Chemical Equilibrium

CHEMICAL EQUILIBRIUM

C1 Reaction is set to be equilibrium reaction where the rate of the forward reaction is equal to the rate of backward reaction. Chemical equilibrium at a given temperature there is a constancy of certain observable properties such as pressure, concentration and density. Chemical equilibrium can be approach from another side. A catalyst can hasten the approach of equilibrium but does not alter the state of equilibrium. Chemical equilibrium is dynamic in nature.

C2A Expression of equilibrium constant K_c and K_p :

Expression of K_c for $aA(g) + bB(g) \rightleftharpoons cC(g) + dD(g)$

$K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$. If any component in solid state or in excess its conc. is 1.

$K_p = \frac{[P_D]^d[P_C]^c}{[P_A]^a[P_B]^b}$, P → partial pressure can be expressed as $P_A = \frac{nRT}{V}$, $P_A = P_T X_A$

X_A → mole fraction

P_T → Total pressure

C2B RELATION BETWEEN K_p and K_c

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

Δn = moles of gaseous product - moles of gaseous reactants.

Practice Problems :

1. A sample of HI (g) is placed in flask at a pressure of 0.2 atm. At equilibrium, the partial pressure of HI (g) is 0.04 atm. What is K_p for the given equilibrium ?

   $2HI (g) \rightleftharpoons H_2(g) + I_2(g)$

2. One of the reactions that takes place in produceing steel from iron ore is reduction of iron (II) oxide by the carbon monoxide to give iron metal and CO_2.

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

   K_p = 0.265 atm at 1050 K

   What are the equilibrium partial pressures of CO and CO_2 at 1050 K if the initial partial pressures are : p_{CO} = 1.4 atm and p_{CO_2} = 0.80 atm ?

3. Dihydrogen gas used in Haber's process is produced by reacting methane from natural gas with high temperature steam. The first stage of two stage reaction involves the formation of CO and H_2. In second state, CO formed in first stage is reacted with more steam in water gas shift reaction.

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

   If a reaction vessel at 400 ^{0}C is charged with an equimolar mixture of CO and steam such that $p_{CO} = p_{H_2O} = 4.0$ bar, what will be the partial pressure of H_2O at equilibrium ? K_p = 10.1 at 400 ^{0}C.

4. For the reversible reaction, $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ at 500^{0}C, the value of K_p is 1.44×10^{-5} when partial pressure is measured in atmosphere. The corresponding value of K_c, with concentration in mole litre^{-1}, is

   (a) $1.44 \times 10^{-5}/(0.082 \times 500)^{-2}$ (b) $1.44 \times 10^{-5}/(8.314 \times 733)^{-2}$

   (c) $1.44 \times 10^{-5}/(0.082 \times 773)^{2}$ (d) $1.44 \times 10^{-5}/(0.082 \times 773)^{-2}$

[Answers : (1) 4.0 (2) $p_{CO_2} = 1.74$ atm , $p_{CO} = 0.46$ atm (3) p = 0.96 bar (4) d]

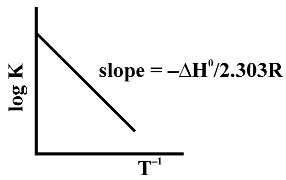
C3 FACTORS AFFECTING EQUILIBRIUM CONSTANT

1. **Methods of representing the equation :**

$N_2 + 3H_2 \rightleftharpoons 2NH_3$, K_c, on reversing the reaction new equilibrium constant $K'_C = \dfrac{1}{K_C}$

2. If a reaction is multiplied by coefficient 'n' then $K'_C = (K_C)^n$ and if reaction is divided by coefficient n then $K'_C = (K_C)^{1/n}$.

3. Effect of temperature : $K_{eq} = A_0 e^{-\Delta H/RT}$, $\log \dfrac{K_2}{K_1} = \dfrac{\Delta H}{2.303R}\left[\dfrac{T_2 - T_1}{T_1 T_2}\right]$



Practice Problems :

1. K_p for the equilibrium, $FeO(s) + CO(g) \rightleftharpoons Fe(s) + CO_2(g)$ at 1000^0C is 0.4. If CO(g) at a pressure of 1 atm and excess FeO(s) are placed in a container at 1000^0C, the pressures of $CO_2(g)$ when equilibrium is attained is

(a) 0.714 atm (b) 2.745 atm (c) 3.222 atm (d) 4.202 atm

2. One mole of hydrogen iodide is heated in a closed container of 2 litre. At equilibrium half mole of hydrogen iodide has dissociated. The equilibrium constant is

(a) 1.0 (b) 0.5 (c) 0.25 (d) 0.75

3. When S in the form of S_8 is heated at 90^0 K, the initial pressure of 1 atmosphere falls by 29% at equilibrium. This is because of the conversion of some gaseous S_8 to gaseous S_2. The K_p for the reaction is

(a) 2.55 atm^3 (b) 1 atm^3 (c) 5 atm^3 (d) 9.55 atm^3

4. The equilibrium constant for the reaction $2SO_2 + O_2 \rightleftharpoons 2SO_3$ at 1000K is 3.5. What would the partial pressure of oxygen gas have to be to give equal moles of SO_2 and SO_3?

(a) 0.29 atm (b) 3.5 atm (c) 0.53 atm (d) 1.87 atm

5. For the reaction $NH_2COONH_4(s) \rightleftharpoons 2NH_3(g) + CO_2(g)$. The equilibrium constant $K_p = 2.9 \times 10^{-5}$ atm^3. The total pressure of gases at equilibrium when 1.0 mole of reactant was heated will be

(a) 0.0194 atm (b) 0.0388 atm (c) 0.0580 atm (d) 0.0667 atm

6. For the reaction $N_2O_4(g) \rightleftharpoons 2NO_2(g)$, the relation connecting the degree of dissociation (α) of $N_2O_4(g)$ with equilibrium constant K_p is

(a) $\alpha = \dfrac{K_p/p}{4 + K_p/p}$ (b) $\alpha = \dfrac{K_p}{4 + K_p}$

(c) $\alpha = \left(\dfrac{K_p/P}{4 + K_p/P}\right)^{1/2}$ (d) $\alpha = \left(\dfrac{K_p/P}{4 + K_p}\right)^{1/2}$

7. **At temperature, T, a compound $AB_2(g)$ dissociates according to the reaction**

$2AB_2(g) \rightleftharpoons 2AB(g) + B_2(g)$ with a degree of dissociation x, which is small compared with unity. The expression of K_p, in terms of x and the total pressure, P is

(a) $\frac{Px^3}{2}$ **(b)** $\frac{Px^2}{3}$ **(c)** $\frac{Px^3}{3}$ **(d)** $\frac{Px^2}{2}$

8. **If K_1 and K_2 are the respective equilibrium constants for the two reactions,**

$XeF_6(g) + H_2O(g) \rightleftharpoons XeOF_4(g) + 2HF(g)$

$XeO_4(g) + XeF_6(g) \rightleftharpoons XeOF_4(g) + XeO_3F_2(g)$

The equilibrium constant for the reaction,

$XeO_4(g) + 2HF(g) \rightleftharpoons XeO_3F_2(g) + H_2O(g)$ is

(a) K_1K_2 **(b)** K_1/K_2^2 **(c)** K_2/K_1 **(d)** K_1/K_2

9. **Determine K_C for the reaction $1/2N_2(g) + 1/2O_2(g) + 1/2Br_2(g) \rightleftharpoons NOBr(g)$**

from the following information (at 298 K)

$2NO(g) \rightleftharpoons N_2(g) + O_2(g)$; **$K_1 = 2.4 \times 10^{30}$**

$NO(g) + 1/2Br_2(g) \rightleftharpoons NOBr(g)$; **$K_2 = 1.4$**

(a) 6.45×10^{-16} **(b)** 9.03×10^{-16} **(c)** 3×10^{-8} **(d)** 1.7×10^{-4}

10. **For the reaction $2NO_2(g) + ½ O_2(g) \rightleftharpoons N_2O_5(g)$**

if the equilibrium constant is K_p, then the equilibrium constant for the reaction.

$2N_2O_5(g) \rightleftharpoons 4NO_2(g) + O_2(g)$ would be

(a) K_P^2 **(b)** $2/K_P$ **(c)** $1/K_P^2$ **(d)** $1/\sqrt{K_P}$

11. **At 700 K, equilibrium constant for the reaction : $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ is 54.8. If 0.5 mol L^{-1} of HI(g) is present at equilibrium at 700 K, what are the concentration of $H_2(g)$ and $I_2(g)$ assuming that we initially started with HI (g) and allowed it to reach equilibrium at 700 K.**

[Answers : (1) a (2) c (3) a (4) a (5) c (6) c (7) a (8) c (9) b (10) c (11) concentration of $H_2(g)$ and $I_2(g)$ is equal to 0.0675 mol L^{-1}]

C4 **<u>REACTION QUOTIENT (Q_C)</u>**

It is an expression that has the same form as the equilibrium constant expression, but all concentration values are not necessarily those at equilibrium.

$$aA + bB \rightleftharpoons cC + dD, \quad Q_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

i) **If $Q_c > K_c$, backward reaction takes place**

ii) **If $Q_c < K_c$, forward reaction takes place**

iii) **If $Q_c = K_c$, the reaction mixture is at equilibrium**

Practice Problems :

1. A mixture of 1.57 mol of N_2, 1.92 mol of H_2 and 8.13 mol of NH_3 is introduced into a 20 L reaction vessel at 500 K. At this temperature, the equilibrium constant, K_c for the reaction

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \text{ is } 1.7 \times 10^2$$

Is the reaction mixture at equilibrium ? If not, what is the direction of net reaction ?

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

$$CH_3COOH\,(l) + C_2H_5OH\,(l) \rightleftharpoons CH_3COOC_2H_5\,(l) + H_2O\,(l)$$

(i) Write the concentration ratio (reaction quotient) Q_c, for this reaction. (Note that water is not in excess and is not a solvent in this reaction).

(ii) At 293 K, if one starts with 1.00 mol of acetic acid and 0.18 of ethanol, there is 0.171 mol of ethyl acetate in the final equilibrium mixture. Calculate the equilibrium constant.

(iii) Starting with 0.5 mol of ethanol and 1.0 mol of acetic acid and maintaining it at 293 K, 0.214 mol of ethyl acetate is found after sometime. Has equilibrium been reached ?

3. Equilibrium constant, K_c for the reaction,

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \text{ at 500 K is 0.061.}$$

At a particular time, the analysis shows that composition of the reaction mixture is 3.00 mol L^{-1} N_2, 2.0 mol L^{-1} H_2, and 0.5 mol L^{-1} NH_3. Is the reaction at equilibrium ? If not, in which direction does the reaction tend to proceed to reach equilibrium ?

4. At a certain temperature, K_C for $SO_{2(g)} + NO_{2(g)} \rightleftharpoons SO_{3(g)} + NO_{(g)}$ is 16. If we take one mole of each of all the four gases in one litre container, what would be the equilibrium concentrations of NO and NO_2 are respectively

(a) 0.6, 0.4 (b) 1.6, 0.6 (c) 1.6, 0.4 (d) 0.4, 0.6

[Answers : (1) 2.38×10^3, As $Q_c > K_c$, the net reaction will be in the backward direction (2) (ii) $K_c = 3.919$ (iii) $Q_c = 0.2037$ (3) $Q_c = 0.010$, as $Q_c < K_c$ the reaction moves in the right hand direction to reach the equilibrium (4) c]

C5 THERMODYNAMICS OF CHEMICAL EQUILIBRIUM

Spontaneous of natural process is a process that occurs in a system left to itself once started; no action from outside the system is necessary to make the process continued.

Gibbs Free Energy Change and Spontaneity :

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

For a process occuring at constant T and P, if

(i) $\Delta G < 0$ (negative) the process is spontaneous

(ii) $\Delta G > 0$ (positive) the process is nonspontaneous

(iii) $\Delta G = 0$ (zero) the process is at equilibrium

Relation of ΔG^0 to the equilibrium constant K :

$\Delta G^0 = -2.303\ RT \log K$

C6 LE-CHATELIER'S PRINCIPLE

It states that "When a system at equilibrium is subjected to some stress (such as a change in concentration, temperature, pressure) then the equilibrium adjusted itself in such a way so as to nullify the effects of the stress". With the help of this principle it is possible to predict favourable conditions for the reactions.

CONCLUSIONS

i) If endothermic reaction $K_{eq}\uparrow, T\uparrow$ and $K_{eq}\downarrow, T\downarrow$

ii) In exothermic reaction $K_{eq}\downarrow, T\uparrow$ and $K_{eq}\uparrow, T\downarrow$

iii) If $P\uparrow$ reaction will move to that side where $V\downarrow$ i.e. where no. of mole of gaseous components is less.

iv) If concentration of reactant decreases then reaction takes place in backward reaction.

By chance of conc. pressure, volume, value of K_p and K_c does not change it only changes with temperature.

Addition of an Inert Gas at Constant Volume of Constant Pressure :

i) **At Constant Volume :** The addition of an inert gas at constant volume has no effect. It only increase the total pressure but does not alter the partial pressure of various species.

ii) **At Constant Pressure :** The addition of an inert gas at constant pressure will favour the direction of reaction where total no. of moles at equilibrium show an increase.

Practice Problems :

1. The equilibrium constant for the reaction, $Br_2 \rightleftharpoons 2Br$ at 500 K and 700 K and 1×10^{-10} and 1×10^{-5} respectively. The reaction is

(a) Endothermic (b) Exothermic (c) Fast (d) Slow

2. For an equilibrium reaction $A(g) + B(g) \rightleftharpoons C(g) + D(g)$, ΔH = +ve, an increase in temperature would cause

(a) an increase in the value of K_{eq}

(b) a decrease in the value of K_{eq}

(c) no change in the value of K_{eq}

(d) a change in K_{eq} which cannot be qualitatively predicated

3. Given the following reaction at equilibrium $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

Some inert gas is added at constant volume. Predict which of the following facts will be affected ?

(a) More of NH_3 (g) is produced

(b) Less of NH_3(g) is produced

(c) No effect on the degree of advancement of the produced reaction at equilibrium

(d) K_p of the reaction is increased.

4. Predict which of the following facts for the equilibrium reaction $2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$ holds good ?

(a) K_p of the reaction is changed with increase in pressure of the system

(b) K_p of the reaction remains unaffected with increase in pressure of the system

(c) More of NH_3(g) is decreased with increase in pressure

(d) Less of H_2(g) is formed as compared to N_2(g)

5. The oxidation of SO_2 by O_2 to SO_3 is an exothermic reaction. The yield of SO_3 will be maximum if

(a) temperature is increased and pressure is kept constant

(b) temperature is reduced and pressure is increased

(c) both temperature and pressure are increased

(d) both temperature and pressure arereduced

6. For a chemical reaction $3X(g) + Y(g) \rightleftharpoons X_3Y(g)$, the amount of $X_3Y(g)$ at equilibrium is affected by

(a) temperature and pressure (b) temperature only

(c) pressure only (d) temperature, pressure & catalyst

7. When $NaNO_3(s)$ is heated in a closed vessel, oxygen is liberated and $NaNO_2(s)$ is left behind. At equilibrium

(a) addition of $NaNO_2$ favours reverse reaction

(b) addition of $NaNO_3$ favours forward reaction

(c) increasing temperature favours forward reaction

(d) increasing pressure favours reverse reaction

8. For the gas phase reaction $C_2H_4 + H_2 \rightleftharpoons C_2H_6$ $\Delta H = -136.8$ kJ mol^{-1} carried out in a vessel, the equilibrium concentration of C_2H_4 can be increased by

(a) increasing the temperature (b) decreasing the pressure

(c) removing some H_2 (d) all of above

9. PCl_5 is 50% dissociated into PCl_3 and Cl_2 at 1 atmosphere. It will be 40% dissociated at

(a) 1.75 atm (b) 1.84 atm (c) 2.00 atm (d) 1.25 atm

10. The equilibrium constant for the following reaction is 1.6×10^5 at 1024 K.

$$H_2(g) + Br_2(g) \rightleftharpoons 2HBr(g)$$

Find the equilibrium pressure of all gases if 10.0 bar of HBr is introduced into a sealed container at 1024 K.

[Answers : (1) a (2) a (3) c (4) b (5) b (6) a (7) c (8) d (9) a (10) $p_{H_2} = p_{Br_2} = 2.5 \times 10^{-2}$ bar, $p_{HBr} = 10.0$ bar]