

# Chapter 7. Equilibrium

## Question-1

Why is vapour pressure independent of initial amount?

### Solution:

Vapour pressure of liquid is defined as pressure exerted by liquid at equilibrium at a given temperature. Different amounts of liquids exert same equilibrium pressure at a given temperature.

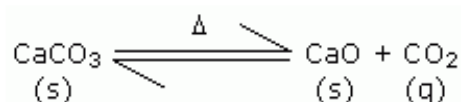
At equilibrium, rate of evaporation = rate of condensation

Different amounts of liquid will give same ratio of amount of evaporation to amount of condensation.

## Question-2

Write  $K_p$  for  $\text{CaCO}_3$  decomposition.

### Solution:



$K_p = p_{\text{CO}_2}$  where  $p_{\text{CO}_2}$  - Partial vapor pressure.

## Question-3

At 500 k, 1.04 g of hydrogen, and 12,060 g of  $\text{I}_2$  are in equilibrium with 5.058 g of hydrogen iodide in a vessel of capacity 1 lit. Calculate the equilibrium constant.

### Solution:

$$[\text{H}_2] = \frac{1.04}{2} \text{ g/mole } [\text{H I}] = \frac{5.058}{128} \text{ g/mole } (\text{H}_2 = 2; \text{I}_2 = 254; \text{HI} = 128)$$



$$K_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = \frac{\left(\frac{5.058}{128}\right)^2}{\left(\frac{1.04}{2}\right)\left(\frac{12060}{254}\right)} = 6.48$$

$$K_c = 6.48.$$

### Question-4

If the value of  $K_c$  be 50.21, for the reaction  $H_2 + I_2 \rightleftharpoons 2HI$  how much HI would be present at the equilibrium, if we start with 5.30 mol of  $I_2$  and 7.94 mol of  $H_2$ ?

#### Solution:

At equilibrium of  $2x$  mol HI is formed,  $x$  mol  $H_2$  and  $x$  mole of  $I_2$  should be consumed.

At equilibrium  $[HI] = 2x$ ;  $[H_2] = [7.94 - x]$

$[I_2] = [5.30 - x]$

$$K_c = \frac{[HI]^2}{[H_2][I_2]}$$

$$50.21 = \frac{[2x]^2}{[7.94 - x][5.30 - x]}$$

$$4x^2 = 2112.93 - 664.78x + 50.21 x^2$$

$$46.21 x^2 - 664.78 x + 2112.93 = 0;$$

$$x^2 - 14.3 x + 46 = 0$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$x = \frac{14.3 \pm \sqrt{205 - 184}}{2}$$

$$x = \frac{14.3 \pm 4.58}{2}$$

$$2x = 9.72 \text{ moles}$$

At equilibrium  $[HI] = 9.72$  moles.

### Question-5

$K_c$  for  $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$  is 61. What is  $K_c$  for  $2NH_3 \rightleftharpoons N_2(g) + 3H_2(g)$ ?

#### Solution:

Equilibrium constant for the reverse reaction is the inverse of the equilibrium constant for the reaction in the forward reaction.

$K'_c$  for  $2NH_3 \rightleftharpoons N_2(g) + 3H_2(g)$  is  $\frac{1}{61}$ .

### Question-6

For the equilibrium  $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$   $K_p$  is  $6.8 \times 10^5$  at 298 K. What is the  $K_c$  value for the same equilibrium?

#### Solution:

For the reaction  $\Delta n = 2 - (1 + 3) = -2$

$$K_p = K_c (RT)^{\Delta n};$$

$$6.8 \times 10^5 = K_c \times (0.0831 \times 298)^{-2}$$

$$6.8 \times 10^5 = K_c \times \frac{1}{(0.0831 \times 298)^2}$$

$$(\text{i.e.}) K_c = 6.8 \times 10^5 \times (0.0831 \times 298)^2 = 4170.1 \times.$$

### Question-7

If the reaction between iron and steam proceeds as:  $3\text{Fe} + 4\text{H}_2\text{O} \rightleftharpoons \text{Fe}_3\text{O}_4 + 4\text{H}_2$  and the partial pressure of steam be 50 mm and of hydrogen 940 mm at  $250^\circ$ . Calculate the pressure of steam at equilibrium when the partial pressure of hydrogen is 1800 mm.

#### Solution:



$$K_p = \frac{(p_{\text{H}_2})^4}{(p_{\text{H}_2\text{O}})^4} = \frac{(940)^4}{(50)^4}$$

When  $p_{\text{H}_2} = 1800$  mm

$$K_p = \frac{(940)^4}{(50)^4} = \frac{(1800)^4}{x^4} \text{ where } x \text{ is } p_{\text{H}_2\text{O}}$$

$$x = \frac{50 \times 1800}{940} = 95.7.$$

$\therefore$  Partial pressure of steam is 95.7 mm.

### Question-8

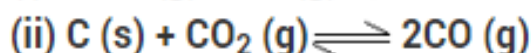
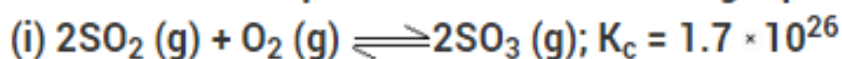
Why is NaCl precipitated by passing HCl gas in a NaCl saturated solution?

#### Solution:

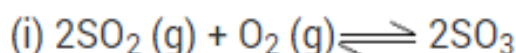
$\text{NaCl} \rightleftharpoons \text{Na}^+ \text{Cl}^-$ , when HCl is passed,  $[\text{Cl}^-]$  is more. To decrease the concentration of  $\text{Cl}^-$  backward reaction takes place. Hence NaCl is precipitated. This could also be attributed to common ion effect.

### Question-9

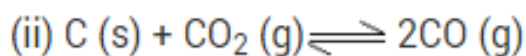
What is effect of pressure for the following equilibrium?



#### Solution:



[When equilibrium pressure is increased, to annul the effect, the reaction in which pressure is consumed will take place. Pressure is used to decrease the volume (i.e.) forward reaction will take place where 3 moles are reduced to 2 moles. The equilibrium is shifted to forward direction.



When pressure increased the reaction in which number of moles reduced will take place. (i.e.) equilibrium is shifted to reverse direction.

### Question-10

$\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$  ;  $\Delta H^\circ = -92.38 \text{ kJ mole}^{-1}$ , what happens temp is increased at equilibrium?

#### Solution:

When temperature is increased at equilibrium, the reaction in which heat is consumed will take place to annul the effect of increase in temperature. Backward reaction is a heat consuming reaction. Hence, decomposition of ammonia takes decomposition when temp is increased.

### Question-11

Explain the dynamic equilibrium between ice and water.

#### Solution:

The dynamic equilibrium consists of a forward reaction in which ice melts to give water and a reverse reaction in which water solidifies to ice.

$\text{Ice} \rightleftharpoons \text{water}$ ,

At 273K, both ice and water are in equilibrium. Both forward and backward reactions occur at the same rate. At  $T > 273\text{K}$ , more water is present and  $\Delta G < 0$ . At  $T < 273\text{K}$ , more ice is present and  $\Delta G > 0$ .

### Question-12

Explain why the equilibrium constant for a gaseous reaction can be written in terms of partial pressures instead of concentrations.

#### Solution:

The molar concentration of a gas is directly proportional to its partial pressure at a fixed temperature. Therefore, it is convenient to express the composition of a gaseous reaction mixture in terms of the partial pressures of the components rather than in terms of their molar concentrations.

### Question-13

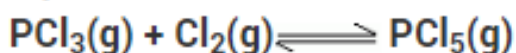
The equilibrium constant of a reaction decrease with increase in temperature. Is the reaction exothermic or endothermic?

#### Solution:

Exothermic because with increase in temperature, the equilibrium shifts in the backward direction.

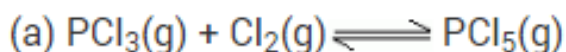
### Question-14

(a) Predict the direction of reaction when chlorine gas is added to an equilibrium mixture of  $\text{PCl}_3$ ,  $\text{PCl}_5$  and  $\text{Cl}_2$ . The reaction is

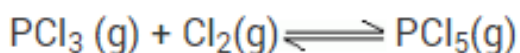


(b) What is the direction of reaction when chlorine gas is removed from an equilibrium mixture of these gases?

#### Solution:



(a) When  $\text{Cl}_2$  is added to the reaction mixture, increasing its concentration, the reaction goes in the forward direction (more  $\text{PCl}_5$  is formed).



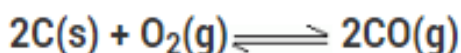
(b) When  $\text{Cl}_2$  is removed from the reaction mixture, lowering its concentration, the reaction goes in the reverse direction (more  $\text{PCl}_5$  dissociates to  $\text{PCl}_3$  and  $\text{Cl}_2$ ) to partially restore the  $\text{Cl}_2$  that was removed.





### Question-15

What is the effect of reducing the volume on the system described below?



#### Solution:

The forward reaction is accompanied by increase in volume. Hence according to Le-Chatelier's principle, reducing the volume will shift the equilibrium in the forward direction.

### Question-16

Consider the reaction:



Indicate the direction in which the equilibrium will shift when

(i) a catalyst is added

(ii) pressure is decreased

#### Solution:

(i) **A catalyst is added:** The equilibrium will not shift in any direction because both the forward and backward rates are increased to the same extent.

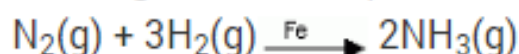
(ii) **Pressure is decreased:** The equilibrium will shift to the left to produce more number of moles of the reactants.

### Question-17

What is the effect of catalyst on the equilibrium? Give an example.

#### Solution:

A catalyst is a substance that increases the rate of a reaction but is not consumed by it. However, the presence of a catalyst speeds the reverse reaction as well as the forward reaction, leaving the equilibrium constant unchanged. For example,



### Question-18

Classify conjugate pairs among the following:

Q.  $\text{HCl}$ ,  $\text{HS}^-$ ,  $\text{HSO}_4^{2-}$ ,  $\text{H}_2\text{O}$ ,  $\text{HCO}_3^-$ ,  $\text{H}_2\text{S}$ ,  $\text{HPO}_4^{2-}$ ,  $\text{NH}_3$ ,  $\text{Cl}^-$ ,  $\text{H}_3\text{O}^+$ ,  $\text{NH}_4^+$ ,  $\text{SO}_4^{2-}$ .

#### Solution:

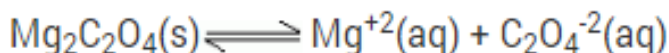
$\text{HCl}$  and  $\text{Cl}^-$ ,  $\text{H}_2\text{S}$  and  $\text{HS}^-$ ,  $\text{HSO}_4^{2-}$  &  $\text{SO}_4^{2-}$ ,  $\text{H}_3\text{O}^+$  and  $\text{H}_2\text{O}$ .

### Question-19

The solubility of magnesium oxalate,  $\text{MgC}_2\text{O}_4$ , in water is  $0.0093 \text{ mol/L}$ .

Calculate  $K_{\text{sp}}$ .

#### Solution:



Starting                      0                      0

Equilibrium                 $9.3 \times 10^{-3}$      $9.3 \times 10^{-3}$

$$[\text{Mg}^{+2}] = 9.3 \times 10^{-3} \text{ mol L}^{-3}, [\text{C}_2\text{O}_4^{2-}] = 9.3 \times 10^{-3} \text{ mol L}^{-1}$$

$$K_{\text{sp}} = [\text{Mg}^{+2}][\text{C}_2\text{O}_4^{2-}] = (9.3 \times 10^{-3})(9.3 \times 10^{-3}) = 8.65 \times 10^{-5} \text{ M}^2.$$

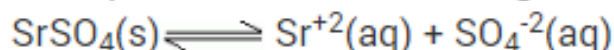


### Question-20

What is the solubility of strontium sulphate,  $\text{SrSO}_4$ , in 0.15 M sodium sulphate,  $\text{Na}_2\text{SO}_4$ ?  $K_{\text{sp}}$  of  $\text{SrSO}_4 = 2.5 \times 10^{-7}$

#### Solution:

The equation for the dissolving  $\text{SrSO}_4$  is



In this solution there are two sources of  $\text{SO}_4^{-2}(\text{aq})$ . The soluble  $\text{Na}_2\text{SO}_4$  is completely dissociated into  $\text{Na}^+$  ions and  $\text{SO}_4^{-2}(\text{aq})$  ions, and the small amount of  $\text{SrSO}_4$  that dissolves also provides  $\text{SO}_4^{-2}(\text{aq})$  ions. The  $\text{SO}_4^{-2}(\text{aq})$  ion is common to both the insoluble electrolyte  $\text{SrSO}_4$  and the soluble salt  $\text{Na}_2\text{SO}_4$ . There is, however, only one source of  $\text{Sr}^{+2}$  ions, namely the dissolution of solid  $\text{SrSO}_4$

Let

$S$  = molar solubility of  $\text{SrSO}_4$  in 0.15 M  $\text{Na}_2\text{SO}_4$

Then,  $[\text{Sr}^{+2}] = S$  and  $[\text{SO}_4^{-2}] = 0.15 + S$

$$K_{\text{sp}}(\text{SrSO}_4) = [\text{Sr}^{+2}] [\text{SO}_4^{-2}] = S(0.15 + S)$$

$$2.5 \times 10^{-7} = 0.15S + S^2$$

Assuming  $S$  to be small compared to 0.15 and that

$$\therefore 2.5 \times 10^{-7} = 0.15S$$

$$\text{or } S = 1.67 \times 10^{-6} \text{ M.}$$

### Question-21

The solubility product of  $\text{Fe}(\text{OH})_3$  is  $1 \times 10^{-36}$ . What is the minimum concentration of  $\text{OH}^-$  ions required to precipitate  $\text{Fe}(\text{OH})_3$  from a 0.001 M solution of  $\text{FeCl}_3$ ?

#### Solution:

$$K_{\text{sp}} = [\text{Fe}^{3+}] [\text{OH}^-]^3$$

Precipitation will occur when ionic product,  $[\text{Fe}^{3+}] [\text{OH}^-]^3$  becomes greater than  $K_{\text{sp}}$

$$[\text{Fe}^{3+}] = [\text{FeCl}_3] = 0.001 \text{ M}$$

The concentration of  $\text{OH}^-$  ions required to start the precipitation is

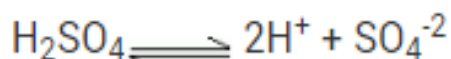
$$[\text{OH}^-]^3 = \frac{K_{\text{sp}}}{[\text{Fe}^{3+}]} = \frac{1 \times 10^{-36}}{0.001} = 1 \times 10^{-11}$$

$$\therefore [\text{OH}^-] = (1 \times 10^{-11})^{1/3} = 1 \times 10^{-11} \text{ mol L}^{-1}.$$

### Question-22

Calculate the pH of 0.5 molar solution of sulphuric acid.

**Solution:**



In a 0.5 m  $\text{H}_2\text{SO}_4$  solution

$$[\text{H}^+] = 2 \times 0.5 \text{ mol L}^{-1} = 1 \text{ mol L}^{-1}$$

$$\therefore \text{pH} = -\log [\text{H}^+] = -\log (1) = 0$$

### Question-23

The pH of 0.05M aqueous solution of diethyl amine is 12.0 calculate its  $K_b$ .

**Solution:**

$$\text{pH} = 12.0; \text{pOH} = 14 - 12.00 = 2.00$$

$$[\text{OH}^-] = 10^{-2} \text{M}; K_b = \frac{x^2}{c}$$

$$K_b = \frac{(10^{-2})(10^{-2})}{5 \times 10^{-2}} = 0.2 \times 10^{-2} = 2 \times 10^{-3}.$$

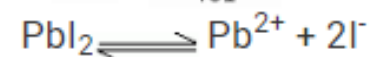
### Question-24

The solubility of lead iodide in water is 0.63 gm/litre. Calculate the solubility product of lead iodide (At mass of Pb = 207; I = 127).

**Solution:**

Solubility of lead iodide in moles / litre

$$= \frac{0.63}{461} = \frac{630 \times 10^{-3}}{461} = 1.36 \times 10^{-3} \text{ moles / litres}$$



$$K_{SP} = [\text{Pb}^{2+}][\text{I}^-]^2$$

$$= [1.36 \times 10^{-3}][2 \times 1.36 \times 10^{-3}]^2$$

$$= 4 \times (1.36 \times 10^{-3})^3$$

$$= 4 \times (10^{-3})^3 (1.36)^3$$

$$= 4 \times 10^{-9} \times 1.4 \times 1.4 \times 1.4$$

$$= 4 \times 10^{-9} \times 1.4 \times 1.4 \times 1.4$$

$$= 10.9 \times 10^{-9}$$

$$K_{SP} = 1.09 \times 10^{-8} \text{ mol}^{-3} \text{ L}^{-3}.$$

### Question-25

How many moles of AgBr ( $K_{SP} = 5 \times 10^{-13} \text{ mol}^{-2} \text{ L}^{-2}$ ) will dissolve in 0.01M NaBr solution?



$K_{SP} = [x] [x + 0.01]$  where  $x$  = solubility of  $\text{Ag}^+$  or  $\text{Br}^-$ .

#### Solution:

$5 \times 10^{-13} \equiv (x) (10^{-2})$  (compare to 0.01,  $x$  is small)

$$\text{(i.e.) } x = \frac{5 \times 10^{-13}}{10^{-2}} = 5 \times 10^{-11} \text{ mol L}^{-1}.$$

### Question-26

Two moles of HI when heated at  $44.4^\circ\text{C}$  until equilibrium is reached, were found to be 22% dissociated. Calculate the equilibrium constant for the reaction.

#### Solution:



$$x = 22\% \text{ (i.e.) that } \frac{22}{100} = 0.22$$



0.22 dissociate to give 0.11 moles of  $\text{H}_2$  and 0.11 mole of  $\text{I}_2$

Equilibrium concentration =  $(1 - 0.22) = 0.78$  moles / litre

Equilibrium concentration of HI = 0.78 moles / litre.

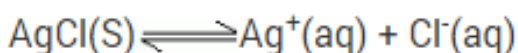
$$K_c = \frac{[\text{H}_2][\text{I}_2]}{[\text{HI}]^2} = \frac{0.11 \times 0.11}{(0.78)^2}$$

$$K_c = 0.0198.$$

### Question-27

How does the solubility of AgCl change in the presence of NaCl solution?  
( $S = 1.3 \times 10^{-5} \text{M}$ )

#### Solution:



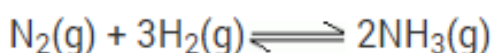
$$K_{\text{SP}} = [\text{Ag}^+][\text{Cl}^-]$$

Addition of NaCl to saturated solution of AgCl increases the concentration of  $\text{Cl}^-$  ions. According to Le Chatelier's  $\text{AgCl}(s)$ , there by reducing the  $\text{Ag}^+$  concentration by precipitating AgCl. Thus solubility of AgCl in NaCl solution is lower than water, due to common ion effect.

### Question-28

A 50.0 L reaction vessel contains 1.00 mol  $\text{N}_2$ , 3.00 mol  $\text{H}_2$ , and 0.055 mol  $\text{NH}_3$ . Will more ammonia, ( $\text{NH}_3$ ), be formed or will it dissociate when the mixture goes to equilibrium at  $400^\circ\text{C}$ ? The equation is  $\text{N}_2(g) + 3\text{H}_2(g) \rightleftharpoons 2\text{NH}_3(g)$   $K_c$  is 0.500 at  $400^\circ\text{C}$ .

#### Solution:



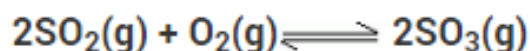
$$\text{Concentrations } \frac{1.00}{50.0} \frac{3.00}{50.0} \frac{0.055}{50.0} = 0.0200 \text{ M}, 0.0600 \text{ M}, 0.0011 \text{ M}$$

$$\therefore Q_c = \frac{[\text{NH}_3]^2}{[\text{H}_2]^3[\text{N}_2]} = \frac{(0.0011)^2}{(0.0600)^3(0.0200)} = 0.2801$$

Because  $Q_c = 23.1$  is greater than  $K_c = 0.500$ , the reaction will go to the left as it approaches equilibrium. Therefore, ammonia will dissociate.

### Question-29

Consider the exothermic formation of sulphur trioxide from sulphur dioxide and oxygen in the gas-phase.



At 900 K,  $K_p$  for this reaction is  $40.5 \text{ atm}^{-1}$  and  $\Delta H = -198 \text{ kJ}$

(a) Write the expression for the equilibrium constant for this reaction.

(b) Will the equilibrium constant for this reaction at room temperature (300 K) be greater than, less than, or equal to the equilibrium constant at 900 K? Explain your answer.

(c) How will the equilibrium be affected if the volume of the vessel containing the three gases is reduced, keeping the temperature constant: what happens?

(d) What is the effect of adding one mole of  $\text{He}(\text{g})$  to a flask containing  $\text{SO}_2$ ,  $\text{O}_2$  and  $\text{SO}_3$  at equilibrium at constant temperature?

**Solution:**

$$(a) K_p = \frac{P_{\text{SO}_3}^2}{P_{\text{SO}_2}^2 P_{\text{O}_2}}$$

(b) The equilibrium constant at 300 K will be greater than the equilibrium constant at 900 K. This is an exothermic reaction. If we decrease the temperature from 900 to 300 K, the equilibrium will be displaced to the right, releasing heat, more  $\text{SO}_3$  is produced and  $\text{SO}_2$  and  $\text{O}_2$  are used up. The equilibrium constant increases.

(c) Decreasing the volume of the vessel will increase the partial pressure of each gas and therefore increase the total pressure. The system will shift to the side with fewer numbers of moles of gas. Since there are two moles of gas on the right, but three on the left, the system will shift to the right. More  $\text{SO}_3$  will be produced, and some  $\text{SO}_2$  and  $\text{O}_2$  will be used up.

(d) Adding  $\text{He}(\text{g})$  has no effect at all. The partial pressures of  $\text{SO}_2$  and  $\text{O}_2$  and  $\text{SO}_3$  are unchanged by the addition of helium. The total pressure in the container increases, but as the partial pressure of the gases involved in the equilibrium are unaffected, the equilibrium does not shift.



### Question-30

Suppose we mix  $25.0 \text{ cm}^3$  of  $0.001 \text{ M AgNO}_3(\text{aq})$  with  $75.0 \text{ cm}^3$  of  $0.001 \text{ M Na}_2\text{CO}_3(\text{aq})$ . Does a precipitate of  $\text{Ag}_2\text{CO}_3$  form? The  $K_{\text{sp}}$  of  $\text{Ag}_2\text{CO}_3$  is  $6.2 \times 10^{-12}$  at  $298 \text{ K}$ .

#### Solution:

At the instant of mixing,

$$\text{Conc. Of } [\text{Ag}^+] = \frac{(0.025\text{L})(0.001\text{M})}{(0.100\text{L})} = 2.5 \times 10^{-4} \text{ M}$$

$$\text{Conc. Of } [\text{CO}_3^{2-}] = \frac{(0.075\text{L})(0.001\text{M})}{(0.100\text{L})} = 7.5 \times 10^{-4} \text{ M}$$

We are considering the reaction



$$K_i = [\text{Ag}^+]^2 [\text{CO}_3^{2-}] = (2.5 \times 10^{-4})^2 (7.5 \times 10^{-4})$$

$$K_i = 4.69 \times 10^{-11}$$

Since,  $K_i > K_{\text{sp}}$ , the solution is saturated and  $\text{Ag}_2\text{CO}_3$  will form.

### Question-31

Which of the following are Lewis bases?

$\text{H}_2\text{O}$ ,  $\text{BF}_3$ ,  $\text{H}^+$ ,  $\text{Ag}^+$ ,  $\text{NH}_3$  &  $\text{CO}$ .

#### Solution:

$\text{H}_2\text{O}$ ,  $\text{NH}_3$  and  $\text{CO}$  are Lewis bases as they have lone pairs of electrons to donate to Lewis acids.

### Question-32

Which of the following act both as Bronsted acids and bases?

$\text{HSO}_4^-$ ,  $\text{NH}_3$ ,  $\text{CO}$ ,  $\text{H}_2\text{O}$ ,  $\text{SO}_4^{2-}$ .

#### Solution:

$\text{HSO}_4^-$ ,  $\text{NH}_3$ ,  $\text{H}_2\text{O}$  can donate as well as accept a proton. Hence these can act as Bronsted acids and bases.

$\text{CO}$ ,  $\text{SO}_4^{2-}$  can only accept proton, hence they are Bronsted's bases.



### Question-33

A solution has a hydroxide concentration of  $1.0 \times 10^{-5}$  M at  $25^\circ$  C. Is the solution acidic, natural or basic?

#### Solution:

$$[\text{OH}^-] = 1.0 \times 10^{-5} \text{ M};$$

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

$$[\text{H}^+] = \frac{1 \times 10^{-14}}{1 \times 10^{-5}} = 1.0 \times 10^{-9} \text{ M}$$

as  $[\text{H}^+]$  is less than  $1 \times 10^{-7}$  M, the solution is basic.

### Question-34

Calculate the pH value of mixture containing 50cc M-HCl and 30cc M-NaOH solution assuming both to be completely ionised.

#### Solution:

$$\text{Total volume after mixing} = 50 + 30 = 80 \text{ cc}$$

$$\text{Molarity of HCl after mixing} = \frac{50}{80} \text{ M}$$

$$\text{Molarity of NaOH after mixing} = \frac{30}{80} \text{ M}$$

$$\text{Net molarity of HCl after mixing} = \frac{50}{80} - \frac{30}{80} = 0.25 \text{ M}$$

$$[\text{H}^+] = 0.25 = 2.5 \times 10^{-1}$$

$$\text{pH} = -\log (2.5 \times 10^{-1}) = 0.6021.$$

### Question-35

The dissociation constant of an acid HA is  $1.6 \times 10^{-5}$ . Calculate  $\text{H}_3\text{O}^+$  ion concentration of its 0.01 M solution.

#### Solution:

$$K_a = \frac{C\alpha^2}{1-\alpha}; K_a = C \alpha^2$$

$$\alpha = \sqrt{\frac{K_a}{C}}$$

$$\alpha = \sqrt{\frac{1.6 \times 10^{-5}}{1 \times 10^{-2}}} = \sqrt{1.6 \times 10^{-3}} = \sqrt{10^{-4} \times 16} = 4 \times 10^{-2}$$

$$[\text{H}^+] = \alpha \times C = (4 \times 10^{-2}) \times 10^{-2} = 4 \times 10^{-4} \text{ mol. L}^{-1}.$$

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### Question-36

Calculate the concentration of  $\text{H}_3\text{O}^+$  ion in a mixture of 0.02 M acetic acid and 0.2 M sodium acetate. (Given  $K_a$  for acetic acid is  $1.8 \times 10^{-5}$ )

**Solution:**



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

$$[\text{CH}_3\text{COO}^-] = 0.2 \text{ M} + x \approx 0.2 \text{ M}$$

$$[\text{CH}_3\text{COOH}] = 0.02 \text{ M} - x \approx 0.02 \text{ M}$$

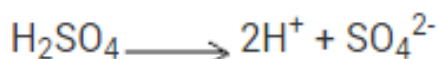
$$1.8 \times 10^{-5} = \frac{[\text{H}_3\text{O}^+][0.2]}{[0.02]}$$

$$(\text{i.e.}) \text{H}_3\text{O}^+ = \frac{1.8 \times 10^{-5} \times 0.02}{0.2} = 1.8 \times 10^{-6} \text{ mol. L}^{-1}.$$

### Question-37

Calculate pH of features  $10^{-2} \text{ M H}_2\text{SO}_4$ .

**Solution:**



One mole of  $\text{H}_2\text{SO}_4$  gives 2 moles of  $\text{H}^+_{(\text{aq})}$  ions.

$$[\text{H}^+] = 2[\text{H}_2\text{SO}_4]$$

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

$$\text{pH} = -\log [2 \times 10^{-2}]$$

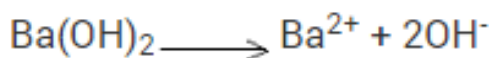
$$= 2 - \log 2 = 2 - 0.3010$$

$$\text{pH} = 1.699.$$

### Question-38

Calculate pH of 0.001 M Ba (OH)<sub>2</sub>.

**Solution:**



Each mole of Ba(OH)<sub>2</sub> gives 2[OH<sup>-</sup>] moles.

∴ 0.001 m Ba(OH)<sub>2</sub> gives 2 × [0.001 m] OH<sup>-</sup> ions

$$[\text{H}^+] = \frac{10^{-14}}{2 \times 10^{-3}} = \frac{10^{-11}}{2} = 0.5 \times 10^{-11}$$

$$[\text{H}^+] = 5 \times 10^{-12}$$

$$\text{pH} = -\log_{10} [5 \times 10^{-12}]$$

$$\text{pH} = -[\log_{10} 5 + \log 10^{-12}]$$

$$= -(-12) \log 10 - \log 5$$

$$= 12 \times 1 - 0.6990$$

$$\text{pH} = 11.301.$$

### Question-39

How many grams of NaOH must be dissolved in one litre of solution to give it a pH of 12?

**Solution:**

$$\text{pH} = 12; -\log [\text{H}^+] = 12; [\text{H}^+] = \text{antilog of } -12 = 1 \times 10^{-12}.$$

$$[\text{OH}^-] = \frac{K_w}{[\text{H}^+]} = \frac{1 \times 10^{-14}}{1 \times 10^{-12}} = 1 \times 10^{-2} = 0.01 \text{ moles/litre}$$

We know, weight per litre  $\equiv$  molarity  $\times$  m.wt.

$$= 0.01 \times 40 = 0.4 \text{ gms/litre.}$$

$$\therefore \text{Weight of NaOH present} = 0.4 \text{ gms/litre.}$$

### Question-40

A buffer solution is prepared by mixing 6 g. of acetic acid and 13.6 g of sodium acetate  $\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}$  and making the total volume 250 ml. Calculate the

(i) pH of the solution and

(ii) pH change on addition of 1 ml of 1M HCl to it.  $K_a = 1.8 \times 10^{-5}$ .

**Solution:**

$$[\text{CH}_3\text{COOH}] = \frac{\text{wt}}{\text{mwt}} = \frac{6}{60} = 0.1 \text{ moles} ; 0.1/0.250 = 0.004$$

$$[\text{CH}_3\text{COONa}] = \frac{\text{wt}}{\text{mwt}} = \frac{13.6}{136} = 0.1 \text{ moles} = 0.004$$

$$\text{pH} = \text{pK}_a + \log_{10} \frac{[\text{Salt}]}{[\text{Acid}]}$$

$$\text{pK}_a = -\log_{10} K_a = -\log 1.8 \times 10^{-5} \equiv 5 - 0.2553 = 4.74$$

$$\text{pH} = 4.74 + \log [0.004]/[0.004]$$

$$\text{pH} = 4.74 + \log_{10} 1 = 4.74 + 0 = 4.74.$$

### Question-41

Calculate the amount of  $(\text{NH}_4)_2 \text{SO}_4$  in gms which must be added to 500 ml of 0.200 M  $\text{NH}_3$  to yield a solution with pH 9.35 ( $K_b$  for  $\text{NH}_3 = 1.78 \times 10^{-5}$ )

**Solution:**

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

$$\text{pH} = 9.35$$

$$\text{pOH} = 14 - 9.35 = 4.65; K_b = 1.78 \times 10^{-5}$$

$$\text{pK}_b = 4.7447$$

Number of moles of  $\text{NH}_3$  added: one litre of 0.2 M  $\text{NH}_3$  contain 0.2 mole  
500 ml contains  $0.2 \times \frac{1}{2} = 0.1$  mole

$$\text{Moles of } (\text{NH}_4)_2 \text{SO}_4 = x$$

$$\therefore 4.65 = 4.7447 + \log \left( \frac{x}{0.1} \right)$$

$$\log \left( \frac{x}{0.1} \right) = -0.0947 \text{ or } \log \left( \frac{0.1}{x} \right) = 0.0947$$

$$\frac{0.1}{x} = 1.2436; x = \frac{0.1}{1.2436} = 0.08 \text{ mole}$$

$$\text{M. wt. of } (\text{NH}_4)_2 \text{SO}_4 = \text{mole} \times \text{m.wt} = 0.08 \times 132 = 10.56 \text{ grams.}$$

### Question-43

What would be the pH of a solution that contains 100 ml of 0.1 N HCl and 9.9 ml of 1 N NaOH solution?

#### Solution:

9.9 ml of 1 N solution of NaOH should be converted into 0.1 N NaOH

$$9.9 \times 1 \text{ N} \equiv x \times 0.1; \text{ (i.e.) } x = \frac{9.9 \times 1}{0.1} = 99 \text{ ml.}$$

9.9 ml of 1.0 N NaOH = 99 ml of 0.1 N, NaOH

Volume of HCl left unneutralised  $\equiv (100 - 99 \text{ ml})$  of 0.1 N  $\equiv 1 \text{ ml}$  of 0.1 N

Total volume of solution after mixing  $\equiv 100 + 9.9 = 109.9 \text{ ml} \equiv 110 \text{ ml}$

(app)

Conc. HCl after mixing  $\equiv \frac{0.1}{110} = 9.09 \times 10^{-4} \text{ m}$

$$[\text{H}^+] = 9.09 \times 10^{-4}$$

$$\text{pH} = -\log [9.09 \times 10^{-4}] = 4 - 0.9546 = 3.0454.$$

### Question-44

Calculate the degree of hydrolysis of 0.1M solution of sodium acetate at 25° C ;  $K_a = 1.8 \times 10^{-5}$ .

#### Solution:

Since sodium acetate is a salt of strong base and weak acid

$$K_b = \frac{k_w}{k_a} = \frac{1 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.5 \times 10^{-10}$$

$$\begin{aligned} \text{Since solution is 0.1, } h &= \sqrt{\frac{k_b}{c}} \\ &= \sqrt{\frac{5.5 \times 10^{-10}}{0.1}} = 7.452 \times 10^{-5}. \end{aligned}$$

### Question-45

$K_a$  for butyric acid is  $2.0 \times 10^{-5}$ . Calculate pH and hydroxyl ion concentration of 0.2 M aqueous solution of sodium butyrate.

#### Solution:

For salt of a weak acid with strong base

$$\begin{aligned} \text{pH} &= \frac{1}{2}\text{pK}_w + \frac{1}{2}\text{pK}_a + \frac{1}{2}\log C \\ &= \frac{1}{2} \times 14 + \frac{1}{2}\log \left( \frac{1}{2 \times 10^{-5}} \right) + \frac{1}{2}\log 0.2 \\ &= 7 + 2.3494 - 0.3494 \\ &= 9 \end{aligned}$$

$$\text{pOH} = 14 - 9 = 5$$

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

### Question-46

The pH of blood stream is maintained by a proper balance of  $\text{H}_2\text{CO}_3$  and  $\text{NaHCO}_3$  concentrations. What volume of 5 M  $\text{NaHCO}_3$  solution should be mixed with a 10 ml sample of blood which is 2 M in  $\text{H}_2\text{CO}_3$  in order to maintain a pH of 7.4?  $K_a$  for  $\text{H}_2\text{CO}_3$  in blood is  $7.8 \times 10^{-7}$ .

#### Solution:

Let the amount of  $\text{NaHCO}_3$  mixed = x ml

$$\text{Number of moles of NaHCO}_3 \text{ in x ml of 5 m NaHCO}_3 = \frac{5 \times x}{1000} = 0.005x$$

$$\text{Number of moles of H}_2\text{CO}_3 \text{ in 10 ml of 2 m H}_2\text{CO}_3 = \frac{2 \times 10}{1000} = 0.02$$

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

$$7.4 = -\log 7.8 \times 10^{-7} + \log \left( \frac{0.005x}{0.02} \right)$$

$$x = 78.36 \text{ ml.}$$



### Question-47

To a buffer solution containing 0.02 mole of propionic acid and 0.015 mole of sodium propionate per litre, 0.01 mole / litre of HCl is added. What is the pH of the solution?  $K_a$  propionic acid =  $1.34 \times 10^{-5}$ .

#### Solution:

$$[\text{propionic acid}] = (0.02 + 0.01)\text{M}$$

$$[\text{propionate}] = (0.015 + 0.010)\text{M}$$

$$\text{pH} = \text{p}K_a + \log [\text{salt}] / [\text{Acid}]$$

$$\text{pH} = -\log (1.34 \times 10^{-5}) + \log \frac{0.025}{0.03} = 4.9528.$$

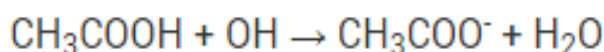
### Question-48

A buffer solution of acetic acid and sodium acetate of 1 M concentration was prepared. Calculate pH of the system when 0.01 mole of NaOH is added per litre of the above solution.  $K_a = 1.8 \times 10^{-5}$ .

#### Solution:

NaOH ionises fully: Hence  $\text{OH}^-$  ions added will react with  $\text{CH}_3\text{COOH}$  of the buffer system.

Molar conc. before adding NaOH



Molar conc. after adding 0.01 mole of  $(1 - 0.01) = 0.99$

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

$$= -\log 1.8 \times 10^{-5} + \log \frac{[1.01]}{[0.99]}$$

$$= 4.74 + 0.01 = 4.75.$$

### Question-49

The solubility product of AgCl in water is  $1.5 \times 10^{-10}$ . Calculate its solubility in 0.01 M NaCl aqueous.

#### Solution:

Let the solubility of AgCl in 0.01 M NaCl solution =  $x$  g mole  $L^{-1}$

$[Ag^+]$  in NaCl solution =  $x$  mol  $L^{-1}$

$[Cl^-]$  in 0.01 M NaCl solution  $\equiv x + 0.01$  M  $L^{-1}$

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

$(x)(x + 0.01) = 1.5 \times 10^{-10}$

$0.01x + x^2 = 1.5 \times 10^{-10}$

Since value of  $x$  is small  $x^2$  is neglected.

$0.01x = 1.5 \times 10^{-10}$

$x = 1.5 \times 10^{-8}$  mol  $L^{-1}$ .