Equilibrium

A state of equilibrium is attained when two opposing process (forward and reverse)occur simultaneously at the same rate. The criterion for equilibrium for the reaction aA+bB$\rightleftarrows cC + dD$ is $\Delta_r G$ is zero . $\Delta_r G^{\emptyset}$ can never be zero because it is calculated from the $\Delta_r G^{\emptyset}$ of the reactants and products. The $\Delta_r G^{\emptyset}$ is related to equilibrium constant K_c or K_p as follows :

0=$\Delta_r G^{\emptyset} - 2.303RTlogK$

And $\Delta_r G^{\emptyset} = \Delta_r H^{\emptyset} - T\Delta_r S^{\emptyset} = -2.303RTlogK$

Law of equilibrium :

$K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$ and $K_p = \frac{p_C^c p_D^d}{p_A^a p_B^b}$

(where K_c and K_p are equilibrium constants in terms of molar concentration and pressure respectively .)

Where $K_p = K_c(RT)^{\Delta ng}$

$\Delta ng = [sum\ of$ stoichiometric coefficients of gaseous products – sum of stoichiometric coefficients of gaseous reactants]

Predicting the direction of reaction : The direction of reaction can be predicted by the value of reaction quotient Q_c which is defined the same way as equilibrium constant K_c except that the concentrations in Q_c are not necessary equilibrium values . If $Q_c > K_c$ the reaction proceeds in the reverse direction and if $Q_c < K_c$, the reaction will proceed in the forward direction . If $Q_c = K_c$, no net reaction occurs .

Magnitude of equilibrium constant depends upon the way in which a reaction is written .

Chemical equation	Equilibrium constant
aA+bB$\rightleftarrows cC + dD$	K
cC+dD$\rightleftarrows aA + bB$	$K_1 = \frac{1}{K}$
naA+nbB$\rightleftarrows ncC + ndD$	$K_2 = K^n$
$\frac{a}{n}A + \frac{b}{n}B \rightleftarrows \frac{c}{n}C + \frac{d}{n}D$	$K_3 = K^{1/n}$

When individual balanced equations are combined , multiply their equilibrium constants to obtain the equilibrium constant for the net reaction . For example ,

$N_2 + O_2 \rightleftarrows 2NO; K_1$

2NO+$O_2 \rightleftarrows 2NO_2;\ K_2$

$N_2 + 2O_2 \rightleftarrows 2NO_2\,; K = K_1 \times K_2$

Le Chatelier's principle : When a system at equilibrium is subjected to a change in temperature , pressure or concentration of a reacting species, the system changes in a way that it reduces or counteracts the effect of the change while reaching a new state of equilibrium . Le Chatelier's principle can be used to study the effect of various factors such as temperature , concentration , pressure, catalyst and addition of inert gases on the direction of equilibrium and to control the yield of products by controlling these factors.

Use of a catalyst does not effect the equilibrium composition of a reaction mixture but increases the rate of chemical reaction by making available a new lower energy pathway for conversion of reactants to products and vice versa

The pH scale :

Activity of hydrogen $(a_{H^+}) = [H^+]/molL^{-1}$

pH=-loga_H+=-log$\{[H^+]/molL^{-1}\}$

pOH=-log$\{[OH^-]/molL^{-1}\}$

and pH+pOH=14

$\because [H^+][OH^-] = 1.0 \times 10^{-14}$ at 298K

Ionisation constant of water and its ionic product

The following equilibrium exists in pure water

$H_2O + H_2O \rightleftarrows H_3O^+ + OH^-$

At 298k, $[H^+] = [OH^-] = 1 \times 10^{-7} M$

$k_w = [H^+] \times [OH^-] = 10^{-14}$ at 298K

Ionisation constants of Acids and Bases (Acid Base Equilibrium)

HX$\rightleftarrows H^+ + X^-$

$$K_a = \frac{[H^+][X^-]}{[HX]} = \frac{C\alpha.C\alpha}{C(1-\alpha)} = \frac{C\alpha^2}{1-\alpha}$$

Similarly for base MOH$\rightleftarrows M^+ + OH^-$

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

Product of ionisation constants of an acid (K_a) and its conjugate base (K_b) is equal to ionic product of water i.e. $K_a \times K_b = K_w$

Ionisation of di and polybasic acids and di and polyacidic bases :

For example for diabasic acid (H_2X):

$H_2 \rightleftarrows H^+ + HX^-$

$K_{a_1} = \frac{[H^+][HX^-]}{[H_2X]}$

And $HX^- \rightleftarrows H^+ + X^{2-}$

$K_{a_2} = \frac{[H^+][X^{2-}]}{[HX^-]}$

Higher order ionisation constants are always smaller than lower order ionisation constants.

Common ion effect : The depression of ionisation of weak electrolyte by the presence of common ion from a strong electrolyte is called common ion effect.

Hydrolysis of salts and pH of their solutions : Hydrolysis of salt is defined as the reaction of cation or anion with water as a result of which the pH of water changes .

1. Salts of strong acids and strong bases (e.g. NaCl)do not hydrolyse ,
   The solution pH=7
2. Salts of weak acids and strong bases (e.g. CH_3COONa) hydrolyse , pH>7. (The anion acts as a base)
   $X^- + H_2O \rightleftarrows HX \quad + \quad OH^-$
   (Weak acid) (Strong base)
   pH=7+1/2 $(pK_a + \log c)$
3. Salt of strong acids and weak bases (e.g. , NH_4Cl) hydrolyse ,
   pH<7 . (The cation acts as an acid)
   $M^+ + H_2O \rightleftarrows MOH + H^+$
   $pH = 7 - \frac{1}{2}(pK_b + \log c)$

4. Salts of weak acids and weak base (e.g. , $CH_3COO\ NH_4$) hydrolyse . The cation acts as an acid anion as a bases but whether the solution is acidic or basic depends upon the relative values of K_a and K_b for these ions.

$M^+ + X^- + H_2O \rightleftarrows MOH + HX$

pH=7+$\frac{1}{2}(pK_a - pK_b)$

Buffer solutions : The solutions , which resist the change in pH on dilution or addition of small amounts of acid or base , are called buffer solutions .

Basic buffer :Solution of weak base and its salt with strong acid e.g. , $NH_4OH + NH_4Cl$

Acidic buffer : Solution of weak acid and its salt with strong base, e.g.,

$CH_3COOH + CH_3COO\ Na$

Solubility product constant (K_{sp}): The equilibrium constant that represent the equilibrium between undissolved salt (solute) and its ions in a saturated solution is called solubility product constant (K_{sp}). In the absence of equilibrium , i.e., if the concentration of one or more species is not the equilibrium concentration , the product of concentration of ions raised to powers equal to respective stoichiometric coefficients appearing in balanced chemical equation is called Q_{sp} , the ionic product of salt .

Ca$F_2(s) \leftrightharpoons Ca^{2+}(aq) + 2F^-(aq)$

$K_{sp} = [Ca^{2+}][F^-]^2$

$If\ the$ concentration of any one of the ions is increased , it will combine with the ion of opposite charge and some of the salt will be precipitated till once again $K_{sp} = Q_{sp}$ and if the concentration of any one of their ions is decreased more salt will dissolve to increase the concentration of both the ions till once again $K_{sp} = Q_{sp}$

1 Mark Questions

1. Define physical equilibrium . Give an example also .
2. Justify the statement : ‘Both physical and chemical equilibria are dynamic in nature.’
3. At what temperature the solid and liquid phase of the same substance are in equilibrium with each other ?
4. State the law of chemical equilibrium .
5. Name the indicator used for titration of strong acid versus strong base.
6. Mention the effect of temperature on solubility of a gas in liquid
7. State Henry’s law
8. Write the expression for K_c for the following reaction :
   C$H_3COOC_2H_5(aq) + H_2O(l) \leftrightharpoons$ C$H_3COOH(aq) + C_2H_5OH(aq)$
9. Write the expression for K_p for the following reaction :
   Cu$(NO_3)_2(s) \leftrightharpoons 2CuO(s) + 4NO_2(g) + O_2(g)$
10. For the following equilibrium $K_c = 6.3 \times 10^{14}$ at 1000K :
    NO(g)+$O_3(g) \rightleftharpoons NO_2(g) + O_2(g)$
    Find the value of K_c for the following
    $\frac{1}{2}NO(g) + \frac{1}{2}O_3(g) \leftrightharpoons \frac{1}{2}\ NO_2(g) + \frac{1}{2}O_2(g)$
11. Equilibrium constant (K_c) for the reaction $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ at 500K is 0.061. Calculate the value of K_c for the reversible reaction .
12. Give an example of a heterogeneous equilibrium
13. $N_2(g) + 3H_2(g) \rightleftharpoons\ 2NH_3(g) + Heat$
    $What$ is the effect of increasing temperature on the value of K
14. $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$
    $Write$ the relationship between K_p and K_c for the given reaction

15. Why a catalyst does not affect the magnitude of equilibrium constant ?
16. Define solubility product
17. What is meant by ionic product of water ?
18. Calculate the pH of 0.01M NaOH solution
19. Why does BF_3 act as a Lewis acid ?
20. Write the conjugate acid of NH_3

21. Write the expression of K_{sp} for Ag_2CrO_4
22. Define common ion effect
23. How does common ion effect affect the solubility of salts?
24. Define dissociation constant of a base
25. Predict the direction of reaction when $Q_c > K_c$
26. NH_3 acts as Arrhenius base as well as Bronsted base . Explain
27. Give the relationship between K_a , C and α where K_a is the dissociation constant of acid, C is the initial concentration of acid and α is its degree of dissociation . Write the condition when α is neglected in comparison to C.
28. Arrange the following acids in increasing order of their pK_a values
    HCl , HBr, HF and HI
29. Write the unit of K_p for the following equilibrium
    N_2O_4(g) $\rightleftharpoons$2 $NO_2(g)$
30. Define Le Chatlier's principle
31. If K_a value for hydrofluoric acid (HF) is 6.8$\times 10^{-4}$, what is the K_b value of its conjugate base at 298K . Given $K_w = 1.0 \times 10^{-14}$ at 298K

    [Ans $K_b(F^-) = 1.5 \times 10^{-11}$]
32. Explain why pure NaCl precipitates out when HCl gas is passed in brine solution

2 – Mark Questions

1. (a) Write an expression for K_p for the following reaction :
   Ca$CO_3(s) \leftrightharpoons CaO(s) + CO_2(g)$
   (b)Mention the effect of decreasing the concentration of CO_2 on direction of reaction .

2. For an endothermic reaction , how does the value of K_c change when :

(a)temperature is increased ?

(b)pressure is increased ?

3. (a)Define buffer solution

(b)Give one example each of an acidic buffer and a basic buffer

4. Write the conjugate bases for the following acids :

a)HF b)NH_4^+ c)HCO_3^- d)H_2SO_4

5. With the help of examples explain the factors affecting the strength of an acid

6. (a) vapour pressure of water , acetone and ethanol at 293K are 2.34, 12.36 and 5.85kPa respectively . Which of these have the lowest and highest boiling point?

(b)At 293 K, which of these will evaporate least in a sealed container before equilibrium is reached ?

7. The concentration of hydrogen ion in soft drink is 3.8x10^{-3} mol L^{-1}. Calculate its pH

[Ans pH=2.42]

8. For the general reaction :

aA(g)+bB(g)->cC(g)+dD(g)

Derive the relationship between K_c and K_p

9. Assign reasons for the following :

(a)A solution of NH_4Cl in water shows pH less than 7

(b)In qualitative analysis NH_4Cl is added before adding NH_4OH for testing Fe^{3+} or Al^{3+} ions

10. (a) Mention the difference between a weak electrolyte and a strong electrolyte.
(b)Which of the following species is a strong electrolyte.
CH_3COOH and CH_3COONa
11. Calculate th pH of 1.0x$10^{-8}M$ solution of HCl. [Ans : pH=6.98]
12. (a) Write the hydrolysis reaction of ammonium acetate .
(b)The p K_a of acetic acid and pK_b of ammonium hydroxide are 4.76 and 4.75 respectively . Calculate the pH of ammonium acetate solution. [Ans pH=7.005]
13. (a) Write the conjugate acid and conjugate base of H_2O
(b)Write the relationship between equilibrium constant and standard Gibbs energy
14. If 0.561 g of KOH is dissolved in water to give 200mL of solution at 298K, calculate the pH of this solution . (Molar mass of KOH=56g mol^{-1})
[Ans pH=12.70]
15. The value of K_c for the reaction :
$3O_2(g) \leftrightharpoons 2O_3(g)$
Is 2.0x10^{-5} at 25°C . If the equilibrium concentration of O_2 in air at25°C is 1.6x10^{-2}M,calculate the concentration of O_3
16. Calculate the minimum volume of water required to dissolve 1g CaSO_4 at 298 K? (For CaSO_4 K_{sp}=9.1x10^{-6}) [Ans : 2.46L of water]
17. The pH of 0.1 M monobasic acid is 4.50. Calculate the concentration of species H_3O^+, A^- *and* HA at equilibrium . [Ans. $[H_3O^+] = [A^-] = 3.16 \times 10^{-5}, [HA] = 0.1]$
18. The cations of strong bases like $Na^+, K^+, Ca^{2+}, Ba^{2+}, etc.$ and anions of strong acids like $Cl^-, Br^-, NO_3^-, ClO_4^-$ etc. get hydrated in water but do not hydrolyse . Explain why?

3 Mark Questions

1. A) Which of the following will act as LEWIS acid :
   H_2O ,BF_3, and H^+
   (b) Equal volumes of 0.02M CaCl_2 and 0.0004M Na_2SO_4 are mixed . Will a precipitate form ? Given : K_{sp} for CaSO_4 =2.4x10^{-5}
   [Ans : Precipitate will not form]
2. (a) Assign reasons to the following :
   (i) Pure liquids and solids can be ignored while writing the equilibrium constant expression
   (ii) H_2S is passed in acidic medium to precipitate group II cations .
   (b) Write the effect of temperature on ionic product of water
3. (a) Explain the hydrolysis of salts
   (b) For the reaction :
   2NOCl$\rightleftharpoons 2NO(g) + Cl_2(g)$
   The value of $K_c = 3.75 \times 10^{-6}$ at 1069 K. Calculate K_p at this temperature
   [Ans kp=3.33x10^{-2}]

4.(a) Define reaction quotient
(b) A mixture of H_2 , N_2 and NH_3 with molar concentrations of 3.0x10^{-3} molL^{-1} and 2.0x10^{-3} molL^{-1} respectively was prepared at 500K . Predict whether at this stage the concentration of NH_3 will increase or decrease .
Given the value of K=61 for the reaction

$N_2(g) + 3H_2(g) \rightleftharpoons 3\ NH_3$(g) at 500K

5. Consider the reaction :

$2SO_2(g) + O_2(g) \rightleftharpoons 3SO_3(g)\quad \Delta_r H^\circ = -190KJ/mol$

Indicate the direction in which the equilibrium will shift when :

(a) Temperature is increased
(b) Pressure is decreased
(c) An inert gas is added at constant pressure ?
(d) Inert gas is added at constant pressure ?

6. (a) Classify the following as homogeneous or heterogeneous equilibria :
(i) 2NO(g) +$O_2(g) \rightleftharpoons 2NO_2(g)$
(ii) Mg(s)+ $O_2(g) \rightleftharpoons 2MgO(s)$
(b) Consider the following transformations

A$\rightleftharpoons B$	$K_1 = 1$
B$\rightleftharpoons C$	$K_2 = 2$
C$\rightleftharpoons D$	$K_3 = 3$

Calculate the value of K for A$\rightleftharpoons$D

7.(a)Give one example each of a lewis and a Lewis base
(b) All Lewis bases are also Bronsted bases . Explain why ?
(c) K_b for NH_4OH and CH_3NH_2 are 1.8x10^{-5}, 4.4x10^{-4} respectively Which of them is stronger base and why ?

8. Ammonia is prepared by Haber's process in which the following reaction occurs :
$N_2 + 3H_2 \rightleftharpoons 2NH_3 + 93.6KJ$
Mention the effect of following on the equilibrium concn. Of ammonia :
(a) Increasing pressure
(b) Increasing temperature
(c) Use of a catalyst at an optimum temperature

9. Calculate the pH of following solution :

(i) 0.3g of Ca$(OH)_2$ dissolved in water to give 500 mL of solution

(ii)1.0mL of 13.6M HCl is diluted with water to give 1.0L solution

(iii) 10mL of 0.1M H_2SO_4 +10 mL of 0.1M KOH

[Ans. (i) 12.21 (ii) 1.87 (iii) 3.00

10. At 700K, equilibrium constant for the reaction :
$H_2(g) + I_2(g) \leftrightharpoons 2HI(g)$

is 54.8. If 0.5mol $L^{-1}$of HI(g) is present at equilibrium at 700K, calculate the concentrations of H_2(g) and $I_2(g)$, assuming that we initially started with HI(g) and allowed it to reach an equilibrium at 700K.

[Ans. $[H_2] = [I_2] = 0.068M]$

11. One mole of H_2O and one mole of CO are taken in a vessel and heated to 725 K. At equilibrium 40% (by mass) of water reacts with CO according to the equation :

H_2O (g)+CO(g)$\rightleftharpoons$ $H_2(g) + CO_2(g)$

Calculate the equilibrium constant for the reaction . [Ans 0.44]

12. The following reaction takes place in the blast furnace during the extraction of iron from haematite ore:

FeO(s)+CO(g) $\rightleftharpoons$Fe(s)+ $CO_2(g)$

$K_p = 0.265$ atm at 1050K

a) If the initial partial pressures are $p_{co} = 1.4\ atm$ and $P_{co2} = 0.80$ atm, predict the direction of reactor. [Ans. The reaction moves backwards
b) Calculate the equilibrium partical pressures of CO and CO_2 at 1050K.

[Ans $[p_{co}] = 1.139\ atm. [P_{co2}] = 0.461atm.$

13. Equal volumes of 0.002M solutions of sodium iodate and cupric chlorate are mixed together. Will it lead to precipitation of copper iodate Cu$(IO_3)_2$?
For cupric iodate , $K_{sp} = 7.4 \times 10^{-8}$

[Ans. Ionic product = 1x10^{-9}, No precipitation]

14. The pH of 0.1M solution of an acid (HA) is 2.34. Calculate the ionisation constant of the acid and its degree of ionization in solution .

[Ans. Ka=2.09x10^{-4} $\alpha = 0.0457$]

15. The solubility of Sr$(OH)_2$ at 298K is 19.23g/L of solution . Calculate the molar concentrations of strontium and hydroxyl ions and the pH of the solution
[Molar mass of Sr$(OH)_2$=121.67g/mol].

[Ans . $[Sr^{2+}] = 0.1581\ M, pH = 13.50, [OH^-] = 0.3162M$

5 Mark Questions

1.(a) K_{a_2} of oxalic acid has much lower value than K_{a_1} . Explain
(b) The following species act as both Bronsted acids and bases. Write the conjugate acid and conjugate base formed by them:
H_2O and HSO_4^-

(c) At 450K , $K_p = 2.0 \times 10^{10}\ bar^{-1}$ for the following reaction :

2S$O_2(g) + O_2(g) \leftrightharpoons 2SO_3(g)$

Calculate the value of K_c at this temperature . [Ans. $K_c = 7.47 \times 10^{11} M^{-1}$]

2.(a) Predict whether the following inorganic salts will give acidic , basic or neutral solutions. Give appropriate reasons.

N$H_4Cl, NaCN, NaCl$

(b) Calculate the pH of a 0.10M ammonia solution . Calculate the pH after 50.0 mL of this solution is treated with 25.0mL of 0.10M HCl. The dissociation constant of ammonia (

(b) Calculate the pH of a 0.10M ammonia solution . Calculate the pH after 50.0 mL of this solution is treated with 25.0mL of 0.10M HCl. The dissociation constant of ammonia (K_b) is 1.77$\times 10^{-5}$. [Ans 11.12, 9.24]

3. Ethyl acetate is formed by the reaction between ethanol and acetic acid and the equilibrium is represented as:

$CH_3COOH(l) + C_2H_5OH(l) \leftrightharpoons CH_3COOC_2H_5(l) + H_2O(l)$

(i) Write the reaction quotient , Q_c for this reaction.

(ii) At 293K, if one starts with 1.0mol of acetic acid and 0.18 mol of ethanol, there is 0.171 mol of ethyl acetate in the final equilibrium mixture. Calculate the equilibrium constant. [Ans. $K_c = 22.9$]

(iii) Starting with 0.5 mol of ethanol and 1.0 mol of acetic and maintaining it at 293K, 0.214 mol of ethyl acetate is found after sometime . Has the equilibrium been attained? [Ans: $Q_c < K_c$, therefore, equilibrium is not reached]

4. For the reaction, $\Delta_r H$ is positive :
$CH_4(g) + H_2O(g) \leftrightharpoons CO(g) + 3H_2(g)$
How will the value of K_p and composition of equilibrium mixture be affected by:
(a) Increasing the pressure
(b) Increasing the temperature
(c) Using a catalyst?

5. (a) Arrange the following in the increasing order of K_a :
HF, H_2O, NH_3, CH_4
(b) The K_b value for dimethylamine , $(CH_3)_2NH$, is 5.4x10^{-4}
Calculate its degree of ionization in its 0.02M solution . [Ans: $\alpha = 0.162$]

(c) Calculate the percentage of dimethylamine ionized if the solution is also 0.1M in NaOH [Ans: $\alpha = 0.0054$]