

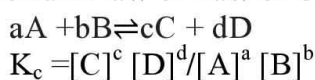
## CHAPTER-7

### EQUILIBRIUM

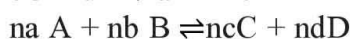
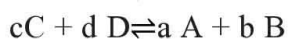
- Equilibrium state- When rate of formation of a product in a process is in competition with rate of formation of reactants, the state is then named as "Equilibrium state".

- Equilibrium in physical processes:  $\text{solid} \rightleftharpoons \text{liquid} \rightleftharpoons \text{gas}$   
 $\text{H}_2\text{O}_{(s)} \rightleftharpoons \text{H}_2\text{O}_{(l)} \rightleftharpoons \text{H}_2\text{O}_{(vap)}$

- Law of chemical equilibrium: At a given temperature, the product of concentrations of the reaction products raised to the respective stoichiometric coefficient in the balanced chemical equation divided by the product of concentrations of the reactants raised to their individual stoichiometric coefficients has a constant value. This is known as the Equilibrium Law or Law of Chemical Equilibrium.



#### Chemical equation



#### Equilibrium constant

$$K$$

$$K' = (1/K)$$

$$K'' = (K^n)$$

Concentrations or partial pressure of pure solids or liquids do not appear in the expression of the equilibrium constant. In the reaction,



- If  $Q_c > K_c$ , the reaction will proceed in the direction of reactants (reverse reaction). If  $Q_c < K_c$ , the reaction will proceed in the direction of the products (forward reaction)
- $K_p$  is equilibrium constant in terms of partial pressure of gaseous reactants and products.
- $K_c$  is equilibrium constant in terms of molar concentration of gaseous reactants and products.
- $K_p = K_c (RT)^{\Delta n}$  here **R** is gas constant, **T** is temperature at which the process is carried out &  $\Delta n$  is no. of moles of gaseous product minus no. of moles of gaseous reactants.
- If  $K_c > 10^3$ ;  $K_c$  is very high i.e. the reaction proceeds nearly to completion.
- If  $K_c < 10^{-3}$ ;  $K_c$  is very small i.e. the reaction proceeds rarely.
- If  $K_c$  is ranging in the range of  $10^3$  to  $10^{-3}$ ; i.e. reactants and products are just in equilibrium.
- $\Delta G^0 = -RT \ln K$  or  $\Delta G^0 = -2.303RT \log K$
- Factors affecting equilibrium constant:- temperature, pressure, catalyst and molar concentration of reactants and products.

- **Le Chatelier's principle:-** It states that a change in any of the factors that determine the equilibrium conditions of a system will cause the system to change in such a manner so as to reduce or to counteract the effect of the change.
- Arrhenius acids are the substances that ionize in water to form  $\text{H}^+$ .
- Arrhenius bases are the substances that ionize in water to form  $\text{OH}^-$ .
- Lewis acids are lone pair (of  $e^-$ ) accepters while Lewis bases are lone pair donors.
- Proton donor are acids while proton accepters are bases (Bronsted-Lowry concept).
- The acid-base pair that differs only by one proton is called a **conjugate acid-base pair**. If Brønsted acid is a strong acid then its conjugate base is a weak base and *viceversa*.
- **Ionic product of water.**  $K_w = [\text{H}^+][\text{OH}^-]$
- **pH =  $-\log [\text{H}^+]$  ; here  $[\text{H}^+]$  is molar concentration of hydrogen ion.**
- **pH + pOH = 14**
- **pKa + pKb = 14**
- **$K_a \times K_b = K_w$  = ionic product of water =  $1 \times 10^{-14}$**
- **Buffer solution :** The solutions which resist change in pH on dilution or with the addition of small amounts of acid or alkali are called Buffer Solutions.
- **common ion effect:** It can be defined as a shift in equilibrium on adding a substance that provides more of an ionic species already present in the dissociation equilibrium.
- **Hydrolysis of Salts:** process of interaction between water and cations/anions or both of salts is called hydrolysis.
- The cations (e.g.,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Ba}^{2+}$ , etc.) of strong bases and anions (e.g.,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{NO}_3^-$ ,  $\text{ClO}_4^-$  etc.) of strong acids simply get hydrated but do not hydrolyse, and therefore the solutions of salts formed from strong acids and bases are neutral i.e., their pH is 7.
- Salts of weak acid and strong base e.g.,  $\text{CH}_3\text{COONa}$  are basic in nature.
- Salts of strong acid and weak base e.g.,  $\text{NH}_4\text{Cl}$ , are acidic
- Salts of weak acid and weak base, e.g.,  $\text{CH}_3\text{COONH}_4$ . The pH is determined by the formula  $\text{pH} = 7 + \frac{1}{2} (\text{pK}_a - \text{pK}_b)$
- **Solubility product-** product of the molar concentrations of the ions in a saturated solution, each concentration term raised to the power equal to the no. of ions produced.

## ONE MARK QUESTIONS

Q.1. Mention the factors that affect equilibrium constant.

Ans. Temperature, pressure, catalyst and molar concentration of reactants and products.

Q.2. What are ionic products of water?

Ans.  $K_w = [H^+][OH^-]$

Q.3. Write conjugate acids of  $H_2O$  &  $NH_3$ .

Ans.  $H_3O^+$  &  $NH_4^+$ .

Q.4. Define Arrhenius acids.

Ans. Arrhenius acids are the substances that ionize in water to form  $H^+$ .

Q.5. Define the term degree of ionization.

Ans. Extent up to which an acid/base/salt ionize to form ions.

Q.6. What are Buffer solutions?

Ans. The solutions which resist change in pH on dilution or with the addition of small amounts of acid or alkali are called Buffer Solutions.

Q.7. Write  $K_c$  for the gaseous reaction-  $N_2 + 3H_2 \rightleftharpoons 2NH_3$

Ans.  $K_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$

Q.8. Out of  $H_2O$  &  $H_3O^+$  which is stronger acid?

Ans.  $H_3O^+$ .

Q.9. What is common ion effect?

Ans. Shift in equilibrium on adding a substance that provides more of an ionic species already present in the dissociation equilibrium.

Q.10. Write relationship between  $K_p$  and  $K_c$  for the gaseous reaction -  $N_2 + O_2 \rightleftharpoons 2NO$

Ans.  $K_p = K_c$  as  $\Delta n$  is zero for the above said reaction.

## TWO MARKS QUESTIONS

1. What is effect of catalyst on equilibrium constant ' $K_c$ '?

Ans. A catalyst does not affect equilibrium constant because it speeds up both forward and backward reactions to the same extent.

2. State Le Chatelier's principle.

Ans. It states that a change in any of the factors that determine the equilibrium conditions of a system will cause the system to change in such a manner so as to reduce or to counteract the effect of the change.

3. What is meant by conjugate acid-base pairs? Explain.

Ans:-  $\underset{\text{base}}{H_2O} + \underset{\text{acid}}{HCl} \rightleftharpoons \underset{\text{conjugate acid}}{H_3O^+} + \underset{\text{conjugate base}}{Cl^-}$



4. Classify the following bases as strong and weak bases:  $\text{NaHCO}_3$ ,  $\text{NaOH}$ ,  $\text{KOH}$ ,  $\text{Ca(OH)}_2$ ,  $\text{Mg(OH)}_2$ .

Ans:-strong base  $\text{NaOH}$ ,  $\text{KOH}$  ; weak bases  $\text{NaHCO}_3$ ,  $\text{Ca(OH)}_2$ ,  $\text{Mg(OH)}_2$ .

5. The concentration of hydrogen ion in a sample of soft drink is  $3.8 \times 10^{-3}\text{M}$ . What is its pH ?

Ans:- $\text{pH} = -\log[3.8 \times 10^{-3}]$

$$= -\{\log[3.8] + \log[10^{-3}]\}$$

$$= -\{(0.58) + (-3.0)\} = -\{-2.42\} = 2.42$$

Therefore, the pH of the soft drink is 2.42 and it is acidic.

6. The species:  $\text{H}_2\text{O}$ ,  $\text{HCO}_3^-$ ,  $\text{HSO}_4^-$  and  $\text{NH}_3$  can act both as Bronsted acids and bases. For each case give the corresponding conjugate acid and conjugate base.

Ans:-

Species	Conjugate acid	Conjugate base
$\text{H}_2\text{O}$	$\text{H}_3\text{O}^+$	$\text{OH}^-$
$\text{HCO}_3^-$	$\text{H}_2\text{CO}_3$	$\text{CO}_3^{2-}$
$\text{HSO}_4^-$	$\text{H}_2\text{SO}_4$	$\text{SO}_4^{2-}$
$\text{NH}_3$	$\text{NH}_4^+$	$\text{NH}_2^-$

7. Explain Lewis acids and bases with suitable examples.

Ans:-Lewis acids are lone pair (of  $e^-$ ) accepters while Lewis bases are lone pair donators.

$\text{AlCl}_3$  is a Lewis acid while  $\text{NH}_3$  is a Lewis base.

8. What is difference between alkali and bases? Give examples.

Ans:- An alkali is a water soluble base. All the alkalis are bases but all the bases are not alkali.

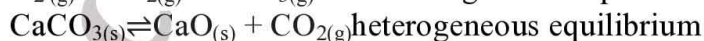
Ex-  $\text{NaOH}$  is an alkali/base.

$\text{Ca(OH)}_2$  is a base but not an alkali.

9. Explain homogeneous and heterogeneous equilibrium giving examples.

Ans:- If all the reactants and products present in an equilibrium mixture are in same phase  $\rightarrow$  homogeneous equilibrium.

If all the reactants and products present in an equilibrium mixture are in different phase  $\rightarrow$  heterogeneous equilibrium.



## THREE MARK QUESTIONS

1. The pH of some common substances is given below. Classify the substances as acidic/basic

Name of fluid	pH
Lime water	10
Milk of magnesia	10
Human saliva	6.4
Lemon juice	2.2
Sea water	7.8
Vinegar	3
milk	6.8

Ans.: acidic-Human saliva, Lemon juice, milk, vinegar

Basic- Lime water, sea water, milk of magnesia.

2. Explain general characteristics of acids and bases.

Ans.: Most of the acids taste sour. Acids are known to turn blue litmus paper into red and liberate dihydrogen on reacting with some metals.

Bases are known to turn red litmus paper blue, taste bitter and feel soapy.

3. Water is amphoteric in nature. Explain.

Ans.: Water can react with acid as well as base



4. Describe the effect of :

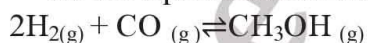
a) addition of  $\text{H}_2$

b) addition of  $\text{CH}_3\text{OH}$

c) removal of  $\text{CO}$

d) removal of  $\text{CH}_3\text{OH}$

on the equilibrium of the reaction:



Ans.: a) addition of  $\text{H}_2$

equilibrium will shift on RHS

b) addition of  $\text{CH}_3\text{OH}$

equilibrium will shift on LHS

c) removal of  $\text{CO}$

equilibrium will shift on LHS

d) removal of  $\text{CH}_3\text{OH}$

equilibrium will shift on RHS

5. Classify the following species into Lewis acids and Lewis bases and show how these act as such:

(a)  $\text{HO}^-$  (b)  $\text{F}^-$  (c)  $\text{H}^+$  (d)  $\text{BCl}_3$

**Solution**

(a) Hydroxyl ion is a Lewis base as it can donate an electron lone pair ( $:\text{OH}^-$ ).

(b) Fluoride ion acts as a Lewis base as it can donate any one of its four electron lone pairs.

(c) A proton is a Lewis acid as it can accept a lone pair of electrons from bases like hydroxyl ion and fluoride ion.

(d)  $\text{BCl}_3$  acts as a Lewis acid as it can accept a lone pair of electrons from species like ammonia or amine molecules.

6. For the equilibrium,  $2\text{NOCl(g)} \rightleftharpoons 2\text{NO(g)} + \text{Cl}_2\text{(g)}$  the value of the equilibrium constant,  $K_c$  is  $3.75 \times 10^{-6}$  at 1069 K. Calculate the  $K_p$  for the reaction at this temperature?

**Solution**

We know that,  $K_p = K_c(RT)^{\Delta n}$

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

$K_p = 3.75 \times 10^{-6} (0.0831 \times 1069)$

$K_p = 0.033$ .

7. Hydrolysis of sucrose gives,  $\text{Sucrose} + \text{H}_2\text{O} \rightarrow \text{Glucose} + \text{Fructose}$   
Equilibrium constant  $K_c$  for the reaction is  $2 \times 10^{13}$  at 300K. Calculate  $\Delta G^0$  at 300K.

**Solution**

$\Delta G^0 = -RT \ln K_c$

$\Delta G^0 = -8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 300 \text{ K} \times \ln(2 \times 10^{13})$

$\Delta G^0 = -7.64 \times 10^4 \text{ J mol}^{-1}$

8. Explain the following :

(i) Common ion effect      (ii) solubility products      (iii) pH

Ans. (i) Suppression of ionization of weak electrolyte by adding a strong electrolyte having an ion common.

(ii) Product of the molar concentrations of the ions in a saturated solution, each concentration term raised to the power equal to the no. of ions produced.

(iii) Negative logarithm of hydrogen ion concentration.

9. The values of  $K_{sp}$  of two sparingly soluble salts  $\text{Ni(OH)}_2$  and  $\text{AgCN}$  are  $2.0 \times 10^{-15}$  and  $6 \times 10^{-17}$  respectively. Which salt is more soluble? Explain.

**Solution**

$\text{AgCN} \rightleftharpoons \text{Ag}^+ + \text{CN}^-$

$K_{sp} = [\text{Ag}^+][\text{CN}^-] = 6 \times 10^{-17}$

$\text{Ni(OH)}_2 \rightleftharpoons \text{Ni}^{2+} + 2\text{OH}^-$

$K_{sp} = [\text{Ni}^{2+}][\text{OH}^-]^2 = 2 \times 10^{-15}$

Let  $[\text{Ag}^+] = S_1$ , then  $[\text{CN}^-] = S_1$

Let  $[\text{Ni}^{2+}] = S_2$ , then  $[\text{OH}^-] = 2S_2$

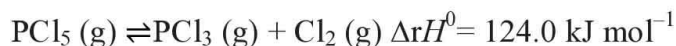
$S_1^2 = 6 \times 10^{-17}$ ,  $S_1 = 7.8 \times 10^{-9}$

$(S_2)(2S_2)^2 = 2 \times 10^{-15}$ ,  $S_2 = 0.58 \times 10^{-4}$

$\text{Ni(OH)}_2$  is more soluble than  $\text{AgCN}$ .

## FIVE MARKS QUESTIONS

1. At 473 K, equilibrium constant  $K_c$  for decomposition of phosphorus pentachloride,  $\text{PCl}_5$  is  $8.3 \times 10^{-3}$ . If decomposition is depicted as,



- a) Write an expression for  $K_c$  for the reaction.  
 b) What is the value of  $K_c$  for the reverse reaction at the same temperature?  
 c) what would be the effect on  $K_c$  if (i) more  $\text{PCl}_5$  is added (ii) pressure is increased (iii) the temperature is increased?

Ans: (a)  $K_c = \frac{[\text{PCl}_3][\text{Cl}_2]}{[\text{PCl}_5]}$

(b) 120.48

(c) (i) equilibrium will shift on RHS

(ii) equilibrium will shift on LHS

(iii) equilibrium will shift on RHS

2. Dihydrogen gas is obtained from natural gas by partial oxidation with steam as per following endothermic reaction:  $\text{CH}_4(\text{g}) + \text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{CO}(\text{g}) + 3\text{H}_2(\text{g})$

- (a) Write an expression for  $K_p$  for the above reaction.  
 (b) How will the values of  $K_p$  and composition of equilibrium mixture be affected by (i) increasing the pressure (ii) increasing the temperature (iii) using a catalyst?

Ans. (a)  $K_p = \frac{p(\text{CO}) \cdot p(\text{H}_2)^3}{p(\text{CH}_4) \cdot p(\text{H}_2\text{O})}$

(b) (i) value of  $K_p$  will not change, equilibrium will shift in backward direction.

(ii) Value of  $K_p$  will increase and reaction will proceed in forward direction.

(iii) no effect.

3. What is meant by the conjugate acid-base pair? Find the conjugate acid/base for the following species:  $\text{HNO}_2$ ,  $\text{CN}^-$ ,  $\text{HClO}_4$ ,  $\text{F}^-$ ,  $\text{OH}^-$ ,  $\text{CO}_3^{2-}$ , and  $\text{S}^{2-}$

Ans. The acid-base pair that differs only by one proton is called a conjugate acid-base pair

Species	Conjugate acid/base
$\text{HNO}_2$	$\text{NO}_2^-$
$\text{CN}^-$	$\text{HCN}$
$\text{HClO}_4$	$\text{ClO}_4^-$
$\text{F}^-$	$\text{HF}$
$\text{OH}^-$	$\text{H}_2\text{O}$
$\text{CO}_3^{2-}$	$\text{HCO}_3^{2-}$



$S^{2-}$	$HS^-$
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## HOTS QUESTIONS

1. The value of  $K_c$  for the reaction  $2A \rightleftharpoons B + C$  is  $2 \times 10^{-3}$ . At a given time, the composition of reaction mixture is  $[A] = [B] = [C] = 3 \times 10^{-4}$  M. In which direction the reaction will proceed?

### Solution

For the reaction the reaction quotient  $Q_c$  is given by,  $Q_c = [B][C] / [A]^2$

as  $[A] = [B] = [C] = 3 \times 10^{-4}$  M

$$Q_c = (3 \times 10^{-4})(3 \times 10^{-4}) / (3 \times 10^{-4})^2 = 1$$

as  $Q_c > K_c$  so the reaction will proceed in the reverse direction.

2.  $PCl_5$ ,  $PCl_3$  and  $Cl_2$  are at equilibrium at 500 K and having concentration 1.59 M  $PCl_3$ , 1.59 M  $Cl_2$  and 1.41 M  $PCl_5$ . Calculate  $K_c$  for the reaction,  $PCl_5 \rightleftharpoons PCl_3 + Cl_2$

### Solution

The equilibrium constant  $K_c$  for the above reaction can be written as,

$$K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]}$$

$$= (1.59)^2 / 1.41 = 1.79$$

3. Why is ammonia termed as a base though it does not contain  $OH^-$  ions?  
 Ans. ammonia is termed as a base on the basis of Lewis concept it can donate a lone pair of electrons.