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: solid $\rightleftharpoons$ liquid $\rightleftharpoons$ gas
  $H_2O_{(s)} \rightleftharpoons H_2O_{(l)} \rightleftharpoons H_2O_{(vap)}$
- Law of chemical equilibrium: At a given temperature, the product ofconcentrations of the reaction productsraised to the respective stoichiometriccoefficient in the balanced chemicalequation divided by the product ofconcentrations of the reactants raised totheir individual stoichiometric coefficientshas a constant value. This is known asthe Equilibrium Law or Law of ChemicalEquilibrium.

  $aA + bB \rightleftharpoons cC + dD$

  $K_c = [C]^c\,[D]^d/[A]^a\,[B]^b$

Chemical equation	**Equilibriumconstant**
$aA + b\,B \rightleftharpoons c\,C + D$	K
$cC + d\,D \rightleftharpoons a\,A + b\,B$	$K'c = (1/Kc)$
$na\,A + nb\,B \rightleftharpoons ncC + ndD$	$K'''c = (Kc^n)$

Concentrations or partial pressure of pure solids orliquids do notappear in the expression of the equilibriumconstant. In the reaction,

$Ag_2O(s) + 2HNO_3(aq) \rightleftharpoons 2AgNO_3(aq) + H_2O(l)$ $\boldsymbol{Kc = \frac{[AgNO3]^2}{[HNO3]^2}}$

- If $Qc > Kc$, the reaction will proceed in thedirection of reactants (reverse reaction).If $Qc < Kc$, the reaction will proceed in thedirection of the products (forward reaction)
- Kp is equilibrium constant in terms of partial pressure of gaseous reactants and products.
- Kc is equilibrium constant in terms of molar concentration of gaseous reactants and products.
- $Kp = Kc\,(RT)^{\Delta n}$ here **R** is gas constant, **T** is temperature at which the process is carried out &**Δn** is no. of moles of gaseous product minus no. of moles of gaseous reactants.
- If $Kc > 10^3$; Kc is very high i.e. the reaction proceeds nearly to completion.
- If $Kc < 10^3$; Kc is very small i.e. the reaction proceeds rarely.
- If Kcis 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.

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- **Le Chatelier's principle**:- It states that a **change in any of the factors thatdetermine the equilibrium conditions of asystem will cause the system to changein such a manner so as to reduce or tocounteract the effect of the change.**

- Arrhenius acids are the substances that ionize in water to form H^+.
- Arrhenius bases are the substances that ionize in water to form OH^-.
- Lewis acids are lone pair (of e-) accepters while Lewis bases are lone pair donators.
- Proton donor are acids while proton accepters are bases(Bronsted-Lowry concept).
- The acid-base pair thatdiffers only by one proton is called a **conjugateacid-base pair**. IfBrönsted acid is a strong acid then **itsconjugate base is a weak base and *viceversa*.**
- **Ionic product of water**.$K_w = [H^+][OH^-]$
- **pH = -log $[H^+]$; here$[H^+]$** is molar concentration of hydrogen ion.
- **pH + pOH =14**
- **pKa + pKb =14**
- **Ka x Kb = Kw =** ionic product of water**=1 x 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 andcations/anions or both of salts is calledhydrolysis.
- The cations (e.g., Na^+, K^+,Ca^{2+}, Ba^{2+}, etc.) of strong bases and anions(e.g., Cl^-, Br^-, NO^{3-}, ClO^{4-} etc.) of strong acids simply get hydrated but do not hydrolyse, andtherefore the solutions of salts formed fromstrong acids and bases are neutral i.e., theirpH is 7.
- Salts of weak acid and strong base e.g.,CH_3COONa are basic in nature.
- Salts of strong acid and weak base e.g.,NH_4Cl, are acidic
- Salts of weak acid and weak base, e.g.,CH_3COONH_4. The pH is determined by the formula $pH = 7 + ½ (pK_a – pK_b)$
- 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.

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

Q.2. Whatis ionic products of water?

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

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 $\mathbf{H^+}$.

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 Kc for the gaseous reaction- $N_2 + 3H_2 \rightleftharpoons 2NH_3$

Ans. $Kc=[NH_3]^2/[N_2]\ [H_2]^3$

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 Kp and Kc for the gaseous reaction - $N_2 + O_2 \rightleftharpoons 2NO$

Ans.Kp = Kc asΔn is zero for the above said reaction.

TWO MARKS QUESTIONS

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

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'r principle.
   Ans.It states that a change in any of the factors thatdetermine the equilibrium conditions of asystem will cause the system to changein such a manner so as to reduce or tocounteract 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: $NaHCO_3$, NaOH, KOH, $Ca(OH)_2$, $Mg(OH)_2$.
   Ans:-strong base NaOH, KOH ; weak bases $NaHCO_3$, $Ca(OH)_2$, $Mg(OH)_2$.

5. The concentration of hydrogen ion in a sample of soft drink is 3.8×10^{-3}M. What is its pH ?
   Ans:-$pH = -\log[3.8 \times 10^{-3}]$
   $= -\{\log[3.8] + \log[10^{-3}]\}$
   $= -\{(0.58) + (-3.0)\} = -\{-2.42\} = 2.42$
   Therefore, the pH of the soft drink is 2.42and it is acidic.

6. The species: H_2O, HCO_3^-, HSO_4^- and NH_3can act both as Bronsted acids and bases.For each case give the correspondingconjugate acid and conjugate base.

Ans:-

Species	Conjugate acid	Conjugate base
H_2O	H_3O^+	OH^-
HCO_3^-	H_2CO_3	CO_3^{2-}
HSO_4^-	H_2SO_4	SO_4^{2-}
NH_3	NH_4^+	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.
   $AlCl_3$ is a Lewis acid while 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- NaOH is an alkali/base. $Ca(OH)_2$ 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→homogeneous equilibrium.
   If all the reactants and products present in an equilibrium mixture are in different phase→ heterogeneous equilibrium.
   $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$ homogeneous equilibrium
   $CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$heterogeneous equilibrium

THREE MARK QUESTIONS

1. The pH of some common substances is given bellow. 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, tastebitter and feel soapy.

3. Water is amphoteric in nature. Explain.

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

$H_2O + HCl \rightarrow H_3O^+ + Cl^-$ water is basic

$H_2O + NH_3 \rightarrow OH^- + NH_4^+$ water is acidic

4. Describe the effect of :

a) addition of H_2
b) addition of CH_3OH
c) removal of CO
d) removal of CH_3OH
on the equilibrium of the reaction:

$2H_{2(g)} + CO_{(g)} \rightleftharpoons CH_3OH_{(g)}$

Ans.:- a) addition of H_2 equilibrium will shift on RHS
b) addition of CH_3OH equilibrium will shift on LHS
c) removal of CO equilibrium will shift on LHS
d) removal of CH_3OH equilibrium will shift on RHS

5. Classify the following species into Lewisacids and Lewis bases and show howthese act as such:
(a) HO^- (b)F^- (c) H^+ (d) BCl_3

Solution

(a) Hydroxyl ion is a Lewis base as it candonate an electron lone pair ($:OH^-$).
(b) Flouride ion acts as a Lewis base asit can donate any one of its fourelectron lone pairs.

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(c) A proton is a Lewis acid as it canaccept a lone pair of electrons frombases like hydroxyl ion and fluorideion.
(d) BCl_3 acts as a Lewis acid as it canaccept a lone pair of electrons fromspecies like ammonia or aminemolecules.

6. For the equilibrium, $2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2(g)$ the value of the equilibrium constant, K_c is 3.75×10^{-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, Sucrose + H_2O → Glucose + Fructose
Equilibrium constant K_c for the reaction is 2×10^{13} at 300K. Calculate ΔG^0 at 300K.

Solution

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

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

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

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 solublesalts $Ni(OH)_2$ and AgCN are 2.0 $\times 10^{-15}$ and 6×10^{-17} respectively. Which salt ismore soluble? Explain.

Solution

$AgCN \rightleftharpoons Ag^+ + CN^-$

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

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

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

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

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

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

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

$Ni(OH)_2$ is more soluble than AgCN.

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FIVE MARKS QUESTIONS

1. At 473 K, equilibrium constant Kc for decomposition of phosphorus pentachloride, PCl_5 is 8.3×10^{-3}. If decomposition is depicted as,

   PCl_5 (g) $\rightleftharpoons$ PCl_3 (g) + Cl_2 (g) ΔrH^0 = 124.0 kJ mol^{-1}
   a) Write an expression for Kc for the reaction.
   b) What is the value of Kc for the reaction at the same temperature?

   c) what would be the effect on Kc if (i) more PCl_5 is added (ii) pressure is increased (iii) the temperature is increased ?

   Ans: (a) $Kc = \frac{[PCl_3][Cl_2]}{[PCl_5]}$

   (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 asper following endothermic reaction: CH_4 (g) + H_2O (g) $\rightleftharpoons$ CO (g) + $3H_2$ (g)
   (a) Write as expression for Kp for the above reaction.
   (b) How will the values of Kp and composition of equilibrium mixture be affectedby (i) increasing the pressure (ii) increasing the temperature (iii) using a catalyst?
   Ans. (a) $K_p = p(CO).p(H_2)^3 / p(CH_4).p(H_2O)$
   (b)(i) value of Kp will not change, equilibrium will shift in backward direction.
   (ii) Value of Kp 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/basefor the following species: HNO_2, CN^-, $HClO_4$, F^-, OH^-, CO_3^{2-}, and S^{2-}
   Ans. The acid-base pair thatdiffers only by one proton is called a conjugate acid-base pair

Species	Conjugate acid/base
HNO_2	NO_2^-
CN^-	HCN
$HClO_4$	ClO_4^-
F^-	HF
OH^-	H2O
CO_3^{2-}	HCO_3^{2-}

S^{2-}	HS^{-}

HOTS QUESTIONS

1. The value of *Kc*for the reaction2A $\rightleftharpoons$B + C is 2 × 10^{-3}. At a given time,the composition of reaction mixture is[A] = [B] = [C] = 3 × 10^{-4} M. In whichdirection the reaction will proceed?

Solution

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

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

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

as$Qc>Kc$so the reaction will proceed inthe reverse direction.

2. PCl_5, PCl_3 and Cl_2 are at equilibrium at500 K and having concentration 1.59M PCl_3, 1.59M Cl_2 and 1.41 M PCl_5. Calculate *Kc*for the reaction,$PCl_5 \rightleftharpoons PCl_3 + Cl_2$

Solution

The equilibrium constant *Kc*for the abovereaction can be written as,

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

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

3. Why is ammonia termed as a base though it does not contain OH^- ions?

Ans.ammona is termed as a base on the basis of Lewis concept it can donate a lone pair of electrons.