frac{1}{2} [\text{pK}_w - \text{pK}_b - \log C]$$

- (D) When  $\text{Na}_3\text{PO}_4$  (aq) is titrated with HCl (aq), the pH of solution at second equivalent point is calculated by  $\frac{1}{2} [\text{pK}_{a1} + \text{pK}_{a2}]$

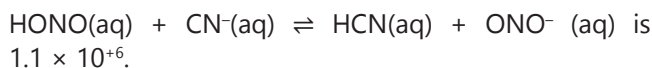
**Q.21** Which of the following is true for alkaline aqueous solution?

- (A)  $\text{pH} > \frac{\text{pK}_w}{2}$       (B)  $\text{pH} > \text{pOH}$   
 (C)  $\text{pOH} < \frac{\text{pK}_w}{2}$       (D)  $\text{pH} < \text{pOH}$

**Q.22** An acid-base indicator has a  $K_a$  of  $3.0 \times 10^{-5}$ . The acid form of the indicator is red and the basic form is blue, then:

- (A) pH is 4.05 when indicator is 75% red  
 (B) pH is 5.00 when indicator is 75% blue.  
 (C) pH is 5.00 when indicator is 75% red  
 (D) pH is 4.05 when indicator is 75% blue.

**Q.23** The equilibrium constant for the reaction



From the magnitude of this  $K_{\text{eq}}$  one can conclude that

- (A)  $\text{CN}^-$  is stronger base than  $\text{ONO}^-$   
 (B) HCN is a stronger acid than HONO  
 (C) The conjugate base of HONO is  $\text{ONO}^-$   
 (D) The conjugate acid of  $\text{CN}^-$  is HCN

**Q.24** Which of the following are acid-base conjugate pairs:

- (A)  $\text{HF}, \text{F}^-$       (B)  $\text{H}_3\text{O}^+, \text{OH}^-$   
 (C)  $\text{CH}_3\text{NH}_3^+, \text{CH}_3\text{NH}_2$       (D)  $\text{HS}^-, \text{S}_2^-$

**Q.25** Which of the following will suppress the ionization of phthalic acid in an aqueous solution.

- (A) KCl      (B)  $\text{H}_2\text{SO}_4$       (C)  $\text{HNO}_3$       (D) NaOH

**Match the Columns**

**Q.26 Match the following**

List I	List II weak
(A) $\text{CH}_3\text{COOH}$	(p) Base
(B) $\text{H}_2\text{SO}_4$	(q) Weak acid
(C) NaOH	(r) Strong acid
(D) $\text{NH}_3$	(s) Strong base



## Q.27

Column I (pH of resultant solution)	Column II (Exist between Colour transition range of an indicator)
(A) 200 ml of $\text{H}_2\text{SO}_4$ solution (specific gravity 1.225 containing 25% $\text{H}_2\text{SO}_4$ by weight) + 800 ml of 0.525 M strong triacidic base $\text{X}(\text{OH})_3$	(p) Phenol Red (6.8 to 8.4)
(B) 50 ml of 0.1 M $\text{HCO}_3^-$ + 50 ml of 0.8 M $\text{CO}_3^{2-}$ ( $\text{H}_2\text{CO}_3$ : $K_{a1} = 4 \times 10^{-7}$ , $K_{a2} = 2 \times 10^{-11}$ )	(q) Propyl red (4.6 to 6.4)
(C) 50 ml of 0.2 M $\text{HA}(\text{aq})$ ( $K_a = 10^{-5}$ ) + 50 ml of 0.1 M $\text{HCl}(\text{aq})$ + 100 ml of 0.13 M $\text{NaOH}(\text{aq})$	(r) Phenolphthalein (8.3 to 10.1)
	(s) Malachite green (11.4 to 13)

## Previous Years' Questions

**Q.1** Pure ammonia is placed in a vessel at a temperature where its dissociation constant ( $\alpha$ ) is appreciable. At equilibrium  $\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3$  (1984)

- (A)  $K_p$  does not change significantly with pressure  
 (B)  $\alpha$  does not change with pressure  
 (C) Concentration of  $\text{NH}_3$  does not change with pressure  
 (D) Concentration of hydrogen is less than that of nitrogen

**Q.2** A certain buffer solution contains equal concentration of  $\text{X}^-$  and  $\text{HX}$ . The  $K_b$  for  $\text{X}^-$  is  $10^{-10}$ . The pH of the buffer is (1984)

- (A) 4      (B) 7      (C) 10      (D) 14

**Q.3** A certain weak acid has a dissociation constant of  $1.0 \times 10^{-4}$ . The equilibrium constant for its reaction with a strong base is (1984)

- (A)  $1.0 \times 10^{-4}$       (B)  $1.0 \times 10^{-10}$   
 (C)  $1.0 \times 10^{10}$       (D)  $1.0 \times 10^{14}$

**Q.4** Solubility product constant ( $K_{sp}$ ) of salts of types  $\text{MX}$ ,  $\text{MX}_2$  and  $\text{M}_3\text{X}$  at temperature 'T' are  $4.0 \times 10^{-8}$ ,  $3.2 \times 10^{-14}$  and  $2.7 \times 10^{-15}$ , respectively. Solubilities ( $\text{mol. dm}^{-3}$ ) of the salts at temperature 'T' are in the order (2008)

- (A)  $\text{MX} > \text{MX}_2 > \text{M}_3\text{X}$     (B)  $\text{M}_3\text{X} > \text{MX}_2 > \text{MX}$   
 (C)  $\text{MX}_2 > \text{M}_3\text{X} > \text{MX}$     (D)  $\text{MX} > \text{M}_3\text{X} > \text{MX}_2$

**Q.5** 2.5 mL of  $\frac{2}{5}$  M weak monoacidic base

( $K_b = 1 \times 10^{-12}$  at  $25^\circ\text{C}$ ) is titrated with  $\frac{2}{15}$  M

$\text{HCl}$  in water at  $25^\circ\text{C}$ . The concentration of  $\text{H}^+$  at equivalence point is ( $K_w = 1 \times 10^{-14}$  at  $25^\circ\text{C}$ ) (2008)

- (A)  $3.7 \times 10^{-13}$  M      (B)  $3.2 \times 10^{-7}$  M  
 (C)  $3.2 \times 10^{-2}$  M      (D)  $2.7 \times 10^{-2}$  M

**Q.6** Aqueous solutions of  $\text{HNO}_3$ ,  $\text{KOH}$ ,  $\text{CH}_3\text{COOH}$ , and  $\text{CH}_3\text{COONa}$  of identical concentrations are provided. The pair(s) of solutions which form a buffer upon mixing is(are) (2010)

- (A)  $\text{HNO}_3$  and  $\text{CH}_3\text{COOH}$   
 (B)  $\text{KOH}$  and  $\text{CH}_3\text{COONa}$   
 (C)  $\text{HNO}_3$  and  $\text{CH}_3\text{COONa}$   
 (D)  $\text{CH}_3\text{COOH}$  and  $\text{CH}_3\text{COONa}$

**Q.7** The equilibrium  $2 \text{Cu}^{\text{I}} + \text{Cu}^{\text{II}}$  in aqueous medium at  $25^\circ\text{C}$  shifts towards the left in the presence of. (2011)

- (A)  $\text{NO}_3^-$       (B)  $\text{Cl}^-$       (C)  $\text{SCN}^-$       (D)  $\text{CN}^-$

**Q.8** The solubility of  $\text{Mg}(\text{OH})_2$  in pure water is  $9.57 \times 10^{-3}$  g/L. Calculate its solubility (in g/L) in 0.02M  $\text{Mg}(\text{NO}_3)_2$  solution. (1986)

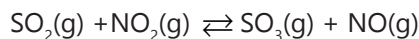
**Q.9** What is the pH of the solution when 0.20 moles of  $\text{HCl}$  is added to one litre of a solution containing:

- (i) 1 M each of acetic acid and acetate ion  
 (ii) 0.1 M each of acetic acid and acetate ion

Assume the total volume is one litre.  $K_a$  for acetic acid =  $1.8 \times 10^{-5}$  (1987)



**Q.10** At a certain temperature, equilibrium constant ( $K_c$ ) is 16 for the reaction;



If we take one mole of each of all the four gases in a one litre container, what would be the equilibrium concentrations of NO and  $\text{NO}_2$ ? **(1987)**

**Q.11 Statement-I:** In water, orthoboric acid behaves as a weak monobasic acid.

**Statement-II:** In water, orthoboric acid acts as a proton donor. **(2007)**

(A) Statement-I is True, statement-II is True; statement-II is a correct explanation for statement-I.

(B) Statement-I is True, statement-II is True; statement-II is NOT a correct explanation for statement-I.

(C) Statement-I is True, statement-II is False.

(D) Statement-I is False, statement-II is True.

**Q.12** The INCORRECT statement among the following, for this reaction, is **(2016)**

(A) Decrease in the total pressure will result in formation of more moles of gaseous X.

(B) At the start of the reaction, dissociation of gaseous  $X_2$ , takes place spontaneously.

(C)  $\beta_{\text{equilibrium}} = 0.7$

(D)  $K_C < 1$

**Q.13** In 1 L saturated solution of AgCl [ $K_{sp}(\text{AgCl}) = 1.6 \times 10^{-10}$ ], 0.1 mol of CuCl [ $K_{sp}(\text{CuCl}) = 1.0 \times 10^{-6}$ ] is added. The resultant concentration of  $\text{Ag}^+$  in the solution is  $1.6 \times 10^{-x}$ . The value of "x" is **(2011)**

**Q.14** The solubility product ( $K_{sp}$ ;  $\text{mol}^3\text{dm}^{-9}$ ) of  $\text{MX}_2$  at 298 based on the information available the given concentration cell is (take  $2.303 \times \frac{298}{F} = 0.059$  V) **(2012)**

(A)  $1 \times 10^{-15}$  (B)  $4 \times 10^{-15}$

(C)  $1 \times 10^{-12}$  (D)  $4 \times 10^{-12}$

**Q.15** The compound that does NOT liberate  $\text{CO}_2$ , on treatment with aqueous sodium bicarbonate solution, is **(2013)**

(A) Benzoic acid (B) Benzenesulphonic acid

(C) Salicylic acid (D) Carboic acid (phenol)

**Q.16** The initial rate of hydrolysis of methyl acetate (1 M) by a weak acid (HA, 1M) is 1/100th of that of a strong acid (HX, 1M), at 25° C. The  $K_a$  of HA is **(2013)**

(A)  $1 \times 10^{-4}$  (B)  $1 \times 10^{-5}$

(C)  $1 \times 10^{-6}$  (D)  $1 \times 10^{-3}$

**Q.17** The  $K_{sp}$  of  $\text{Ag}_2\text{CrO}_4$  is  $1.1 \times 10^{-12}$  at 298K. The solubility (in mol/L) of  $\text{Ag}_2\text{CrO}_4$  in a 0.1M  $\text{AgNO}_3$  solution is **(2013)**

(A)  $1.1 \times 10^{-11}$  (B)  $1.1 \times 10^{-10}$

(C)  $1.1 \times 10^{-12}$  (D)  $1.1 \times 10^{-9}$

**Paragraph 1:** Thermal decomposition of gaseous  $X_2$  to gaseous X at 298 K takes place according to the following equation:  $X_2(\text{g}) \rightleftharpoons 2X(\text{g})$

The standard reaction Gibbs energy,  $\Delta_r G^\circ$  of this reaction is positive. At the start of the reaction, there is one mole of  $X_2$  and no X. As the reaction proceeds, the number of moles of X formed is given by b. Thus,  $b_{\text{equilibrium}}$  is the number of moles of X formed at equilibrium. The reaction is carried out at a constant total pressure of 2 bar. Consider the gases to behave ideally. (Given:  $R = 0.083 \text{ L bar K}^{-1} \text{ mol}^{-1}$ )

**Q.18** The equilibrium constant  $K_p$  for this reaction at 298 K, in terms of  $b_{\text{equilibrium}}$ , is **(2016)**

(A)  $\frac{8\beta_{\text{equilibrium}}^2}{2 - \beta_{\text{equilibrium}}}$  (B)  $\frac{8\beta_{\text{equilibrium}}^2}{4 - \beta_{\text{equilibrium}}^2}$

(C)  $\frac{4\beta_{\text{equilibrium}}^2}{2 - \beta_{\text{equilibrium}}^2}$  (D)  $\frac{4\beta_{\text{equilibrium}}^2}{4 - \beta_{\text{equilibrium}}^2}$

# MASTERJEE Essential Questions

## JEE Main/Boards

### Exercise 1

Q.1      Q.4      Q.6      Q.8  
 Q.13    Q.17    Q.19    Q.28  
 Q.29

### Exercise 2

Q.5      Q.8      Q.9      Q.13  
 Q.17    Q.22    Q.24

### Previous Years' Questions

Q.4      Q.7      Q.11

## JEE Advanced/Boards

### Exercise 1

Q.2      Q.6      Q.9      Q.11  
 Q.16    Q.21    Q.24    Q.25  
 Q.29    Q.30

### Exercise 2

Q.1      Q.4      Q.7      Q.8  
 Q.9      Q.13    Q.16    Q.19  
 Q.21    Q.22

### Previous Years' Questions

Q.3      Q.5      Q.8      Q.10

## Answer Key

## JEE Main/Boards

### Exercise 1

**Q.1** 2.3 mol/lit  
**Q.2.** 1.5 times  
**Q.3**  $1.44 \times 10^{-4}$   
**Q.4**  $2 \times 10^{-8}$   
**Q.5** No  
**Q.6**  $4.11 \times 10^{-4}$  M  
**Q.7**  $5.6 \times 10^{-10}$ ,  $2.4 \times 10^{-4}$ , 5.63  
**Q.8** 1.3  
**Q.9**  $\text{HZ} < \text{HY} < \text{HX}$ ,  $K_a(\text{HY}) = 10^{-5}$  M,  $K_a(\text{HZ}) = 10^{-9}$  M  
**Q.10** (a)  $3.72 \times 10^4 \text{ dm}^3$  (b)  $4 \text{ dm}^3$   
**Q.11**  $K_c = 3.02 \times 10^{-2}$ ,  $S = 0.123$  M

**Q.12** 6.1  
**Q.13** (i) pH = 4.35 (ii)  $1.79 \times 10^{-9}$  mol/lit  
**Q.14** (i) 28.6%  
**Q.15**  $[\text{HS}^-] = 9.54 \times 10^{-5}$ , in 0.1 M HCl  $[\text{HS}^-] = 9.1 \times 10^{-8}$  M,  $[\text{S}^{2-}] = 1.2 \times 10^{-13}$  M, in 0.1 M HCl  $[\text{S}^{2-}] = 1.09 \times 10^{-19}$  M  
**Q.16**  $[\text{Ac}^-] = 0.00093$ , pH = 3.03  
**Q.17**  $[\text{A}^-] = 7.08 \times 10^{-5}$  M,  $K_a = 5.08 \times 10^{-7}$ ,  $\text{p}K_a = 6.29$   
**Q.18** (i) 2.52 (ii) 2.30 (iii) 2.7 (iv) 2.70  
**Q.19** (i) 11.65 (ii) 12.21 (iii) 12.57 (iv) 1.87  
**Q.20** 0.103g  
**Q.21** pH = 9.20,  $k_H = 0.772$ ,  $h = 0.467$   
**Q.22** 11  
**Q.23** 0.082 mol of NaOH can be added

**Exercise 2****Single Correct Choice Type**

Q.1 A	Q.2 C	Q.3 C	Q.4 C	Q.5 B	Q.6 C
Q.7 C	Q.8 D	Q.9 D	Q.10 A	Q.11 D	Q.12 B
Q.13 B	Q.14 C	Q.15 B	Q.16 D	Q.17 A	Q.18 C
Q.19 A	Q.20 B	Q.21 B	Q.22 C	Q.23 A	Q.24 D
Q.25 B	Q.26 A				

**Previous Years Questions**

Q.1 C	Q.2 A	Q.3 A	Q.4 B	Q.5 B	Q.6 D
Q.7 B,C	Q.8 A,C	Q.9 A	Q.10 A	Q.11 C	Q.12 A
Q.13 B	Q.14 C	Q.15 B	Q.16 B	Q.17 D	Q.18 C
Q.19 D	Q.20 B				

**JEE Advanced/Boards****Exercise 1**

Q.1 $6.022 \times 10^7$	Q.2 $1.6 \times 10^{-7}$
Q.3 (i) 6.50 ; (ii) (a) Basic, (b) Acidic	Q.4 6.79
Q.5 (a) 0.522, (b) 2.61	Q.6 0.027 M, 0.073 M, 0.027 M, $10^{-5}$ M
Q.7 0.2116 M, 0.1884 M, 0.0116 M, 0	Q.8 8.7782
Q.9 12.8	
Q.10 (Methyl red), one with pH = 5.22 as midpoint of colour range	
Q.11 $\Delta\text{pH} = 0.95$	Q.12 $[\text{OH}^-] = 6.664 \times 10^{-6}$
Q.13 pH = 4.477	Q.14 $5.12 \times 10^{-6}$ M
Q.15 8.86	Q.16 $\text{QX}_2$ is more soluble
Q.17 $4 \times 10^{-7}$ mol/L AgBr, $9 \times 10^{-7}$ mol/L AgSCN	Q.18 $K_a = 1.25 \times 10^{-2}$
Q.19 $[\text{S}^{2-}] = 2.5 \times 10^{-15}$	Q.20 $V = 2.77 \times 10^4$ litre
Q.21 Acetic acid, salt-acid molar ratio 1.8: 1	Q.22 9.168
Q.23 (a) pH = 3.83 (b) pH = 3.85, (c) = 3.99	

**Exercise 2****Single Correct Choice Type**

Q.1 A	Q.2 C	Q.3 D	Q.4 B	Q.5 B	Q.6 D
Q.7 C	Q.8 B	Q.9 A	Q.10 D	Q.11 A	Q.12 A
Q.13 A	Q.14 B	Q.15 C	Q.16 C		

**Multiple Correct Choice Type**

- Q.17 A, B      Q.18 B, C      Q.19 B, C      Q.20 A, B, C      Q.21 A, B, C      Q.22 A, B  
 Q.23 A, C, D      Q.24 A, D      Q.25 B, C, D

**Match the Columns**

- Q.26 A → q; B → r; C → s; D → p      Q.27 A → s; B → s; C → q

**Previous Years Questions**

- Q.1 A      Q.2 A      Q.3 C      Q.4 D      Q.5 D      Q.6 C, D  
 Q.7 B, C, D      Q.8  $8.7 \times 10^{-4} \text{ gL}^{-1}$       Q.9 (i) 4.56 (ii) 1      Q.10  $[\text{NO}] = 0.80\text{M}$ ;  $[\text{NO}_2] = 0.20\text{M}$       Q.11 C  
 Q.12 C      Q.13 7      Q.14 B      Q.15 D      Q.16 A      Q.17 B  
 Q.18 B

**Solutions****JEE Main/Boards****Exercise 1**

Sol 1:  $\alpha = \sqrt{\frac{K_a}{C}}$

∴  $\alpha$  will be equal, equate the terms on R.H.S. for both the acids.

$$\frac{K_a}{C} \quad \text{HNO}_2$$

Sol 2:

Blood	Spinal fluid
$[\text{H}^+] = 10^{-7.36}$ $= 4.36 \times 10^{-8}$	$[\text{H}^+] = 10^{-7.53}$ $= 2.95 \times 10^{-8}$

Sol 3: The freezing point depression is given by  $\Delta T = K_f \times m$

$1.86 \text{ K mol}^{-1} \text{ kg} \times m = 0.758 \text{ K}$  so,  $m = 0.40752 \text{ mol kg}^{-1}$ . If this can be taken to be  $0.40752 \text{ mol L}^{-1}$  for this question.

The van't Hoff factor  $i = \frac{0.40752}{0.400} = 1.0188$

Ans: van't Hoff factor  $i = 1.02$

(ii) Formic acid ionizes in water according to:  $\text{HCOOH} \rightleftharpoons \text{HCOO}^- + \text{H}^+$

If the initial concentration before ionization is  $0.400 \text{ mol L}^{-1}$  and  $x \text{ mol L}^{-1}$  ionizes then the final number of particles in the solution is

$$(0.400 \text{ mol L}^{-1} - x \text{ mol L}^{-1}) + 2x \text{ mol L}^{-1} = 0.400 \text{ mol L}^{-1} + x \text{ mol L}^{-1}$$

$$\text{Now, } 0.400 \text{ mol L}^{-1} + x \text{ mol L}^{-1} = 0.40752 \text{ mol L}^{-1}$$

$$x \text{ mol L}^{-1} = 7.52 \times 10^{-3} \text{ mol L}^{-1} = [\text{H}^+] = [\text{HCOO}^-]$$

$$K_a = \frac{[\text{H}^+][\text{HCOO}^-]}{[\text{HCOOH}]} = \frac{[7.52 \times 10^{-3} \text{ mol L}^{-1}]}{[0.400 - 7.52 \times 10^{-3}] \text{ mol L}^{-1}} = 1.44 \times 10^{-4}$$

Sol 4:  $2\text{AgCl}(s) + \text{CO}_3^{2-} \rightleftharpoons \text{Ag}_2\text{CO}_3(s) + 2\text{Cl}^-$

$$K = \frac{[\text{Cl}^-]}{[\text{CO}_3^{2-}]} = \frac{[\text{Cl}^-]^2}{[\text{CO}_3^{2-}]} \times \frac{[\text{Ag}^+]^{-2}}{[\text{Ag}^+]^{-2}} = \frac{[K_{sp}(\text{AgCl})]^2}{K_{sp}(\text{Ag}_2\text{CO}_3)}$$

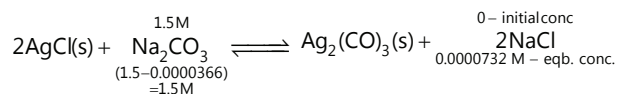
$$[\text{Cl}^-] = \frac{0.0026}{35.5} \text{ M} = 7.5 \times 10^{-5} \text{ M}$$

The above concentration of  $\text{Cl}^-$  indicates that  $[\text{CO}_3^{2-}]$  remains almost unchanged.

$$\Rightarrow \frac{7.3 \times 10^{-5}}{1.5} = \frac{[K_{sp}(\text{AgCl})]^2}{8.2 \times 10^{-12}} \Rightarrow K_{sp}(\text{AgCl}) = 2 \times 10^{-8}$$

**Sol 5:** Initial  $[\text{Na}_2\text{CO}_3] = [\text{CO}_3^{2-}] = 1.5 \text{ M}$

$$\text{Equilibrium } [\text{Cl}^-] = [\text{NaCl}] = \frac{0.0026}{35.5} = 0.0000732 \text{ M}$$



$$[\text{Ag}^+] = \sqrt{\frac{K_{sp}(\text{Ag}_2\text{CO}_3)}{[\text{CO}_3^{2-}]}} = \sqrt{\frac{8.2 \times 10^{-12}}{1.5}}$$

$$= 2.338 \times 10^{-6} \text{ M}$$

$$\therefore K_{sp} = [\text{Ag}^+][\text{Cl}^-] = (2.338 \times 10^{-6})(0.0000732)$$

$$= 1.71 \times 10^{-10}$$

Precipitate of AgCl will not be formed.

**Sol 6:** The hydrogen ion concentrations of the given pH range are

$$\text{pH} = 3.1 = -\log\left\{\frac{[\text{H}^+]}{\text{M}}\right\}$$

$$\text{i.e. } \log\left\{\frac{[\text{H}^+]}{\text{M}}\right\} = -3.1 = \bar{4}.9$$

$$\text{Hence, } [\text{H}^+] = 7.9 \times 10^{-4} \text{ M}$$

$$\text{pH} = 4.5 \text{ i.e. } \log\left\{\frac{[\text{H}^+]}{\text{M}}\right\} = -4.5 = \bar{5}.5$$

$$\text{Hence, } [\text{H}^+] = 3.2 \times 10^{-5} \text{ M}$$

The average of these two hydrogen ion concentration is

$$\frac{7.9 \times 10^{-4} \text{ M} + 3.2 \times 10^{-5} \text{ M}}{2} = 4.11 \times 10^{-4} \text{ M}$$

At this  $\text{H}^+$  concentration,

$$[\text{In}^-] = [\text{HIn}]$$

Therefore,  $\text{pH} = \text{p}K_{\text{HIn}}$

$$\text{Or } [\text{H}^+] = K_{\text{HIn}} = 4.11 \times 10^{-4} \text{ M}$$

**Sol 7:**  $K_b(\text{NH}_4\text{OH}) = 1.8 \times 10^{-5}$ ;  $C = 0.01 \text{ M}$

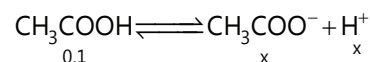
$$\frac{K_w}{K_b} = cx^2 \quad (x = \text{degree of hydrolysis})$$

$$K_h = cx^2 \quad (K_h = \text{hydrolysis constant})$$

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

**Sol 8:**  $C = 0.1 \text{ M}$

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



$$K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]} ; 1.8 \times 10^{-5} = \frac{x^2}{0.1}$$

$$(i) [\text{H}^+] = x \therefore \text{pH} = -\log[\text{H}^+]$$

$$(ii) \text{Vol. of } \text{CH}_3\text{COOH} = 1 \text{ L}$$

Addition of 0.05 mole of HCl increases the concentration of  $\text{CH}_3\text{COOH}$  by 0.05 and reduces the conc. of  $\text{CH}_3\text{COO}^-$  by 0.05 mol / L.

$$\therefore [\text{CH}_3\text{COOH}] = 0.1 + 0.05 = 0.15 \text{ M}$$

$$[\text{CH}_3\text{COO}^-] = 1.34 \times 10^{-3} - 0.05 = 0.05134 \text{ M}$$

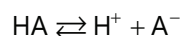
$$\text{pH} = \text{p}K_a + \log \frac{[\text{salt}]}{[\text{acid}]} = -\log 1.8 \times 10^{-5} + \log \frac{0.05134}{0.15}$$

$$\text{pH} = 1.3$$

**Sol 9:** The pH of NaX is 7, thus the acid HX must be a strong acid. The ions  $\text{Y}^-$  and  $\text{Z}^-$  undergo hydrolysis  $\text{Y}^- + \text{H}_2\text{O} \rightleftharpoons \text{HY} + \text{OH}^-$  and  $\text{Z}^- + \text{H}_2\text{O} \rightleftharpoons \text{HZ} + \text{OH}^-$ .

The stronger the base, larger the  $\text{OH}^-$  concentration and thus larger the pH of the solution. Thus  $\text{Z}^-$  is stronger base than  $\text{Y}^-$  and thus conjugate acid HZ will be weaker than HY. Hence, the correct order is  $\text{HX} > \text{HY} > \text{HZ}$

**Sol 10:** We have



$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} = \frac{[\text{H}^+]^2}{[\text{HA}]_0 - [\text{H}^+]} \approx \frac{[\text{H}^+]^2}{[\text{HA}]_0}$$

$$\text{Or } [\text{H}^+] = \sqrt{K_a[\text{HA}]_0} = \left[ (1.8 \times 10^{-5} \text{ M})(0.5 \text{ M}) \right]^{1/2} \\ = 3.0 \times 10^{-3} \text{ M}$$

(a) Now to double the pH, we will have

$$[\text{H}^+] = \text{antilog}(-2 \times 2.523) = 9.0 \times 10^{-6} \text{ M}$$

Now from the expression

$$K_a = \frac{[\text{H}^+]^2}{[\text{HA}]_0 - [\text{H}^+]}$$
 we get

$$1.8 \times 10^{-5} \text{ M} = \frac{(9.0 \times 10^{-6} \text{ M})^2}{[\text{HA}]_0 - (9.0 \times 10^{-6} \text{ M})}$$

$$[\text{HA}]_0 = \frac{(9.0 \times 10^{-6} \text{M})^2 (1.8 \times 10^{-5} \text{M})}{(1.8 \times 10^{-5} \text{M})}$$

$$\text{This given} = \frac{8.0 \times 10^{-11} \text{M}^2 + 1.62 \times 10^{-10} \text{M}^2}{1.8 \times 10^{-5} \text{M}}$$

$$= \frac{2.42 \times 10^{-10} \text{M}^2}{1.8 \times 10^{-5} \text{M}} = 1.344 \times 10^{-5} \text{M}$$

$$\text{Dilution factor} = \frac{0.5 \text{M}}{1.344 \times 10^{-5} \text{M}} = 3.72 \times 10^4$$

(b) To double the  $[\text{OH}^-]$ , we have

$$[\text{H}^+] = \frac{1}{2} \times 3.0 \times 10^{-3} \text{M}$$

$$\text{Hence, } [\text{HA}]_0 = \frac{[\text{H}^+]^2}{K_a} = \frac{(1.5 \times 10^{-3} \text{M})^2}{(1.8 \times 10^{-5} \text{M})} = 0.125 \text{M}$$

$$\text{Dilution factor} = \frac{0.5 \text{M}}{0.125 \text{M}} = 4$$

$$\text{Sol 11: } K_c = \frac{K_{sp}}{K_b^2} = \frac{10^{-11}}{(1.8 \times 10^{-5})^2} = 3.02 \times 10^{-2}$$

$$\text{Sol 12: } \text{pH} = \text{p}K_a^0 + \log \frac{[\text{salt}]}{[\text{acid}]}$$

$$\text{We get } 5.8 = \text{p}K_a^0 + \log \left[ \frac{(10 \text{mL})M_2}{VM_1 - (10 \text{mL})M_2} \right]$$

$$6.402 = \text{p}K_a^0 + \log \left[ \frac{(20 \text{mL})M_2}{VM_1 - (20 \text{mL})M_2} \right]$$

Subtracting Eq. (i) from Eq. (ii), we get

$$6.402 = \left[ \frac{(20 \text{mL})M_2}{VM_1 - (20 \text{mL})M_2} \frac{VM_1 - (10 \text{mL})M_2}{(10 \text{mL})M_2} \right]$$

$$\text{Or } \frac{2[VM_1 - (10 \text{mL})M_2]}{VM_1 - (20 \text{mL})M_2} = 4$$

$$\text{or } \frac{VM_1}{M_2} = \frac{60 \text{mL}}{2} = 30 \text{mL}$$

Substituting this in either Eq. (i) or Eq. (ii) we get

$$\text{p}K_a^0 = 5.8 - \log \left( \frac{10}{30 - 10} \right) = 5.8 + 0.30 = 6.1$$

**Sol 13:** The minimum of concentration  $\text{S}^{2-}$  ion to start of the precipitation is obtained from the  $K_{tp}$  with  $[\text{Mn}^{2+}] = 0.01 \text{M}$ . Therefore, we have

$$[\text{S}^{2-}] = \frac{K_{sp}(\text{MnS})}{[\text{Mn}^{2+}]} = \frac{5.6 \times 10^{-16} \text{M}^2}{(0.01 \text{M})} = 5.6 \times 10^{-14} \text{M}$$

The  $\text{H}^+$  concentration of the solution having the above  $[\text{S}^{2-}]$  can be computed from the expression of  $\text{H}_2\text{S}$  equilibrium:

$$\frac{[\text{H}^+]^2 [\text{S}^{2-}]}{[\text{H}_2\text{S}]} = \frac{[\text{H}^+]^2 (5.6 \times 10^{-14} \text{M})}{(0.10 \text{M})} = 1.1 \times 10^{-21} \text{M}^2$$

This gives

$$[\text{H}^+] = 4.43 \times 10^{-5} \text{M} \text{ or } \text{pH} = 4.35$$

If the  $[\text{H}^+] > 4.43 \times 10^{-5} \text{M}$ , then the  $[\text{S}^{2-}]$  will be less than  $5.6 \times 10^{-14} \text{M}$  and  $\text{MnS}$  will no longer precipitate from the solution.

The concentration of  $\text{Zn}^{2+}$  ion remaining in the solution can be calculated from the solubility product of  $\text{ZnS}$ :

$$[\text{Zn}^{2+}] = \frac{K_{sp}(\text{ZnS})}{[\text{S}^{2-}]} = \frac{1.0 \times 10^{-22} \text{M}^2}{(5.6 \times 10^{-14} \text{M})} = 1.79 \times 10^{-9} \text{M}$$

Thus, by properly adjusting the  $[\text{H}^+]$  in the solution, it is possible to precipitate effectively all of zinc ions from the solution without precipitating any  $\text{Mn}^{2+}$  ion.

**Sol 14:** Since at  $\text{pH} = 2.0$ , half of the indicator is present in the unionized form, therefore

$$[\text{HIn}] = [\text{In}^-]$$

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

$$\text{p}K_{in} = \text{pH} = 2.0$$

$\text{pH}$  of the solution containing  $4.0 \times 10^{-3} \text{M}$  of  $\text{H}^+$  is

$$\text{pH} = -\log(4.0 \times 10^{-3}) = 2.4$$

$$\text{Thus, } \log \left( \frac{[\text{In}^-]}{[\text{HIn}]} \right) = \text{pH} - \text{p}K_{in} = 2.4 - 2.0 = 0.4$$

$$\text{Or } \frac{[\text{In}^-]}{[\text{HIn}]} = 2.5$$

Adding 1 on both sides, we get

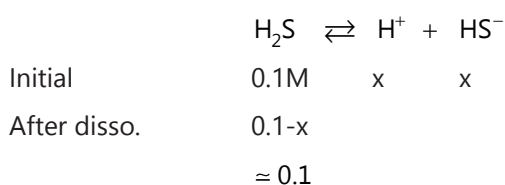
$$\frac{[\text{In}^-] + [\text{HIn}]}{[\text{HIn}]} = 3.5$$

$$\text{or } \frac{[\text{HIn}]}{[\text{In}^-] + [\text{HIn}]} = \frac{1}{3.5} = 0.286$$

Thus, the percentage of indicator in the unionized form = 28.6

**Sol 15:** dissociation constant of  $\text{H}_2\text{S}$  is  $1.2 \times 10^{-13}$ , calculate the concentration of  $\text{S}^{2-}$  under both conditions.

Ans. To calculate  $[\text{HS}^-]$



$$K_a = \frac{x \times x}{0.1} = 9.1 \times 10^{-8} \quad \text{or } x^2 = 9.1 \times 10^{-9}$$

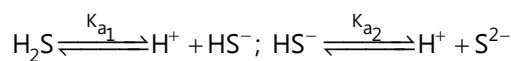
$$\text{or } x = 9.54 \times 10^{-5}$$

In presence of 0.1 M HCl, suppose  $\text{H}_2\text{S}$  dissociated is y. Then at equilibrium,

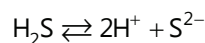
$$[\text{H}_2\text{S}] = 0.1 - y \approx 0.1, [\text{H}^+] = 0.1 + y \approx 0.1, [\text{HS}^-] = y \text{M}$$

$$K_a = \frac{0.1 \times y}{0.1} = 9.1 \times 10^{-8} \text{ (Given) or } y = 9.1 \times 10^{-8} \text{ M}$$

To calculate  $[\text{S}^{2-}]$



For the overall reaction,



$$K_a = K_{a1} \times K_{a2} = 9.1 \times 10^{-8} \times 1.2 \times 10^{-13} = 1.092 \times 10^{-20}$$

$$K_a = \frac{[\text{H}^+]^2 [\text{S}^{2-}]}{[\text{H}_2\text{S}]}$$

In the absence of 0.1 M HCl,  $[\text{H}^+] = 2[\text{S}^{2-}]$

Hence, if  $[\text{S}^{2-}] = x, [\text{H}^+] = 2x$

$$\therefore \frac{(2x)^2 x}{0.1} = 1.092 \times 10^{-20} \quad \text{or } 4x^3 = 1.092 \times 10^{-21} = 273 \times 10^{-24}$$

$$3 \log x = \log 273 - 24 = 2.4362 - 24$$

$$\log x = 0.8127 - 8 = \bar{8}.8127,$$

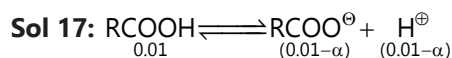
$$\text{Or } x = \text{Antilog } \bar{8}.8127 = 273 \times 10^{-24} = 6.497 \times 10 = 6.5 \times 10^{-8} \text{ M}$$

In presence of 0.1 M HCl, suppose  $[\text{S}^{2-}] = y$ , then

$$[\text{H}_2\text{S}] = 0.1 - y \approx 0.1 \text{M}, [\text{H}^+] = 0.1 + y \approx 0.1 \text{M}$$

$$K_a = \frac{(0.1)^2 \times y}{0.1} = 1.09 \times 10^{-20} \quad \text{or } y = 1.09 \times 10^{-19} \text{M}$$

$$\text{Sol 16: } K_a = 1.74 \times 10^{-5} \quad \sqrt{\frac{K_a}{C}} = \alpha$$



pH = 4.15

conc. = 0.01 M

Get conc. of  $\text{H}^\oplus$  from pH. Calculate  $\alpha$  and  $K_a$ .

**Sol 18:** (i) pH of 0.003 M HCl

$$[\text{H}^+] = 0.003 \text{M}; \text{pH} = -\log(0.003) = 2.52$$

(ii) pH of 0.005 M NaOH

$$[\text{OH}^-] = 0.005 \text{M}; \text{pOH} = -\log(0.005) = 2.30$$

(iii) pH of 0.002 M HBr

$$[\text{H}^+] = 0.002 \text{M}; \text{pH} = -\log(0.002) = 2.70$$

(iv) pH of 0.002 M KOH

$$[\text{OH}^-] = 0.002 \text{M}; \text{pOH} = -\log(0.002) = 2.70$$

**Sol 19:** Calculate  $\text{H}^\oplus / \text{OH}^\ominus$  conc. using the volume and weight. Thus, calculate pH.

**Sol 20:** Calculate solubility and then calculate it using volume of 2.5 L.



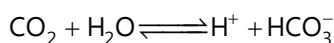
**Sol 21:**

$$K_h = \frac{K_w}{K_a \times K_b} = \frac{10^{-14}}{7.2 \times 10^{-10} \times 1.8 \times 10^{-5}} = 0.772$$

$$h = \frac{\sqrt{K_h}}{1 + \sqrt{K_h}} = \frac{\sqrt{0.772}}{1 + \sqrt{0.772}} = \frac{0.878}{1.878} = 0.467$$

$$\text{pH} = \frac{1}{2} \text{p}K_w + \frac{1}{2} \text{p}K_a - \frac{1}{2} \text{p}K_b = 7.0 + \frac{9.14}{2} - \frac{4.74}{2} = 9.20$$

**Sol 22:**  $\text{CO}_2$  with  $\text{H}_2\text{O}$  forms  $\text{H}_2\text{CO}_3$ .



$$K_1 = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{CO}_2]} = 4.5 \times 10^{-7}$$

Now,  $\text{pH} = -\log[\text{H}^+] = 7.4$ ;  $[\text{H}^+] = 4 \times 10^{-8}$

$$\text{Thus, } \frac{[\text{HCO}_3^-]}{[\text{CO}_2]} = \frac{4.5 \times 10^{-7}}{4 \times 10^{-8}} = 11$$

**Sol 23:** The original  $\text{pOH} = 4.75$ . The  $\text{pOH}$  after addition of  $\text{NaOH}$  cannot be less than 3.75.

$$\text{pOH} = 3.75 = 4.75 + \log \frac{[\text{NH}_4^+]}{[\text{NH}_3]}$$

$$\log \frac{[\text{NH}_4^+]}{[\text{NH}_3]} = -1.00 \quad \text{so} \quad \frac{[\text{NH}_4^+]}{[\text{NH}_3]} = 0.10$$

Hence  $\text{NaOH}$  can be added until the ratio of  $[\text{NH}_4^+]$  to  $[\text{NH}_3]$  is 0.10. Initially  $[\text{NH}_4^+] + [\text{NH}_3] = 0.200$

Although the reaction with  $\text{OH}^-$  converts  $\text{NH}_4^+$  into  $\text{NH}_3$ , the sum of these two concentrations remains 0.200.

$$[\text{NH}_4^+] + [\text{NH}_3] = 0.200$$

$$[\text{NH}_4^+] = 0.10[\text{NH}_3] \quad (\text{From above})$$

$$0.10[\text{NH}_3] + [\text{NH}_3] = 0.200$$

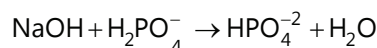
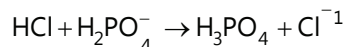
$$\text{so } 1.10[\text{NH}_3] = 0.200 \quad \text{and} \quad [\text{NH}_3] = 0.182\text{M}$$

Hence  $[\text{NH}_4^+] = 0.018\text{M}$  Assuming no change in volume,  $0.100 - 0.018 = 0.082$  mol of  $\text{NaOH}$  can be added without changing the  $\text{pOH}$  by more than 1.00  $\text{pOH}$  unit.

**Exercise 2****Single Correct Choice Type**

**Sol 1: (A)** The conjugate acid has one proton ( $\text{H}^+$ ) more. Hence, for  $\text{NH}_2^-$  the conjugate acid would be  $\text{NH}_3$  (the positive charge of  $\text{H}^+$  and the negative charge of  $\text{NH}_2^-$  cancel each other out).

**Sol 2: (C)**  $\text{H}_2\text{PO}_4^-$  and  $\text{HCO}_3^-$  are amphoteric in nature.



**Sol 3: (C)** Halides and alkaline metals dissociate and do not affect the  $\text{H}^+$  as the cation does not alter the  $\text{H}^+$  and the anion does not attract the  $\text{H}^+$  from water. This is why  $\text{NaCl}$  is a neutral salt. But  $\text{pH}$  of water **decreases** as the temperature **increases**. So option C is correct

$$\text{Sol 4: (C)} \quad \text{No. moles HCl} = \frac{(1 \times 0.1)}{1000} = 10^{-4}$$

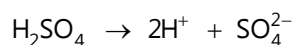
Volume =  $1\text{dm}^3$  Concentration = moles/volume

$= \frac{10^{-4}}{1} = 10^{-4}$  This gives a  $\text{pH}$  of 4 so option (C) is correct.

**Sol 5: (B)**

We have 50mL of  $\frac{\text{M}}{200} \text{H}_2\text{SO}_4$

$$\frac{\text{M}}{200} = 0.005\text{M solution}$$



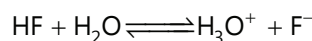
$$\text{Then } [\text{H}^+] = 2 \times 0.005\text{M} = 0.01\text{M}$$

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

$$\text{pH} = -\log 0.01\text{M}$$

$$\text{pH} = 2.00$$

**Sol 6: (C)** The equation for the dissociation of  $\text{HF}$  is as follow:



Here  $\text{p}K_b = 10.83$

$$\Rightarrow -\log K_b = 10.83$$

$$\text{Hence, } K_b = 1.48 \times 10^{-11}$$

Thus Ionization constant of acid  $K_a = K_w / K_b$

$$K_w = 10^{-14}$$

$$K_a = 10^{-14} / 1.48 \times 10^{-11}$$

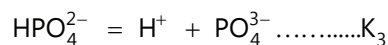
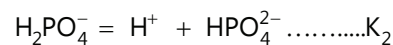
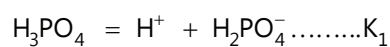
$$K_a = 6.76 \times 10^{-4}$$

Thus Ionization constant of HF is  $6.76 \times 10^{-4}$

**Sol 7: (C)**  $[H_3O^+] = C\alpha = 0.1 \times \frac{1}{100} = 1 \times 10^{-3}$

$$pH = -\log[H_3O^+] = -\log 10^{-3} = 3$$

**Sol 8: (D)**



$$K_3 = [HPO_4^{2-}]$$

$$H^+ = [PO_4^{3-}]$$

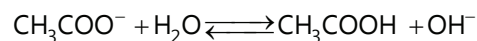
**Sol 9: (D)** Molarity of both acid and base is same. Amount of acid used is thrice the amount of base. Thus the pH of the solution will be highly acidic,

**Sol 10: (A)** Since NaCN is the salt of a weak acid (HCN) and strong base (NaOH), the degree of hydrolysis,

$$\begin{aligned} \alpha &= \sqrt{\frac{K_w}{K_a \times C}} \\ &= \frac{1.0 \times 10^{-14} \times 80}{1.3 \times 10^{-9}} \\ &= \sqrt{6.16 \times 10^{-4}} \\ &= 2.48 \times 10^{-2} \end{aligned}$$

$\therefore$  Percentage hydrolysis of NaCN in N/80 Solution is 2.48

**Sol 11: (D)** Sodium acetate undergoes anionic hydrolysis



**Sol 12: (B)**  $NH_4OH + HCl \rightleftharpoons NH_4Cl$

$NH_4Cl$  Is a salt of weak base and strong acid .so it give s acidic solution with  $pH > 7$

**Sol 13: (B)** The pH of the solution at the equivalence point will be greater than 7 due to salt hydrolysis. So an indicator giving colour on the basic side will be suitable.

**Sol 14: (C)** It is a salt of weak acid and weak base.

$$[H^+] = \sqrt{\frac{K_w \times K_a}{K_b}}$$

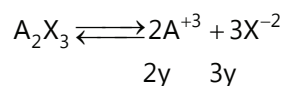
On solving we get

$$pH = 7.01$$

**Sol 15: (B)**  $CH_3COONa + HCl \rightleftharpoons CH_3COOH + NaCl$

It is an example of titration of weak base with strong acid. Observed pH range for the end point is 3.00 to 6.00.

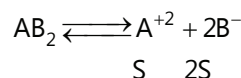
**Sol 16: (D)**



$$K_{sp} = [A^{+3}]^2 [B^{-2}]^3 = (2y)^2 (3y)^3 = 108y^5$$

**Sol 17: (A)** Solubility =  $\sqrt{K_{sp}} = \sqrt{6.4 \times 10^{-5}} = 8 \times 10^{-3}$

**Sol 18: (C)**



$$K_{sp} = [A^{+2}]^2 [B^-]^2 = (S)(2S)^2 = 4(1 \times 10^{-5})^3 = 4 \times 10^{-15}$$

**Sol 19: (A)**  $(AB, AB_2, A_xB_y) K_{sp} = (S^{x+y})X^xY^y$

**Sol 20: (B)** Precipitation takes place when the ionic product of a salt is greater than the solubility product. Solubility product of  $AgCl$  is  $1.8 \times 10^{-10}$ . So, the ionic product of  $AgCl$  should be greater than this value. On using the values given in option (B), the ionic product comes out to be  $1 \times 10^{-10}$ . Hence the correct answer is option (B)

**Sol 21: (B)** Precipitation takes place when the ionic product of a salt is greater than the solubility product. We are given that the solubility product of  $CaF_2$  is  $1.7 \times 10^{10}$ . So, the ionic product of  $CaF_2$  should be greater than this value. The ionic product of  $CaF_2$  can be calculated as follows:

$$= [Ca^{2+}] \times [F^-]^2$$

On using the values given option (A), the ionic product of  $CaF_2$  comes out to be  $1 \times 10^{12}$ , while using the values given in option (C), we get  $1 \times 10^{11}$  as the answer. However, on using the values given in option (B), the ionic product comes out to be

$$= [10^2] \times [10^3]^2$$

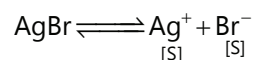
$$= 10^2 \times 10^6$$

$$= 10^8$$

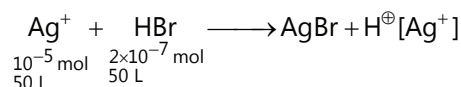
Thus, in this case, the ionic product of  $\text{CaF}_2$  is greater than solubility product. Hence the correct answer is option (b)  $10^2 \text{ M Ca}^{2+}$  and  $10^3 \text{ MF}$ .

**Sol 22: (C)**

$$K_{sp}(\text{AgBr}) = 5 \times 10^{-13}$$



$$K_{sp} = S^2 ; S = \sqrt{K_{sp}} \dots (1)$$



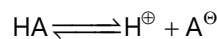
M = mole / V

The obtained  $[\text{Ag}^+]$  should be subtracted from the available 50 L  $\text{Ag}^+$  solution.

$$\text{Sol 23: (A)} \quad \text{pH}(\text{HA}) = 9 \Rightarrow [\text{H}^+] = 10^{-9}$$

$$K_{sp}(\text{AgA}) = [\text{Ag}^+][\text{A}^-]$$

$$K_a(\text{HA}) = 10^{-10}$$



$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} \text{. Get conc. of } [\text{A}^-]$$

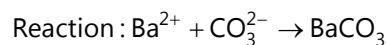
Thus, calculate  $K_{sp}$ .

**Sol 24: (D)**  $\text{Na}_2\text{CO}_3$  is salt of weak acid  $\text{H}_2\text{CO}_3$  and strong base  $\text{NaOH}$  therefore, it has a pH more than 7. Also, it dissociates to give two moles of  $\text{NaOH}$ .

**Sol 25: (B)**

$$\text{Concentration of } \text{Na}_2\text{CO}_3 = [\text{CO}_3^{2-}] = 1.0 \times 10^{-4} \text{ M}$$

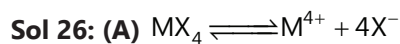
$$K_{sp} \text{ of } \text{BaCO}_3 = 5.1 \times 10^{-9}$$



$$K_{sp} = [\text{Ba}^{2+}][\text{CO}_3^{2-}]$$

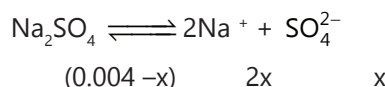
$$[\text{Ba}^{2+}] = \frac{K_{sp}}{[\text{CO}_3^{2-}]} = \frac{5.1 \times 10^{-9}}{1.0 \times 10^{-4}}$$

$$= 5.1 \times 10^{-5}$$



$$\therefore K_{sp} = [\text{S}][4\text{S}]^4 = 256$$

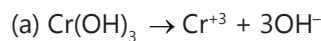
$$S = \left( \frac{K_{sp}}{256} \right)^{1/4}$$

**Previous Years' Questions****Sol 1: (C)**

Since both the solution are isotonic  $0.004 + 2x = 0.01$

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

$$\text{Percent dissociation} = \frac{3 \times 10^{-3}}{0.004} \times 100 = 75\%$$

**Sol 2: (A)**

$$x \quad 3x$$

$$K_{sp} = x.(3x)^3 = 27x^4$$

$$x = \sqrt[4]{\frac{K_{sp}}{27}} ; x = \sqrt[4]{\frac{2.7 \times 10^{-31}}{27}}$$

$$x = 1 \times 10^{-8} \text{ mole/litre.}$$

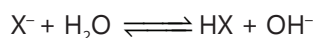
**Sol 3: (A)**

$$(a) \text{pH} = 7 + \frac{1}{2} [\text{p}K_a + \log C]$$

$$= 7 + \frac{1}{2} [4.74 + \log 10^{-2}]$$

$$= 7 + \frac{1}{2} [4.74 - 2]$$

$$= 7 + \frac{2.74}{2} = 8.37$$

**Sol 4: (B)**

$$K_h = \frac{10^{-14}}{10^{-5}} \text{ so } h = \sqrt{\frac{10^{-9}}{10^{-1}}} = 10^{-4}$$

$$100 \times 10^{-4} = 10^{-2}$$

So% of hydrolysis = 0.01%.

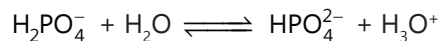
**Sol 5: (B)**  $\text{Na}_2\text{O}$  from  $\text{NaOH}$ . So that it is basic oxide.

**Sol 6: (D)**  $\alpha = 1.9 \times 10^{-9}$ ;  $C = \frac{1000}{18}$

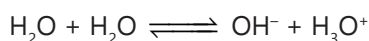
$$K = \frac{[\text{H}^+][\text{OH}^-]}{(\text{H}_2\text{O})} = c\alpha^2$$

$$= 1.9 \times 10^{-9} \times 1.9 \times 10^{-9} \times \frac{1000}{18} = 2.0 \times 10^{-16}$$

**Sol 7: (B, C)** pH of  $1 \times 10^{-8} \text{M}$  is below to 7



Conjugate base of  $\text{H}_2\text{PO}_4^-$  acid



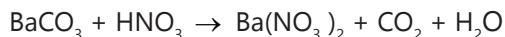
$K$  (Auto protolysis constant of water i.e., with ionic product of water) increases with temperature. For half neutralization of a weak acid by a weak base

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

$$[\text{Salt}] = [\text{Acid}] \therefore \text{pH} = \text{p}K_a.$$

**Sol 8: (A, C)** A buffer solution can be prepared by mixing weak acid/base with salt of its Conjugate base/acid.

**Sol 9: (A)** (a) Barium carbonate is more soluble in  $\text{HNO}_3$  than in water because carbonate is a weak base and reacts with the  $\text{H}^+$  ion of  $\text{HNO}_3$  causing the barium salt to dissociate.



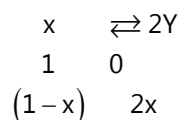
**Sol 10: (A)** (a) The conjugate base of  $\text{CHCl}_3$  is more stable than conjugate base of  $\text{CHF}_3$  ( $\text{CF}_3$ ).  $\text{CCl}_3$  stabilized by  $-I$  effect of chlorine atoms as well as by the electrons. But conjugate base of  $\text{CH}_3(\text{CH}_2)$  is stabilized only by  $-I$  effect of fluorine atoms. Here both assertion and reason are true and reason is correct explanation of assertion.

**Sol 11: (C)** It is a salt of weak acid and weak base

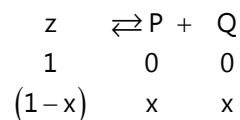
$$[\text{H}^+] = \sqrt{\frac{K_w \times K_a}{K_b}}$$

$$\text{pH} = 7.01$$

**Sol 12: (A)**  $X \rightleftharpoons 2Y$



$$K_{p1} = \frac{(2x)^2}{(1-x)} \left( \frac{P_1}{1+x} \right)^1$$



$$K_{p2} = \frac{x^2}{(1-x)} \left( \frac{P_2}{1+x} \right)^1$$

$$\frac{4 \times P_1}{P_2} = \frac{1}{9} \Rightarrow \frac{P_1}{P_2} = \frac{1}{36}$$

**Sol 13: (B)**  $\text{Ag}^+ + \text{Br}^- \rightleftharpoons \text{AgBr}$

Precipitation starts when ionic product just exceeds solubility product

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

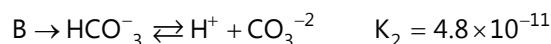
$$[\text{Br}^-] = \frac{K_{sp}}{[\text{Ag}^+]} = \frac{5 \times 10^{-13}}{0.05} = 10^{-11}$$

i.e., precipitation just starts when  $10^{-11}$  moles of  $\text{KBr}$  is added to 1 L  $\text{AgNO}_3$  solution. No. of moles of  $\text{KBr}$  to be added =  $10^{-11}$

$$= 10^{-11} \times 120$$

$$= 1.2 \times 10^{-9} \text{ g}$$

**Sol 14: (C)**



As  $K_2 \ll 1$

$$\text{All major } [\text{H}^+]_{\text{total}} \approx [\text{H}^+]_A$$

**Sol 15: (B)**  $\text{Mg}^{2+} + 2\text{OH}^- \rightleftharpoons \text{Mg}(\text{OH})_2$

$$K_{sp} = [\text{Mg}^{2+}][\text{OH}^-]^2$$

$$[\text{OH}^-] = \sqrt{\frac{K_{sp}}{[\text{Mg}^{2+}]}} = 10^{-4}$$

$$\therefore \text{pOH} = 4 \text{ and } \text{pH} = 10$$

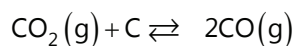
**Sol 16: (B)** Electron releasing groups (Alkyl groups) destabilizes conjugate base.

The + I effect of  $C_3H_7$  is less than - I effect of Cl

$K_a$  of HCOOH is  $17.9 \times 10^{-5}$

$K_a$  of  $CH_3CH_2\underset{\text{Cl}}{\text{CH}}-COOH$  is  $139 \times 10^{-5}$

**Sol 17: (D)**



Initial moles	p	0	
Equilibrium moles	p - x	2x	

Total pressure at equilibrium = 0.8 atm; Total no. of moles = p + x.

Therefore,  $p \propto n$ ;  $\frac{0.5}{0.8} = \frac{p}{p+x} \Rightarrow x = 0.3$

$$K_p = \frac{P_{CO}^2}{P_{CO_2}} = \frac{0.6 \times 0.6}{0.2} = 1.8 \text{ atm}$$

**Sol 18: (C)**  $[H^+] = \sqrt{K_a \cdot C} \Rightarrow 10^{-3} = \sqrt{K_a \cdot 10^{-1}}$

$$\Rightarrow K_a = 10^{-5}$$

**Sol 19: (D)**  $pH = 1 [H^+] = 10^{-1} = 0.1 \text{ M}$

$$pH = 2 [H^+] = 10^{-2} = 0.01 \text{ M}$$

for dilution of HCl  $M_1V_1 = M_2V_2$

$$0.1 \times 1 = 0.01 \times V_2$$

$$V_2 = 10 \text{ lt}$$

Volume of water added = 10 - 1 = 9 litre.

**Sol 20: (B)**

	A	+	B	$\rightleftharpoons$	C	+	D
t=0	1		1		1		1
t <sub>eq</sub>	1-x		1-x		1+x		1+x

$$\Rightarrow \frac{(1+x)^2}{(1-x)^2} = 100 \quad \Rightarrow \frac{1+x}{1-x} = 10$$

$$\Rightarrow 1+x = 10 - 10x \quad \Rightarrow 11x = 9$$

$$\Rightarrow x = \frac{9}{11}$$

$$\Rightarrow [D] = 1 + \frac{9}{11}; \Rightarrow [D] = 1.818$$

## JEE Advanced/Boards

### Exercise 1

**Sol 1:** pH = 13

$$\therefore C = [H^+] = 10^{-13}$$

$$n = \frac{C}{V} = \frac{10^{-13}}{10^3} = 10^{-16}$$

$$\text{No. of } H^+ \text{ ions} = n \times N_A = 10^{-16} \times 6.023 \times 10^{23} = 6.022 \times 10^7$$

**Sol 2:**  $K_w = [H^+][OH^-]$

Substitute in the value for  $K_w$  at 298 K:

$$10^{-14} = [H^+][OH^-]$$

$$\text{Since } [H^+] = [OH^-]$$

$$10^{-14} = [H^+]^2$$

Take the root of both sides of the equation to find

$$[H^+]:$$

$$\sqrt{10^{-14}} = [H^+]$$

$$[H^+] = 10^{-7} \text{ M at 298 K}$$

Similarly At 310 K,

$$2.56 \times 10^{-14} = [H^+]^2$$

$$[H^+] = \sqrt{2.56 \times 10^{-14}} = 1.6 \times 10^{-7} \text{ M at 310 K}$$

**Sol 3:**  $K_w = 9.62 \times 10^{-14}$

$$pK_w = -\log(9.62 \times 10^{-14}) = 13.01$$

$$pH = \frac{1}{2}(pK_w) = \frac{13.01}{2} = 6.50$$

(ii) (a) Basic, (b) Acidic

**Sol 4:**  $K_w = 2.56 \times 10^{-14} \longrightarrow 60^\circ\text{C}$

$$pK_w = -\log(2.56 \times 10^{-14}) = 13.58$$

$$\text{Apply } pH = \frac{1}{2}(pK_w) = \frac{13.58}{2} = 6.79$$

**Sol 5:**

(a) Since  $\text{H}_2\text{SO}_4$  dissociates as  $\text{H}_2\text{SO}_4 \rightleftharpoons 2\text{H}^+ + \text{SO}_4^{2-}$

$$[\text{H}_3\text{O}^+] = \frac{(50 \times 0.2) + (50 \times 0.4)}{50 + 50} = \frac{30}{100} = 0.3$$

$$\text{pH} = -\log(0.3) = 0.522$$

(b) 0.1 M HA + 0.1 M HB

$$K_a = 2 \times 10^{-5} \quad K_b = 4 \times 10^{-5}$$

$$[\text{H}^+] = \sqrt{K_a(\text{HA}) \times C_1 + K_a(\text{HB}) \times C_2}$$

$$= \sqrt{2 \times 10^{-5} \times 0.1 + 4 \times 10^{-5} \times 0.1}$$

$$= 0.00244$$

$$\text{pH} = -\log[\text{H}^+] = -\log(0.00244) = 2.61$$

**Sol 6:** Since the solution is fairly concentrated and  $K_2 / K_1 \approx 10^{-3}$  ( $K_2 \ll K_1$ ), we can use the expression:

$$K_1 = \frac{[\text{H}_3\text{O}^+]^2}{[\text{H}_2\text{A}]_0 - [\text{H}_3\text{O}^+]} \quad (\text{Eq.1.10.10})$$

Which gives

$$[\text{H}_3\text{O}^+] = \frac{-K_1 \sqrt{K_1^2 + 4[\text{H}_2\text{A}]_0 K_1}}{2}$$

Substituting the given values of  $K_1$  and  $[\text{H}_2\text{A}]_0$  in the above expression, we get

$$[\text{H}_3\text{O}^+] = \frac{-(5.9 \times 10^{-2} \text{M}) + \sqrt{(5.9 \times 10^{-2} \text{M})^2 + 4(0.1 \text{M})(5.9 \times 10^{-2} \text{M})}}{2}$$

$$= \frac{-(5.9 \times 10^{-2} \text{M}) + (1.645 \times 10^{-1} \text{M})}{2}$$

$$= 0.0528 \text{M}$$

We can obtain the concentrations of  $\text{H}_2\text{C}_2\text{O}_4$ ,  $\text{HC}_2\text{O}_4^-$  and  $\text{C}_2\text{O}_4^{2-}$  in 0.1 M solution of oxalic acid from the following relations:

$$[\text{H}_2\text{C}_2\text{O}_4] = \frac{[\text{H}_2\text{A}]_0}{1 + \frac{K_1}{[\text{H}_3\text{O}^+]}} = \frac{0.1 \text{M}}{1 + \left( \frac{5.9 \times 10^{-2} \text{M}}{5.28 \times 10^{-2} \text{M}} \right)}$$

$$= \frac{0.1 \text{M}}{1 + 1.118} = 0.0472 \text{M}$$

$$[\text{HC}_2\text{O}_4^-] = \frac{[\text{H}_2\text{A}]_0}{\frac{K_1}{[\text{H}_3\text{O}^+]} + 1} = \frac{0.1 \text{M}}{\left( \frac{5.28 \times 10^{-2} \text{M}}{5.90 \times 10^{-2} \text{M}} \right) + 1}$$

$$= \frac{0.1 \text{M}}{0.8949 + 1} = 0.0528 \text{M}$$

$$[\text{C}_2\text{O}_4^{2-}] = \frac{[\text{H}_2\text{A}]_0}{\frac{K_1 K_2}{[\text{H}_3\text{O}^+]^2} + \frac{K_2}{[\text{H}_3\text{O}^+]}}$$

$$= \frac{0.1 \text{M}}{\frac{(5.28 \times 10^{-2} \text{M})^2}{(5.9 \times 10^{-2} \text{M})(6.4 \times 10^{-5} \text{M})} + \frac{5.28 \times 10^{-2} \text{M}}{6.4 \times 10^{-5} \text{M}}}$$

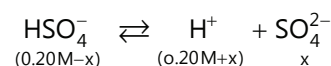
$$= \frac{0.1 \text{M}}{738.3 + 825.0} = 0.000064 \text{M}$$

**Sol 7:** Since the dissociation is strong, therefore, the  $[\text{H}^+]$  due to this dissociation is 0.20 M.

Let x be the amount of  $\text{H}^+$  due to this dissociation. Hence,

$$[\text{H}^+]_{\text{total}} = 0.20 \text{M} + x$$

This in equilibrium gives



$$K = \frac{[\text{H}^+][\text{SO}_4^{2-}]}{[\text{HSO}_4^-]} = \frac{(0.20 \text{M} + x)(x)}{(0.20 \text{M} - x)} = 1.3 \times 10^{-2} \text{M}$$

$$\text{Or } (0.20 \text{M} + x)(x) = (1.3 \times 10^{-2} \text{M})(0.20 \text{M} - x)$$

$$x^2 + (0.20 \text{M} + 1.3 \times 10^{-2} \text{M})$$

$$x - (1.3 \times 10^{-2} \text{M})(0.20 \text{M}) = 0$$

This is quadratic equation in x, which gives

$$x = \frac{-0.213 \text{M} + \sqrt{\{0.213^2 + 4(1.3 \times 10^{-2})(0.20)\} \text{M}^2}}{2}$$

$$= \frac{-0.213 \text{M} + 0.2362 \text{M}}{2} = 0.0116 \text{M}$$

$$\text{Thus, } [\text{H}^+]_{\text{total}} = (0.2 \text{M} + x) = 0.2116 \text{M}$$

$$[\text{HSO}_4^-] = 0.2\text{M} - x = 0.1884\text{M}$$

$$[\text{SO}_4^{2-}] = x = 0.0116\text{M}$$

$$[\text{H}_2\text{SO}_4] = 0$$

**Sol 8:**

$$\text{p}K_a(\text{NH}_4^+) = 9.26$$

$$\therefore \text{p}K_b(\text{NH}_3) = 14 - 9.26 = 4.74$$



Initial	20	15	0
---------	----	----	---

After	5	0	15
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Mixture is a buffer containing 5 millimol of  $\text{NH}_3$  (base)And 15 millimol of  $\text{NH}_4^+$  (conjugate acid)

$$\begin{aligned} \therefore \text{pOH} &= \text{p}K_b + \log \frac{[\text{NH}_4^+]}{[\text{NH}_3]} \\ &= 4.74 + \log 3 \end{aligned}$$

$$\begin{aligned} \therefore \text{pH} &= 14 - \text{pOH} \\ &= 9.26 - \log 3 \\ &= 9.26 - 0.48 = 8.78 \end{aligned}$$

$$\text{Sol 9: } \text{pOH} = \text{p}K_b + \log \frac{[\text{Salt}]}{[\text{Base}]}$$

Final Volume of NaOH after reaction = 50 + 75 = 125 ml

$$M_1V_1 = M_2V_2$$

$$M_2 = \frac{0.1 \times 50}{125} = 0.04\text{M}$$

Final Volume of  $\text{NH}_4\text{Cl}$  = 25 ml

$$M_1V_1 = M_2V_2$$

$$M_2 = \frac{0.2 \times 50}{25} = 0.4\text{M}$$

$$\text{pOH} = 0.2 + \log \frac{[0.4]}{[0.04]} = 0.2 + 1 = 1.2$$

$$\text{pH} = 14 - 1.2 = 12.8$$

**Sol 10:** Methyl red, one with pH = 5.22 as midpoint of colour range.

$$\text{Sol 11: } \text{pH} = \text{p}K_a + \log \frac{[\text{In}^-]}{[\text{HIn}]}$$

Initial concentration of  $[\text{HIn}] = 75\%$ Initial concentration of  $[\text{In}^-] = 25\%$ Final concentration of  $[\text{HIn}] = 25\%$ Initial concentration of  $[\text{In}^-] = 75\%$ 

Thus,

$$\text{pH}_1 = -\log(3 \times 10^{-5}) + \log 75 / 25$$

$$\text{pH}_1 = 5$$

$$[\text{H}^+]_1 = 10^{-5}\text{M}$$

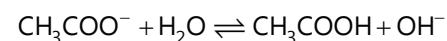
$$\text{pH}_2 = -\log(3 \times 10^{-5}) + \log 25 / 75 = -4.045$$

$$[\text{H}^+]_2 = 8.91 \times 10^{-5}\text{M}$$

$$[\text{H}^+]_2 = 8.91 \times 10^{-5}\text{M}$$

$$[\text{H}^+]_2 - [\text{H}^+]_1 = 7.91 \times 10^{-5}\text{M}$$

$$\text{Sol 12: } K_a(\text{CH}_3\text{COOH}) = 1.8 \times 10^{-5}$$

 $\text{CH}_3\text{COONa}(0.08\text{M})$ 

$$K_w = [\text{H}^+][\text{OH}^-]$$

$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$$

$$\frac{1}{K_a} = \frac{[\text{HA}]}{[\text{H}^+][\text{A}^-]}$$

$$K_b = K_w \times K_a$$

$$K_w = 1 \times 10^{-14}$$

$$k_a = 1.8 \times 10^{-5}$$

$$K_b = 5.6 \times 10^{-20} = \frac{x^2}{(0.08 - x)} = \frac{x^2}{(0.08)}$$

$$x = [\text{OH}^-] = 0.669 \times 10^{-5}\text{M}$$



**Sol 13:**  $K_b(\text{NH}_3) = 1.8 \times 10^{-5}$

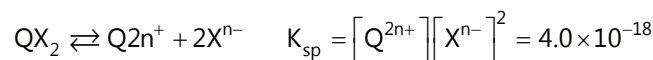
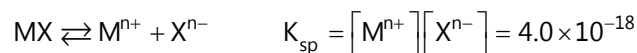
2M  $\text{NH}_4\text{Cl}$  solution of strong acid and weak base.

$$\text{pH} = \frac{1}{2}[\text{p}K_w - \text{p}K_b - \log C] = 4.477$$

**Sol 14:**  $\text{pH} = \frac{1}{2}[\text{p}K_w + \text{p}K_a + \log C]$

**Sol 15:**  $\text{pH} = \frac{1}{2}[\text{p}K_w + \text{p}K_a + \log C] = 8.86$

**Sol 16:**



Solving yield  $[\text{M}^{n+}] = 2.0 \times 10^{-9}$        $[\text{Q}^{2n+}] = 1.0 \times 10^{-6}$

Soluble.

**Sol 17:** Let the simultaneous solubilities of  $\text{AgSCN}$  and  $\text{AgBr}$  be  $s_1$  and  $s_2$  mole per litre

$$[\text{Ag}^+] = s_1 + s_2, [\text{SCN}^-] = s_1 \text{ and } [\text{Br}^-] = s_2$$

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

$$1.0 \times 10^{-12} = (s_1 + s_2) \times s_1 \quad \dots (i)$$

$$5.0 \times 10^{-13} = (s_1 + s_2) s_2 \quad \dots (ii)$$

Dividing Equation (i) by Equation (ii), we get

$$\frac{s_1}{s_2} = 2$$

Or  $s_1 = 2s_2$

Substituting this value in Equation (ii)

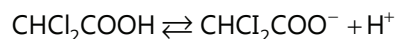
$$5.0 \times 10^{-13} = 3s_2^2$$

$$s_2 = 4.08 \times 10^{-7}$$

$$\therefore s_1 = 8.16 \times 10^{-7}$$

This simultaneous solubilities of  $\text{AgSCN}$  and  $\text{AgBr}$  are  $8.16 \times 10^{-7}$  mole per litre and  $4.08 \times 10^{-7}$  mole per litre respectively.

**Sol 18:** pH will be decided by  $[\text{H}^+]$  furnished by  $\text{HCl}$  and  $\text{CHCl}_2\text{COOH}$ .  $\text{CH}_3\text{COOH}$  being weak does not dissociate due to common ion effect.



Initial conc.	0.09	0	0.09(from HCl)
Final conc.	$(0.09 - x)$	x	$(0.09 + x)$

$$\therefore [\text{H}^+] = 0.09 + x;$$

But  $\text{pH} = 1$

$$\therefore [\text{H}^+] = 10^{-1} = 0.1$$

$$\therefore 0.09 + x = 0.1$$

$$\therefore x = 0.01$$

$K_a$  for  $\text{CHCl}_2\text{COOH}$  can be given as:

$$K_a = \frac{[\text{H}^+][\text{CHCl}_2\text{COO}^-]}{[\text{CHCl}_2\text{COOH}]} = \frac{0.1 \times 0.01}{(0.09 - 0.01)} = 1.25 \times 10^{-2}$$

**Sol 19:**  $\text{H}_2\text{S} \rightleftharpoons \text{H}^+ + \text{HS}^-$

$$K_{a1} = \frac{[\text{H}^+][\text{HS}^-]}{[\text{H}_2\text{S}]} \quad \dots (i)$$

Further  $\text{HS}^- \rightleftharpoons \text{H}^+ + \text{S}^{2-}$

$$K_{a2} = \frac{[\text{H}^+][\text{S}^{2-}]}{[\text{HS}^-]} \quad \dots (ii)$$

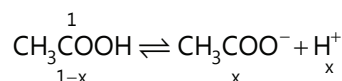
Multiplying both the equations

$$K_{a1} \times K_{a2} = \frac{[\text{H}^+]^2[\text{S}^{2-}]}{[\text{H}_2\text{S}]}$$

Due to common ion, the ionization of  $\text{H}_2\text{S}$  is suppressed and the  $[\text{H}^+]$  in solution is due to the presence of 0.3 M  $\text{HCl}$ .

$$[\text{S}^{2-}] \frac{K_{a1} \times K_{a2} [\text{H}_2\text{S}]}{[\text{H}^+]^2} = \frac{10^{-7} \times 10^{-14} \times (0.1)}{(2 \times 10^{-4})^2} = 2.5 \times 10^{-15}$$

**Sol 20:** Use  $\text{pH} = -\log [\text{H}^+]$  for 1 M.



$$K_a = \frac{x^2}{1-x} = x^2 = 1.8 \times 10^{-5}; x = 4.2 \times 10^{-3} = [\text{H}^+]$$

$$\therefore \text{pH} = -\log[\text{H}^+] = -\log(4.2 \times 10^{-3}) = 2.37$$

Now, let 1 litre of 1 M  $\text{CH}_3\text{COOH}$  be diluted to V litres so that the pH of the solution doubles. Let the concentration of the diluted solution be c moles / litre.

Thus,  $\text{CH}_3\text{COOH} \rightleftharpoons \text{CH}_3\text{COO}^- + \text{H}^+$

$$K_a = \frac{x' \cdot x'}{(c-x')} = 1.8 \times 10^{-5} \quad \dots(i);$$

Further  $\text{pH} = -\log x' = 2 \times 2.37 = 4.74$  (pH doubles on dilution)

$$\text{Or } \log x' = -4.74 = \bar{5}.26; \quad x' = 1.8 \times 10^{-5}.$$

$$\text{Sub. } x' \text{ in (1) we get, } c = 3.6 \times 10^{-5}$$

As the number of moles of  $\text{CH}_3\text{COOH}$  before and after dilution will be the same.

$\therefore$  Moles of  $\text{CH}_3\text{COOH} = \text{Molarity} \times \text{Volume in litres.}$

$$\therefore 3.6 \times 10^{-5} \times V = 1 \times 1 \left( \begin{array}{l} \text{Initial molarity} = 1 \\ \text{Initial volume} = 1 \end{array} \right)$$

$$V = 2.78 \times 10^4 \text{ litres}$$

**Sol 21:** Acetic acid has to use as salt-acid molar ratio is 1.8: 1

**Sol 22:** At the end point, m.e. (on millimoles) of the salt produced

$$= \text{m.e. of NaOH} = 0.1 \times 36.12 = 3.612$$

(Since salt formed will be univalent and so for such salts m.m. = m.e.)

$$\text{m.e. (millimole) of HCl added} = 0.1 \times 18.06 = 1.806$$

The addition of 1.806 m.e. of HCl will produce the same number of m.e. of the unknown acid and reduce the amount of the salt by 1.806 m.e.

$$\therefore \text{m.e. (millimole) of the unknown acid} = 1.806$$

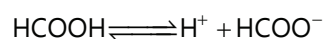
$$\text{And m.e. (or millimole) of the salt} = 3.612 - 1.806 = 1.806.$$

Using,

$$\text{pH} = \text{p}K_a + \log \frac{\text{millimole of salt}}{\text{millimole of acid}}$$

**Sol 23:** Let us find  $[\text{H}^+]$  of  $\text{HCOOH}$  before adding  $\text{HCOONa}$ .

For the equilibrium,



$$K_a = \frac{[\text{H}^+][\text{HCOO}^-]}{[\text{HCOOH}]} = \frac{[\text{H}^+]^2}{[\text{HCOOH}]}$$

$$(\because [\text{H}^+] = [\text{HCOO}^-])$$

$$\therefore [\text{H}^+] = \sqrt{K_a \cdot [\text{HCOOH}]} = \sqrt{1.8 \times 10^{-4} \times 0.2} = 6 \times 10^{-3}$$

Now, on the addition of sodium formate in the acid, we have,

$$[\text{H}^+] = \frac{[\text{acid}]}{[\text{salt}]} = 1.8 \times 10^{-4} \times \frac{0.2}{0.1} = 3.6 \times 10^{-4}$$

Calculate pH.

## Exercise 2

### Single Correct Choice Type

$$\text{Sol 1: (A) } \text{pH} = -\log [4^+] = \frac{1}{\log_{10}[4^+]} \text{ or}$$

$$[4^+] = 10^{-\text{pH}}$$

$$\therefore [4^+] = 10^{-2} \text{ and } [\text{H}^+] = 10^{-6}$$

$$10^{-2} = 10^{-6}$$

$$\therefore \text{Factor} = 10^4$$

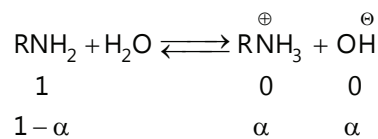
**Sol 2: (C)** Overall dissociation

$$\text{Constant} = 1.0 \times 10^{-5} \times 5.0 \times 10^{-10}$$

$$\text{Acid } (\text{H}_2\text{A}) = 5.0 \times 10^{-15}$$

**Sol 3: (D)**  $k_b = 2 \times 10^{-6}$ ; 0.01 M  $\text{RNH}_2$

$10^{-4}$  M NaOH



Common ion effect due to NaOH

$$k_b = \frac{[\overset{\oplus}{\text{RNH}_3}][\text{OH}^-]}{[\text{RNH}_2]}$$

$$\text{pOH} = -\log k_b + \log \frac{[\text{C.A.}]}{[\text{Base}]}$$

$$= -\log (2 \times 10^{-6}) + \log \frac{(0.01)}{10^{-4}}$$

$$= -\log 2 + 6 + \log 0.01 + 4$$

$$= 10 - 2 - 0.3010 = 7.699$$

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

$$[\text{OH}^-] = 10^{-7.699}$$

**Sol 4: (B)** Salt of WB & WA

Degree of hydrolysis = 50 %; M = 0.1 M

$$M_2 = 0.2 \text{ M}$$

% hydrolysis of salt = ?

$$h_1 = \sqrt{\frac{K_h}{C_1}} \quad h_2 = \sqrt{\frac{K_h}{C_2}}$$

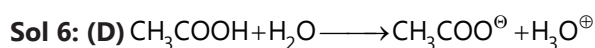
$$h_1^2 C_1 = K_h \quad h_2^2 C_2 = K_h$$

$$h_1^2 C_1 = h_2^2 C_2$$

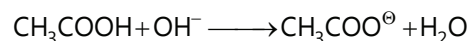


$$K = \frac{x^2}{(0.1-x)^2}; \quad \sqrt{K} = \frac{x}{0.1-x}$$

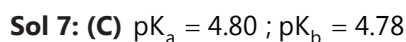
$$\frac{12}{12} = 1$$



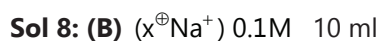
$$K_a = 1.8 \times 10^{-5}$$



$$k_b = \frac{K_w}{K_a} = \frac{10^{-14}}{1.8 \times 10^{-5}} = 5.55 \times 10^{-10}$$



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



HCl 0.1M

$$k_b(x^\ominus) = 10^{-6}$$

$$K_a \times K_b = K_w$$

$$K_a = \frac{K_w}{K_b} = \frac{10^{-14}}{10^{-6}} = 10^{-8}$$

$$K_{in} = K_a = \frac{[\text{H}^+][\text{In}^-]}{[\text{H}_{in}]} = \frac{[\text{H}^+][\text{base}]}{[\text{acid}]}$$

$$[\text{H}^+] = K_a = \frac{[\text{acid}]}{[\text{base}]} = 10^{-9} \frac{[0.1]}{[0.1]}$$

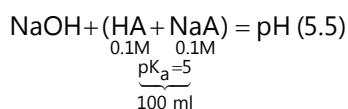
$$\text{pH} = \frac{1}{2} (pK_w - pK_b - \underbrace{\log a}_{pK_a})$$



$$M_{\text{buffer}} = 0.1\text{M}$$

$$\text{pH} = 5.5$$

$$pK_a(\text{HA}) = 5$$



$$\text{pH} = pK_a + \log \frac{[\text{salt}]}{[\text{acid}]} = 5 + \log \frac{[0.1]}{[0.1]} = 5$$

Contributing pH = 0.5 by NaOH

$$0.5 = -\log [\text{H}^+]$$

$$\text{A } \log (-0.5) = [\text{H}^+]$$

$$[\text{H}^+] = 3.16$$

$$[\text{OH}^-] = 10.84 = \frac{\text{no. of moles}}{\text{vol.}}$$



KOH                  HCOOH

0.2M                  0.1M

40ml                  160ml

$$K_a = 2 \times 10^{-4}$$

No. of Millimoles = M × Vol

∴ Millimoles of KOH = 0.2 × 40 = 8

Millimoles of HCOOH = 0.1 × 160 = 16

Millimoles of HCOOK produced = 8

Millimoles of HCOOH remained = 16 - 8 = 8

$$\text{pH} = pK_a + \log \frac{\text{millimoles of salt}}{\text{millimoles of acid}}$$

$$= -\log(2 \times 10^{-4}) + \log \frac{8}{8} = 4 - 0.3010 = 3.699$$

$$\text{pOH} = 14 - 3.699 = 10.3$$



$$\text{pH} = pK_a + \log \frac{[\text{Salt}]}{[\text{Acid}]} = 4.5 + \log \frac{[\text{Salt}]}{[\text{Acid}]}$$

As H A is 50% ionized,  $[\text{Salt}] = [\text{Acid}]$

This is because of the total 100% only %50 is ionized which is equivalent to the concentration of the remaining buffer solution.

If it was 75% then we would consider (100 - 75)%, but in this case  $[\text{Salt}] \neq [\text{Acid}]$ .

$$\text{pH} = 4.5$$

$$\text{pH} + \text{pOH} = 14$$

$$\text{or } \text{pOH} = 14 - 4.5 = 9.5$$

**Sol 12: (A)** C is the conjugate acid of A, and D is the conjugate base of B

**Sol 13: (A)**  $\text{NaH}_2\text{PO}_2$  is not an acid salt.

**Sol 14: (B)** pH of buffer solution is not affected by dilution.

**Sol 15: (C)** Buffer solution constitute of weak acid and its conjugate base or vice versa.

**Sol 16: (C)** Buffer solution constitute of weak acid and its conjugate base or vice versa.

### Multiple Correct Choice Type

**Sol 17: (A, B)** Buffer solution constitute of weak acid and its conjugate base or vice versa.

**Sol 18: (B, C)** (B)  $\text{H}_2\text{PO}_4^- \rightleftharpoons \text{HPO}_4^{2-} + \text{H}^+$   
Acid                      Conjugate Base

(C) Conceptual fact

**Sol 19: (B, C)** Concentration of salt (C) at equivalent point is 0.25 M

Volume of HCl is used at equivalent point is 100 ml

**Sol 20: (A, B, C)** Phenolphthalein is suitable indicator for the titration of weak acid vs strong base and strong acid vs strong base.

**Sol 21: (A, B, C)** All the three relation are correct for alkaline solution.

(A)  $\text{pH} > \frac{\text{p}K_w}{2}$

(B)  $\text{pH} > \text{pOH}$

(C)  $\text{pOH} < \frac{\text{p}K_w}{2}$

**Sol 22: (A, B)**  $\text{pH} = \text{p}K_a + \log \frac{[\text{In}^-]}{[\text{HIn}]}$

Initial concentration of  $[\text{HIn}] = 75\%$

Initial concentration of  $[\text{In}^-] = 25\%$

Final concentration of  $[\text{HIn}] = 25\%$

Final concentration of  $[\text{In}^-] = 75\%$

$$\text{pH}_1 = -\log(3 \times 10^{-5}) + \log \frac{75}{25} = 5$$

$$[\text{H}_1^+] = 10^{-5} \text{M}$$

$$\text{pH}_2 = -\log(3 \times 10^{-5}) + \log \frac{25}{75} = 4.05$$

**Sol 23: (A, C, D)** A very high value of equilibrium constant indicates that the forward is almost complete. Thus  $\text{CN}^-$  is stronger base than  $\text{ONO}^-$ . (C) and (D) are factual.

**Sol 24: (A, D)**



**Sol 25: (B, C, D)**  $\text{H}_2\text{SO}_4$ ,  $\text{HNO}_3$ ,  $\text{NaOH}$  all of them will suppress the ionization of phthalic acid in an aqueous solution.

### Match the Columns

**Sol 26:** A  $\rightarrow$  q; B  $\rightarrow$  r; C  $\rightarrow$  s; D  $\rightarrow$  p

(A)  $\text{CH}_3\text{COOH}$ - Weak acid

(B)  $\text{H}_2\text{SO}_4$ - Strong acid

(C)  $\text{NaOH}$ -Strong base

(D)  $\text{NH}_3$ -Weak base

**Sol 27:** A  $\rightarrow$  s; B  $\rightarrow$  s; C  $\rightarrow$  q

Propyl red and malachite green are suitable indicators for strong acid and strong base titrations.

### Previous Years' Questions

**Sol 1: (A)**  $K_p$  for a given reversible reaction depends only on temperature.

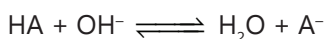
**Sol 2: (A)**  $K_a(\text{HX}) = \frac{K_w}{K_b} = 10^{-4}$

$$\Rightarrow \text{pH} = \text{p}K_a + \log \frac{[\text{X}^-]}{[\text{HX}]}$$

$$= \text{p}K_a$$

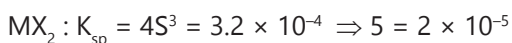
$$[\because [\text{X}^-] = [\text{HX}]] = 4$$

**Sol 3: (C)** The reaction of HA with strong base is :



$$K = \frac{[\text{A}^-]}{[\text{HA}][\text{OH}^-]} \times \frac{[\text{H}^+]}{[\text{H}^+]} = \frac{K_a}{K_w} = \frac{10^{-4}}{10^{-14}} = 10^{10}$$

**Sol 4: (D)** MX:  $K_{sp} = S^2 = 4 \times 10^{-8} \Rightarrow S = 2 \times 10^{-4}$



$$\begin{aligned} \text{M}_3\text{X} : K_{sp} &= 27S^4 \\ &= 2.7 \times 10^{-15} \\ &\Rightarrow S = 10^{-4} \end{aligned}$$

Order of solubility is:



**Sol 5: (D)**  $\text{BOH} + \text{Ha} \rightarrow \text{Ba} + \text{H}_2\text{O} \cdot \text{B}^+ + \text{H}_2\text{O} \rightleftharpoons \text{BOH}_{\text{ch}} + \text{H}^+_{\text{ch}}$

For titration  $N_{\text{acid}_1} V_{\text{acid}_1} = N_{\text{acid}_2} V_{\text{acid}_2}$

$$\begin{aligned} \frac{2}{15} \times v &= 2.5 \times \frac{2}{5} \\ v &= \text{vol g HCl} 7.5 \text{ mL} \end{aligned}$$

In resulting solution, conc. of salt

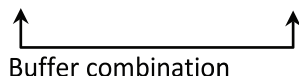
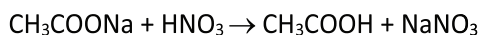
$$[\text{BCl}] = \frac{\frac{2}{5} \times 2.5}{10} = 0.1$$

$$\therefore \frac{ch^2}{1-h} = \frac{k_w}{k_b} \text{ or } h = \sqrt{\frac{k_w}{k_b \times c}} = \sqrt{\frac{10^{-19}}{16^{-12} \times 0.1}}$$

$$h = \sqrt{\frac{1}{10}} \text{ how}$$

$$[\text{H}^+] = ch = 0.1 \times \sqrt{\frac{1}{01}} = 3.16 \times 10^{-2} \text{ M} = 3.2 \times 10^{-2} \text{ M}$$

**Sol 6: (C, D)** In  $\text{HNO}_3$  and  $\text{CH}_3\text{COONa}$  combination, if  $\text{HNO}_3$  is present in limiting amount, it will be neutralised completely, leaving behind some excess of  $\text{CH}_3\text{COONa}$ :



**Sol 7: (B, C, D)**  $\text{Cl}^-$ ,  $\text{CN}^-$  and  $\text{SCN}^-$  forms precipitate with Cu (I), remove Cu (I) ion from equilibrium and reaction shift in backward direction according to Le-Chatelier's principle.

**Sol 8:** In pure water, solubility =  $\frac{9.57}{58} \times 10^{-3}$   
=  $1.65 \times 10^{-4} \text{ M}$

$$K_{sp} = 4S^3 = 4(1.65 \times 10^{-4})^3 = 1.8 \times 10^{-11}$$

$$\begin{aligned} \text{In } 0.02 \text{ M Mg(NO}_3)_2; \\ \text{solubility of Mg(OH)}_2 &= \sqrt{\frac{K_{sp}}{[\text{Mg}^{2+}]}} \times \frac{1}{2} \\ &= 1.5 \times 10^{-5} \text{ mol L}^{-1} \\ &= 1.5 \times 10^{-5} \times 58 \text{ g L}^{-1} \\ &= 8.7 \times 10^{-4} \text{ g L}^{-1} \end{aligned}$$

**Sol 9:** (i) 0.20 mole HCl will neutralise 0.20 mole  $\text{CH}_3\text{COONa}$ , producing 0.20 mol  $\text{CH}_3\text{COOH}$ . Therefore, in the solution

moles of  $\text{CH}_3\text{COOH} = 1.20$

moles of  $\text{CH}_3\text{COONa} = 0.80$

$$\begin{aligned} \text{pH} &= \text{p}K_a + \log \frac{[\text{Salt}]}{[\text{Acid}]} \\ &= -\log(1.8 \times 10^{-5}) + \log \frac{(0.80)}{1.20} = 4.56 \end{aligned}$$

(ii)  $\text{CH}_3\text{COONa} + \text{HCl} \rightarrow \text{CH}_3\text{COOH} + \text{NaCl}$

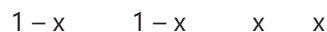
Initial	0.10	0.20	0	0
Final	0	0.10	0.10	0.10

Now the solution has 0.2 mol acetic acid and 0.1 mole HCl. Due to presence of HCl, ionisation of  $\text{CH}_3\text{COOH}$  can be ignored (common mainly due to HCl).

$$\Rightarrow [\text{H}^+] = 0.10$$

$$\Rightarrow \text{pH} = -\log(0.10) = 1.0$$

**Sol 10:**  $\text{SO}_2(\text{g}) + \text{NO}_2(\text{g}) \rightleftharpoons \text{SO}_3(\text{g}) + \text{NO}(\text{g})$



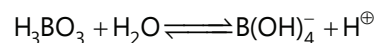
$Q_c = I < K_c$ , ie, reaction proceed in forward direction to attain equilibrium.

$$\Rightarrow 16 = \left( \frac{x}{1-x} \right)^2$$

$$\Rightarrow x = 0.80$$

$$\Rightarrow [\text{NO}] = 0.80 \text{ M}, [\text{NO}_2] = 0.20 \text{ M}$$

**Sol 11: (C)**  $\text{H}_3\text{BO}_3$  (orthoboric acid) is a weak lewis acid.



It does not donate proton rather it acceptors  $\text{OH}^-$  form water.

Hence, (C) is correct.

**Sol 12: (C)** If  $\beta_{\text{eq}} = 0.7$

$$K_p = \frac{8 \times (0.7)^2}{4 - (0.7)^2} = \frac{3.92}{3.51} > 1$$

Which can't be possible as  $\Delta G^\circ > 0$  ( $\Rightarrow K_p < 1$ ).

$\therefore$  Therefore, option (C) is incorrect.

**Sol 13:**

Let the solubility of AgCl is x mol/litre  $\text{AgCl} \rightleftharpoons \text{Ag}^+ + \text{Cl}^-$

Let the solubility of AgCl is x mol/litre  $\text{CuCl} \rightleftharpoons \text{Cu}^+ + \text{Cl}^-$

$$\therefore K_{\text{sp}} \text{ of AgCl} = [\text{Ag}^+][\text{Cl}^-]$$

$$1.6 \times 10^{-10} = x(x + y) \quad \dots \text{(i)}$$

Similarly  $K_{\text{sp}}$  of CuCl =  $[\text{Cu}^+][\text{Cl}^-]$

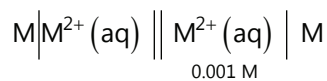
$$1.6 \times 10^{-6} = y(x + y) \quad \dots \text{(ii)}$$

On solving (i) and (ii)

$$[\text{Ag}^+] = 1.6 \times 10^{-7}$$

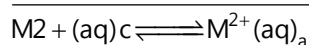
$$\therefore x = 7$$

**Sol 14: (B)**



Anode:  $\text{M} \rightarrow \text{M}^{2+}(\text{aq}) + 2\text{e}^-$

Cathode:  $\text{M}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{M}$



$$E_{\text{cell}} = 0 - \frac{0.059}{2} \log \left\{ \frac{\text{M}^{2+}(\text{aq})_a}{10^{-3}} \right\}$$

$$0.059 = -\frac{0.059}{2} \log \left\{ \frac{\text{M}^{2+}(\text{aq})_a}{10^{-3}} \right\} - 2 = \log \left\{ \frac{\text{M}^{2+}(\text{aq})_a}{10^{-3}} \right\}$$

$$10^{-2} \times 10^{-3} = \text{M}^{2+}(\text{aq})_a = \text{solubility} = s$$

$$K_{\text{sp}} = 4s^3 = 4 \times (10^{-5})^3 = 4 \times 10^{-15}$$

**Sol 15: (D)**  $pK_a$  of PhOH (carboic acid) is 9.98 and that of carbonic acid ( $\text{H}_2\text{CO}_3$ ) is 6.63 thus phenol does not give effervescence with  $\text{HCO}_3^-$  ion.

**Sol 16: (A)** Rate in weak acid =  $\frac{1}{100}$  (rate in strong

acid)

$$\therefore [\text{H}^+]_{\text{weak acid}} = \frac{1}{100} [\text{H}^+]_{\text{strong acid}}$$

$$\therefore [\text{H}^+]_{\text{weak acid}} = \frac{1}{100} \text{M} = 10^{-2} \text{M}$$

$$\therefore C\alpha = 10^{-2}$$

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

Option (A) is correct.

**Sol 17: (B)**  $K_{\text{sp}} = 1.1 \times 10^{-12} = [\text{Ag}^+]^2 [\text{CrO}_4^{2-}]$

$$1.1 \times 10^{-12} = [0.1]^2 [s]$$

$$s = 1.1 \times 10^{-10}$$

**Sol 18: (B)**

	$X_{2(g)} \rightarrow 2X_{(g)}$	
$t = 0$ (No. of moles)	1	0
$t = t$	$1 - \frac{\beta}{2}$	$\beta$
$t = t_{\text{eq}}$	$\left(1 - \frac{\beta_{\text{eq}}}{2}\right)$	$\beta_{\text{eq}}$

$$P_x = 2 \left( \frac{\beta_{\text{eq}}}{1 + \frac{\beta_{\text{eq}}}{2}} \right) \quad n_{\text{Total}} = 1 - \frac{\beta_{\text{eq}}}{2} + \beta_{\text{eq}} = \left(1 + \frac{\beta_{\text{eq}}}{2}\right)$$

$$P_{X_2} = 2 \left( \frac{1 - \beta_{\text{eq}}/2}{1 + \beta_{\text{eq}}/2} \right)$$

$$K_p = \frac{(P_x)^2}{P_{X_2}} = \frac{\left[2 \left(\frac{\beta_{\text{eq}}}{1 + \beta_{\text{eq}}/2}\right)\right]^2}{\left[2 \left(\frac{1 - \beta_{\text{eq}}/2}{1 + \beta_{\text{eq}}/2}\right)\right]^2} = \frac{2\beta_{\text{eq}}^2}{1 - \frac{\beta_{\text{eq}}^2}{4}} = \frac{8\beta_{\text{eq}}^2}{4 - \beta_{\text{eq}}^2}$$