

विध्न विचारत भीरु जन, नहीं आरम्भे काम, विपति देख छोड़े तुरंत मध्यम मन कर श्याम।
पुरुष सिंह संकल्प कर, सहते विपति अनेक, 'बना' न छोड़े ध्येय को, रघुबर राखे टेक।।

रचित: मानव धर्म प्रणेता
सद्गुरु श्री रणछोड़दासजी महाराज

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Topic : CHEMICAL EQUILIBRIUM

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THE KEY

CHEMICAL EQUILIBRIUM

Most of the chemical reaction do not go to completion in a closed system and attain a state of equilibrium. Equilibrium is said to have reached in a physical or chemical system when rate of forward and reverse processes are equal. At equilibrium macroscopic properties of the system like concentration. Pressure ect. become constant at constant temperature.

State of chemical equilibrium is characterised by equilibrium constant. Equilibrium constant have constant value at a given temperature.

UNDERSTANDING EQUILIBRIUM

There are two approaches to understand nature of equilibrium. One stems from kinetics as developed by Gulberg and Wagge (1863). The other approach comes from thermodynaics. Equilibrium criteria is explained on the basis of thermodynamic function like ΔH (change in enthalpy), ΔS (change in entropy) and ΔG (change in Gibb's function).

According to kinetic approaches -The state of equilibrium is characterised by equal rate of forward and backward process.

At equilibrium

$$\text{Rate of forward reaction} = \text{Rate of backward reaction.}$$

Example : Physical equilibria. Solid liquid equilibria
Solid \rightleftharpoons liquid

Example: $\text{H}_2\text{O (s)} \rightleftharpoons \text{H}_2\text{O (l)}$: 273 K ; 1 atm P.

Solid ice and liquid can coexist at 273 K and 1 atm. Solid form is said to be in equilibrium with liquid form. At equilibrium, if heat exchanged from surrounding is zero, amount of solid ice and liquid water will remain unchanged. However it must be noted that, the process of conversion of ice into water and vica-versa-never ceases. At equilibrium

$$\text{Net rate of conversion of ice into water} = \text{Net rate of conversion of water into ice.}$$

OTHER EXAMPLES OF PHYSICAL EQUILIBRIA

The liquid vapour equilibria :

(i) Example : $\text{H}_2\text{O (l)} \rightleftharpoons \text{H}_2\text{O (g)}$ 373 K ; 1 atm pressure.

Equilibrium is characterized by constant value of vapour pressure of $\text{H}_2\text{O (l)}$ at 373 K (= 1 atm)

Net rate of condensation of $\text{H}_2\text{O (g)}$ = net rate of evaporation of $\text{H}_2\text{O (l)}$

(ii) Sugar (s) \rightleftharpoons sugar (aq)

This is example of dissolution equilibria. Equilibrium is characterised by constant molar concentration of sugar at specified temperature. At equilibrium, the solution of sugar in aqueous solution is called saturated solution.

(iii) The dissolution of gas in liquid.

Example $\text{CO}_2 \text{ (g)} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 \text{ (aq)}$

The concentration of gas in liquid is proportional to the pressure of gas over the liquid.

<i>Process</i>	<i>Characteristic constant</i>
H ₂ O (l) ⇌ H ₂ O (g)	P _{H₂O} constant at given temperature
H ₂ O (s) ⇌ H ₂ O (l)	P _{H₂O} constant at given temperature
solute (s) ⇌ solute (sol ⁿ)	concentration of solute is constant at given temperature
gas (g) ⇌ gas (aq)	[Gas(aq)]/[Gas(g)] = constant at given temperature

IMPORTANT CHARACTERISTIC OF EQUILIBRIUM

- (i) Equilibrium is possible only in closed system.
- (ii) The rate of forward process at equilibrium is equal to rate of backward process.
- (iii) All measurable properties of system remain constant over time.
- (iv) When equilibrium is attained for a physical process, it is characterised by constant value of one of its parameter.
- (v) The constant value of these parameters indicate extent to which equilibria is shifted in forward direction.
- (vi) Both, *Kinetic* and *Thermodynamics* theories can be invoked to understand the extent to which a reaction proceed to forward direction. *e.g.* If extent of reaction is too large for forward direction (equilibrium is tilted heavily to forward direction) than
 - (a) Specific rate of forward reaction >>> specific rate of backward reaction
 - (b) Product is thermodynamically very stable as compared to reactant.
 - (c) Gibb's function of product is vary small as compared to Gibb's function of reactant.

EQUILIBRIUM IN CHEMICAL PROCESS

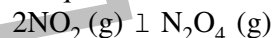
A general equation for a reversible reaction may be written



we can write the reaction quotient, Q for this equation as

$$Q = \frac{[\text{C}]^x [\text{D}]^y \dots}{[\text{A}]^m [\text{B}]^n \dots}$$

where we use bracket to indicate "molar concentration of." The reaction quotient is a ratio of the molar concentrations of the product of the chemical equation (multiplied together) and of the reactants (also multiplied together), each raised to a power equal to the coefficient preceding that substance in the balanced chemical equation. The reaction quotient for the reversible reaction.



is given by the expression $Q = \frac{[\text{N}_2\text{O}_4]}{[\text{NO}_2]^2}$

The numerical value of Q for a given reaction varies ; it depends on the concentration of products and reactants present at the time when Q is determined.

When a mixture of reactants and products of a reaction reaches equilibrium at a given temperature, its reaction quotient always has the same value. This value is called the equilibrium constant, K, of the reaction at that temperature. When a reaction is at equilibrium at a given temperature, the concentration of reactants and products is such that the value of reaction quotient, Q is always equal to the equilibrium constant, K, for that reaction at that temperature.

The mathematical expression that indicates that a reaction quotient always assumes the same value at equilibriums

$$Q = K = \frac{[\text{C}]^x [\text{D}]^y \dots}{[\text{A}]^m [\text{B}]^n \dots}$$

is a mathematical statement of the *law of mass action*. When a reaction has attained equilibrium at a given temperature, the reaction quotient for the reaction always has the same value.

The magnitude of an equilibrium constant is a measure of the yield of a reaction when it reaches equilibrium. A large value for K indicates that equilibrium is attained only after the reactants have been largely converted into products. A small value of K-much less than 1-indicates the equilibrium is attained when only a small proportion of the reactants have been converted into products.

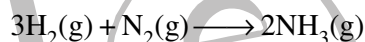
Regardless of the initial mixture of reactants and products in a reversible reaction, the composition of a system will always adjust itself to a condition of equilibrium for which the value of the reaction quotient is equal to the equilibrium constant for the system, provided that the temperature does not change.

An equilibrium can be established either starting from reactants or starting from products. In fact, one technique that is used to determine whether a reaction is truly at equilibrium is to approach equilibrium starting with reactants in one experiment and starting with products in another. If the same value of the reaction quotient is observed when the concentrations stop changing in both experiments, then we may be certain that the system has reached equilibrium.

We should calculate the value of Q or K from the activities of the reactants and products rather than from their concentrations. However, the activity of a dilute solute is usefully approximated by its molar concentration, so we will use concentrations as approximated by its pressure (in atmospheres), so we use pressures for gases. However, we also can use molar concentrations of gases in our equilibrium calculations, because the molar concentration of a gas is directly proportional to its pressure. The activity of a pure solid or pure liquid is 1, and the activity of a solvent in a dilute solution is close to 1. Thus these species (solids, liquids, and solvents) are omitted from reactions quotients and equilibrium calculations.

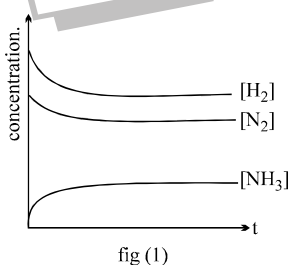
Using concentrations and pressure instead of activities means that we calculate approximate values for reaction quotients and equilibrium constants. However, these approximations hold well for dilute solutions and for gases with pressures less than about 2 atmospheres.

CONCENTRATION VERSES TIME GRAPH FOR HABER PROCESS

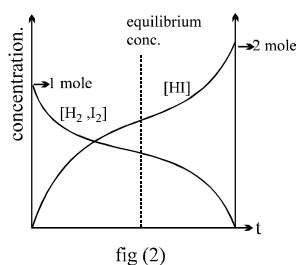


Starting with pure H₂ and N₂ as reaction proceeds in forward direction. Ammonia is formed. At initially conc. of H₂ and N₂ drops and attain a steady value at equilibrium. On the others hand conc. of NH₃ increases and at equilibrium attains a constant value.

Concentration time graphs for



Concentration time graph for H₂ + I₂ ⇌ 2HI

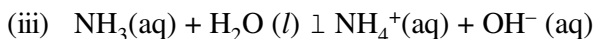
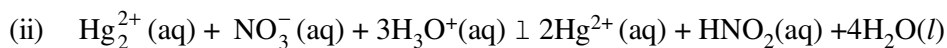
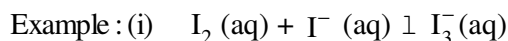


This graph shows how equilibrium state can be achieved from both direction.

HOMOGENEOUS CHEMICAL EQUILIBRIA

A homogeneous equilibrium is equilibrium with in a single phase i.e. when physical state of all the reactants and product are same.

LIQUID PHASE HOMOGENEOUS EQUILIBRIUM



Eq. constants for

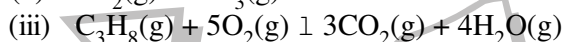
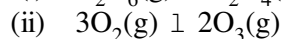
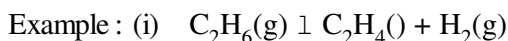
(i)
$$K = \frac{[I_3^-(aq)]}{[I_2(aq)][I^-(aq)]}$$

(ii)
$$K = \frac{[Hg^{2+}]^2[HNO_2]}{[Hg_2^{2+}][NO_3^-][H_3O^+]^3}$$

(iii)
$$K = \frac{[NH_4^+(aq)][OH^-(aq)]}{[NH_3(aq)]}$$

The equilibrium constant in all these cases can be called K_C . The subscript 'C' denoting active masses of solute expressed in terms of molar concentration.

HOMOGENEOUS EQUILIBRIA IN GASES



Equilibrium constant expression for them are

(i)
$$K_C = \frac{[C_2H_4][H_2]}{[C_2H_6]}$$

$$K_P = \frac{P_{C_2H_4} P_{H_2}}{P_{C_2H_6}}$$

[] represents concentration in mol/litre at equilibrium

$P_{C_2H_4}$ & other are partial pressure at equilibrium

(ii)
$$K_C = \frac{[O_3]^2}{[O_2]^3}$$

$$K_P = \frac{P_{O_3}^2}{P_{O_2}^3}$$

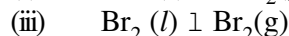
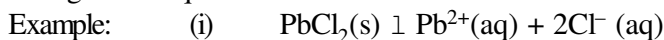
(iii)
$$K_C = \frac{[CO_2]^3 [H_2O]^4}{[C_3H_8] [O_2]^5}$$

$$K_P = \frac{P_{CO_2}^3 \cdot P_{H_2O}^4}{P_{C_3H_8} \cdot P_{O_2}^5}$$

Note : Equilibrium constant for gaseous homogeneous equilibrium can be expressed in two ways viz; K_P and K_C . This means value of equilibrium constant depends upon choice of standard state in which concentration of reactant's and product are expressed.

HETEROGENEOUS EQUILIBRIA

If reactants and product are found in two or more phases, the equilibria describing them is called heterogeneous equilibrium.



Equilibrium expression for them can be written as

(i)
$$K = [Pb^{2+}(aq)][Cl^-(aq)]^2$$

(ii)
$$K_P = \frac{1}{P_{CO_2}} \quad K_C = \frac{1}{[CO_2(g)]}$$

(iii)
$$K_P = P_{Br_2} \quad K_C = [Br_2(g)]$$

Note : Active masses of pure solid and liquid are taken as '1'. It is because as pure solids and liquid took part in reaction, their concentration (or density) remain constant. In thermodynamic sense. We can say this is because Gibb's functions for pure solid and liquid is defined at stipulated pressure of 1.00 bar and as pressure of system changes, Gibb's function for pure solid and liquid remain constant and equal to their value at 1 bar.

UNIT OF EQUILIBRIUM CONSTANT

We have already noted that the value of an equilibrium constant has meaning only when we give the corresponding balanced chemical equation. Its value changes for the new equation obtained by multiplying or dividing the original equation by a number. The value for equilibrium constant, K_C is calculate substituting the concentration in mol/L and for K_p by substituting partial pressure in Pa, kPa, etc. in atm. Thus, units of equilibrium constant will turn out to be units based on molarity or pressure, unless the sum of the exponents in the numerator is equal to the sum of the exponents in the denominator. Thus for the reaction:

$H_2(g) + I_2(g) \rightleftharpoons 2HI$, K_C and K_p do not have any unit

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3$, K_C has unit $(mol/L)^{-2}$ and K_p has unit bar^{-2} or

$N_2O_4(g) \rightleftharpoons 2NO_2$, K_C has unit mol / L and K_p has unit bar

However, these days we express equilibrium constants in dimensionless quantities by specifying the standard state of the reactants and the products. The standard state for pure gas is 1 bar and now the partial pressure are measured with respect to this standard. Thus a pressure of 2 bar in term of this standard state is equal to $2\text{ bar} / 1\text{ bar} = 2$, a dimensionless number. Similarly for a solute the standard state; c_0 , is 1 molar solution and all concentrations are measured with respect to it. The numerical value of equilibrium constant depends on the standard state chosen.

FACTOR'S AFFECTING EQUILIBRIA

Effect of change in concentration on equilibrium. A chemical system at equilibrium can be shifted out of equilibrium by adding or removing one more of reactants or products. Shifting out of equilibrium doesn't mean that value of equilibrium constant change. Any alteration of concentration of reactant or product will disturb the equilibrium and concentration of reactant and product one readjust to one again attain equilibrium concentration.

In other word, as we add or remove reactant (or product) the ratio of equilibrium concentration become 'Q' (reaction quotient) and depending upon.

$Q < K$: equilibrium will shift in forward direction.

$Q > K$: equilibrium will shift in backward direction.

Example : $Fe^{3+}(aq) + SCN^-(aq) \rightleftharpoons Fe(SCN)^{2+}(aq)$

- (i) adding Fe^{3+} or SCN^- will more $\frac{[Fe(SCN)^{2+}]}{[Fe^{3+}][SCN^-]} = Q$ less then K_C and equilibria will shift in forward direction.
- (ii) Removing $Fe(SCN)^{2+}$ will have same effect
- (iii) Adding $Fe(SCN)^{2+}$ from outside source in equilibrium mixture will have effect of increasing 'Q' hence reaction shift in backward direction.

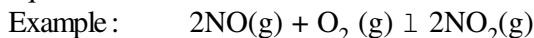
EFFECT OF CHANGE IN PRESSURE

Sometimes we can change the position of equilibrium by changing the pressure on a system. However, changes in pressure have a measurable effect only in system where gases are involved – and then only when the chemical reaction produces a change in the total number of gas molecules in the system.

As we increase the pressure of a gaseous system at equilibrium, either by decreasing the volume of the system or by adding more of the equilibrium mixture, we introduce a stress by increasing the number of molecules per unit of volume. In accordance with Le Chatelier's principle, a chemical reaction that reduces the total number of molecules per unit of volume will be favored because this relieves the stress.

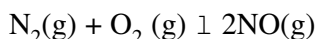
The reverse reaction would be favoured by a decrease in pressure.

Consider what happens when we increase the pressure on a system in which NO, O₂ and NO₂ are in equilibrium.



The formation of additional amounts of NO₂ decreases the total number of molecules in the system, because each time two molecules of NO₂ form, a total of three molecules of NO and O₂ react. This reduces the total pressure exerted by the system and reduces, but does not completely relieve, the stress of the increased pressure. On the other hand, a decrease in the pressure on the system favors decomposition of NO₂ into NO and O₂ which tends to restore the pressure.

Let us now consider the reaction



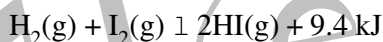
Because there is no change in the total number of molecules in the system during reaction, a change in pressure does not favor either formation or decomposition of gaseous nitric oxide.

EFFECT OF CHANGE IN TEMPERATURE ON EQUILIBRIUM

Changing concentration or pressure upsets an equilibrium because the reaction quotient is shifted away from the equilibrium value. Changing the temperature of a system at equilibrium has a different effect: A change in temperature changes the value of the equilibrium constant. However, we can predict the effect of the temperature change by treating it as a stress on the system and applying Le Chatelier's principle. When hydrogen reacts with gaseous iodine, energy is released as heat is evolved.



Because this reaction is exothermic, we can write it with heat as a product.



Increasing the temperature of the reaction increases the amount of energy present. Thus, increasing the temperature has the effect of increasing the amount of one of the products of this reaction. The reaction shifts to the left to relieve the stress, and there is an increase in the concentration of H₂ and I₂ and a reduction in the concentration of HI. When we change the temperature of a system at equilibrium, the equilibrium constant for the reaction changes. Lowering the temperature in the HI system increases the equilibrium constant from 50.0 at 400°C to 67.5 at 357°C. At equilibrium at the lower temperature, the concentration of HI has increased and the concentrations of H₂ and I₂ have decreased. Raising the temperature decreases the value of the equilibrium constant from 67.5 at 357°C to 50.0 at 400°C.

EFFECT OF TEMPERATURE : VAN'T HOFF EQUATION

$$(a) \frac{d(\ln K)}{dT} = \frac{\Delta H^\circ}{RT^2} \quad (b) \frac{d(\ln K)}{d\left(\frac{1}{T}\right)} = -\frac{\Delta H^\circ}{R} \quad \text{Integrated form } \ln\left(\frac{K_2}{K_1}\right) = -\frac{\Delta H^\circ}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

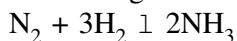
A THERMODYNAMIC RELATIONSHIP :

$$\Delta G^\circ = -RT \ln K.$$

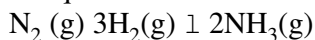
EFFECT OF CATALYST ON EQUILIBRIUM

A catalyst has no effect on the value of an equilibrium constant or on equilibrium concentrations. The catalyst merely increase the rates of both the forward and the reverse reactions to the same extent so that equilibrium is reached more rapidly.

All of these effects change in concentration or pressure, change in temperature, and the effect of a catalyst on a chemical equilibrium play a role in the industrial synthesis of ammonia from nitrogen and hydrogen according to the equation.

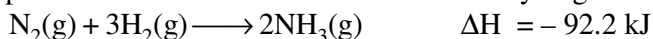


One way to increase the yield of ammonia is to increase the pressure on the system in which N_2 , H_2 and NH_3 are in equilibrium or are coming to equilibrium.



The formation of additional amounts of ammonia reduces the total pressure exerted by the system and somewhat reduces the stress of the increased pressure.

Although increasing the pressure of a mixture of N_2 , H_2 and NH_3 increase the yield ammonia, at low temperatures the rate of formation of ammonia is slow. At room temperature, for example, the reaction is so slow that if we prepared a mixture of N_2 and H_2 , no detectable amount of ammonia would form during our lifetime. Attempts to increase the rate of the reaction by increasing the temperature are counterproductive. The formation of ammonia from hydrogen and nitrogen is an exothermic process:



Thus increasing the temperature to increase the rate lowers the yield. If we lower the temperature to shift the equilibrium to the right to favor the formation of more ammonia, equilibrium is reached more slowly because of the large decrease of reaction rate with decreasing temperature.

Part of the rate of formation lost by operating at lower temperatures can be recovered by using a catalyst to increase the reaction rate. Iron powder is one catalyst used. However, as we have seen, a catalyst serves equally well to increase the rate of a reverse reaction in this case, the decomposition of ammonia into its constituent elements. Thus the net effect of the iron catalyst on the reaction is to cause equilibrium to be reached more rapidly.

In the commercial production of ammonia, conditions of about 500°C and 150–900 atmosphere are selected to give the best compromise among rate, yield and the cost of the equipment necessary to produce and contain gases at high pressure and high temperatures.

APPLICATION OF EQUILIBRIUM CONSTANT

Before we consider the applications of equilibrium constants, let us consider its important features:

- (i) the expression for equilibrium constant, K is applicable only when concentrations of the reactants and products have attained their equilibrium values and do not change with time.
- (ii) The value of equilibrium constant is independent of initial concentration of the reactants and product. Equilibrium constant has one unique value for a particular reaction represented by a balanced equation at a given temperature.
- (iii) The equilibrium constant for the reverse reaction is equal constant for the forward reaction.
- (iv) The equilibrium constant, K for a reaction is related to the equilibrium constant of the corresponding reaction whose equation is obtained by multiplying or dividing the equation for the original reaction by a small integer.

Now we will consider some applications of equilibrium constant and use it to answer question like:

- (i) predicting the extent of a reaction on the basis of its magnitude.
- (ii) predicting the direction of the reaction, and
- (iii) calculating equilibrium concentration.

Predicting the extent of a reaction

The magnitude of equilibrium constant is very useful especially in reactions of industrial importance. An equilibrium constant tells us whether we can expect a reaction mixture to contain a high or low concentration of product(s) at equilibrium. (It is important to note that an equilibrium constant tells us nothing about the rate at which equilibrium is reached). In the expression of K_c or K_p , product of the concentrations of

products is written in numerator and the product of the concentrations of reactants is written in denominator. High value of equilibrium constant indicates that product(s) concentration is high and its low value indicates that concentration of the product(s) in equilibrium mixture is low.

For reaction, $\text{H}_2(\text{g}) + \text{Br}_2(\text{g}) \rightleftharpoons 2\text{HBr}(\text{g})$, the value of

$$K_p = \frac{(P_{\text{HBr}})^2}{(P_{\text{H}_2})(P_{\text{Br}_2})} = 5.4 \times 10^{18}$$

The large value of equilibrium constant indicates that concentration of the product, HBr is very high and reaction goes nearly to completion.

Similarly, equilibrium constant for the reaction $\text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) \rightleftharpoons 2\text{HCl}(\text{g})$ at 300 K is very high and reaction goes virtually to completion.

$$K_c = \frac{[\text{HCl}]^2}{[\text{H}_2][\text{Cl}_2]} = 4.0 \times 10^{31}$$

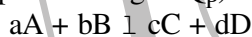
Thus, large value of K_p or K_c (larger than about 10^3), favour the products strongly. For intermediate values of K (approximately in the range of 10^{-3} to 10^3), the concentrations of reactants and products are comparable. Small values of equilibrium constant (smaller than 10^{-3}), favour the reactants strongly. At 298 K for reaction, $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{NO}(\text{g})$

$$K_c = \frac{[\text{NO}]^2}{[\text{N}_2][\text{O}_2]} = 4.8 \times 10^{-31}$$

The very small value of K_c implies that reactants N_2 and O_2 will be the predominant species in the reaction mixture at equilibrium.

Predicting the direction of the reaction.

The equilibrium constant is also used to find in which direction an arbitrary reaction mixture of reactants and products will proceed. For this purpose, we calculate the reaction quotient, Q . The reaction quotient is defined in the same way as the equilibrium constant (with molar concentrations to give Q_c , or with partial pressure to give Q_p) at any stage of reaction. For a general reaction:



$$Q_c = \frac{[\text{C}]^c [\text{D}]^d}{[\text{A}]^a [\text{B}]^b}$$

Then, if $Q_c > K_c$, the reaction will proceed in the direction of reactants (reverse reaction).

if $Q_c < K_c$, the reaction will move in the direction of the products

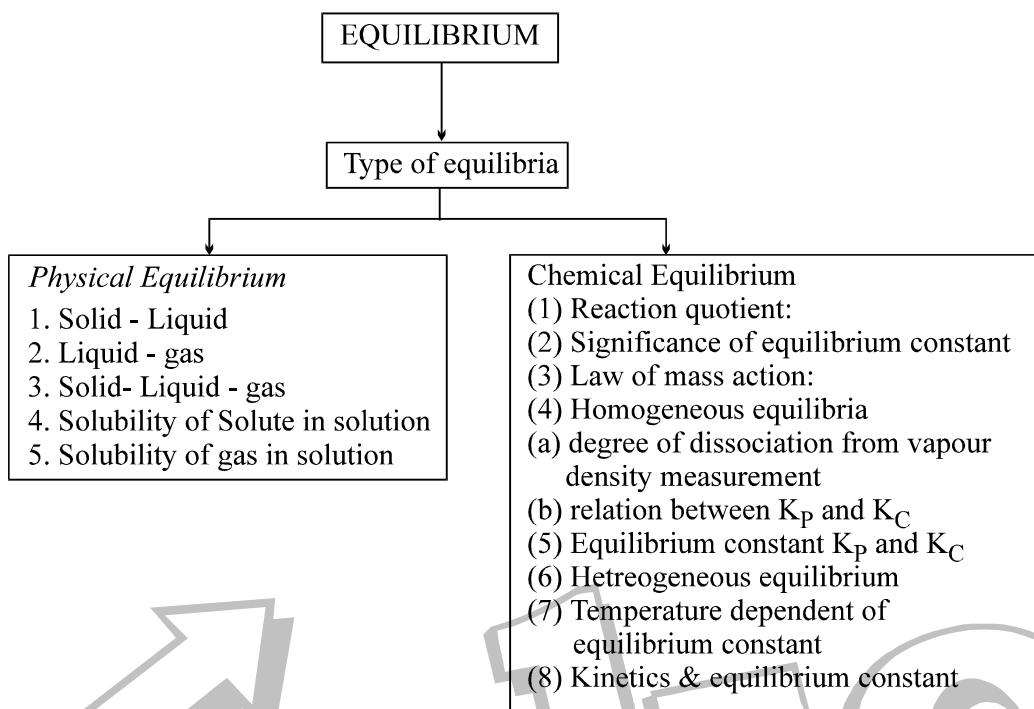
if $Q_c = K_c$, the reaction mixture is already at equilibrium.

In the reaction, $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$, if the molar concentrations of H_2 , I_2 and HI are 0.1 mol L^{-1} respectively at 783 K, then reaction quotient at this stage of the reaction is

$$Q_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = \frac{(0.4)^2}{(0.1)(0.2)} = 8$$

K_c for this reaction at 783 K is 46 and we find that $Q_c < K_c$. The reaction, therefore, will move to right i.e. more $\text{H}_2(\text{g})$ and $\text{I}_2(\text{g})$ will react to form more $\text{HI}(\text{g})$ and their concentration will decrease till $Q_c = K_c$.

THE ATLAS



Application of equilibrium constant

- (i) Predicting extent of reaction
- (ii) Predicting direction of change
- (iii) Calculation of equilibrium concentration

Le Chatleir's principle

Effect of following factor's on equilibrium Once pressure temperature catalyst inert gas

Temperature dependence- Von't Hoff's equation

Understanding equilibrium

- (i) From kinetic's approach (Gulber & Wagge approach)
- (ii) From thermodynamics approach – Criteria for equilibrium in terms of Gibb's function

EXERCISE I

Reaction quotient and equilibrium constant

Q.1 The initial concentrations or pressure of reactants and products are given for each of the following systems. Calculate the reaction quotient and determine the directions in which each system will shift to reach equilibrium.

- (a) $2\text{NH}_3(\text{g}) \rightleftharpoons \text{N}_2(\text{g}) + 3\text{H}_2(\text{g})$ $K = 17$
[NH_3] = 0.20 M ; [N_2] = 1.00 M ; [H_2] = 1.00 M
- (b) $2\text{NH}_3(\text{g}) \rightleftharpoons \text{N}_2(\text{g}) + 3\text{H}_2(\text{g})$ $K_p = 6.8 \times 10^4 \text{ atm}^2$
Initial pressure : $\text{NH}_3 = 3.0 \text{ atm}$; $\text{N}_2 = 2.0 \text{ atm}$; $\text{H}_2 = 1.0 \text{ atm}$
- (c) $2\text{SO}_3(\text{g}) \rightleftharpoons 2\text{SO}_2(\text{g}) + \text{O}_2(\text{g})$ $K = 0.230 \text{ atm}$
[SO_3] = 0.00 M ; [SO_2] = 1.00 M ; [O_2] = 1.00 M
- (d) $2\text{SO}_3(\text{g}) \rightleftharpoons 2\text{SO}_2(\text{g}) + \text{O}_2(\text{g})$ $K_p = 16.5 \text{ atm}$
Initial pressure : $\text{SO}_3 = 1.0 \text{ atm}$; $\text{SO}_2 = 1.0 \text{ atm}$; $\text{O}_2 = 1.0 \text{ atm}$
- (d) $2\text{NO}(\text{g}) + \text{Cl}_2(\text{g}) \rightleftharpoons 2\text{NOCl}(\text{g})$ $K = 4.6 \times 10^4$
[NO] = 1.00 M ; [Cl_2] = 1.00 M ; [NOCl] = 0 M
- (f) $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{NO}(\text{g})$ $K_p = 0.050$
Initial pressure : $\text{NO} = 10.0 \text{ atm}$; $\text{N}_2 = \text{O}_2 = 5 \text{ atm}$

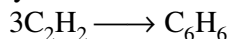
Q.2 Among the solubility rules is the statement that all chlorides are soluble except Hg_2Cl_2 , AgCl , PbCl_2 , and CuCl .

- (a) Write the expression for the equilibrium constant for the reaction represented by the equation.
 $\text{AgCl}(\text{s}) \rightleftharpoons \text{Ag}^+(\text{aq}) + \text{Cl}^-(\text{aq})$
Is K greater than 1, less than 1, or about equal to 1? Explain your answer
- (b) Write the expression for the equilibrium constant for the reaction represented by the equation
 $\text{Pb}^{2+}(\text{aq}) + 2\text{Cl}^-(\text{aq}) \rightleftharpoons \text{PbCl}_2(\text{s})$
Is K greater than 1, less than 1, or about equal to 1? Explain your answer.

Q.3 Among the solubility rules is the statement that carbonates, phosphates, borates, arsenates, and arsenites, except those of the ammonium ion and the alkali metals are insoluble.

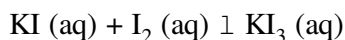
- (a) Write the expression for the equilibrium constant for the reaction represented by the equation
 $\text{CaCO}_3(\text{s}) \rightleftharpoons \text{Ca}^{2+}(\text{aq}) + \text{CO}_3^{2-}(\text{aq})$
Is K greater than 1, less than 1, or about equal to 1? Explain your answer
- (b) Write the expression for the equilibrium constant for the reaction represented by the equation.
 $3\text{Ba}^{2+}(\text{aq}) + 2\text{PO}_4^{3-}(\text{aq}) \rightleftharpoons \text{Ba}_3(\text{PO}_4)_2(\text{s})$
Is K greater than 1, less than 1, or about equal to 1? Explain your answer.

Q.4 Benzene is one of the compounds used as octane enhancers in unleaded gasoline. It is manufactured by the catalytic conversion of acetylene to benzene.



Would this reaction be most useful commercially if K were about 0.01, about 1, or about 10? Explain your answer.

Q.5 Show the complete chemical equation and the net ionic equation for the reaction represented by the equation



give the same expression for the reaction quotient. KI_3 is composed of the ions K^+ and I_3^- .

Using the equilibrium constant

- Q.6 Which of the following reactions goes almost all the way to completion, and which proceeds hardly at all?
- (a) $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{NO}(\text{g}); K_c = 2.7 \times 10^{-18}$
- (b) $2\text{NO}(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g}); K_c = 6.0 \times 10^{13}$
- Q.7 For which of the following reactions will the equilibrium mixture contain an appreciable concentration of both reactants and products?
- (a) $\text{Cl}_2(\text{g}) \rightleftharpoons 2\text{Cl}(\text{g}); K_c = 6.4 \times 10^{-39}$
- (b) $\text{Cl}_2(\text{g}) + 2\text{NO}(\text{g}) \rightleftharpoons 2\text{NOCl}(\text{g}); K_c = 3.7 \times 10^8$
- (c) $\text{Cl}_2(\text{g}) + 2\text{NO}_2(\text{g}) \rightleftharpoons 2\text{NO}_2\text{Cl}(\text{g}); K_c = 1.8$
- Q.8 The value of K_c for the reaction $3\text{O}_2(\text{g}) \rightleftharpoons 2\text{O}_3(\text{g})$ is 1.7×10^{-56} at 25°C . Do you expect pure air at 25°C to contain much O_3 (ozone) when O_2 and O_3 are in equilibrium? If the equilibrium concentration of O_2 in air at 25°C is 8×10^{-3} M, what is the equilibrium concentration of O_3 ?
- Q.9 At 1400 K, $K_c = 2.5 \times 10^{-3}$ for the reaction $\text{CH}_4(\text{g}) + 2\text{H}_2\text{S} \rightleftharpoons \text{CS}_2(\text{g}) + 4\text{H}_2(\text{g})$. A 10.0 L reaction vessel at 1400 K contains 2.0 mol of CH_4 , 3.0 mol of CS_2 , 3.0 mol of H_2 and 4.0 mol of H_2S . Is the reaction mixture at equilibrium? If not, in which direction does the reaction proceed to reach equilibrium?
- Q.10 The first step in the industrial synthesis of hydrogen is the reaction of steam and methane to give water gas, a mixture of carbon monoxide and hydrogen.
- $\text{H}_2\text{O}(\text{g}) + \text{CH}_4(\text{g}) \rightleftharpoons \text{CO}(\text{g}) + 3\text{H}_2(\text{g}) K_c = 4.7$ at 1400 K
- A mixture of reactants and product at 1400 K contains 0.035 M H_2O , 0.050 M CH_4 , 0.15 M CO , and 0.20 M H_2 . In which direction does the reaction proceed to reach equilibrium?
- Q.11 An equilibrium mixture of N_2 , H_2 , and NH_3 at 700 K contains 0.036 M N_2 and 0.15 M H_2 . At this temperature, K_c for the reaction $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$ is 0.29. What is the concentration of NH_3 ?
- Q.12 The air pollutant NO is produced in automobile engines from the high temperature reaction $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{NO}(\text{g}); K_c = 1.7 \times 10^{-3}$ at 2300 K. If the initial concentrations of N_2 and O_2 at 2300 K are both 1.40 M, what are the concentrations of NO, N_2 , and O_2 when the reaction mixture reaches equilibrium?
- Q.13 At a certain temperature, the reaction $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$ has an equilibrium constant $K_c = 5.8 \times 10^{-2}$. Calculate the equilibrium concentrations of PCl_5 , PCl_3 and Cl_2 if only PCl_5 is present initially, at a concentration of 0.160 M.
- Q.14 At 700 K, $K_p = 0.140$ for the reaction $\text{ClF}_3(\text{g}) \rightleftharpoons \text{ClF}(\text{g}) + \text{F}_2(\text{g})$. Calculate the equilibrium partial pressure of ClF_3 , ClF , and F_2 if only ClF_3 is present initially, at a partial pressure of 1.47 atm.

Homogeneous equilibria degree of dissociation, vapour density and equilibrium constant

- Q.15 The degree of dissociation of N_2O_4 into NO_2 at 1.5 atmosphere and 40°C is 0.25. Calculate its K_p at 40°C . Also report degree of dissociation at 10 atmospheric pressure at same temperature.
- Q.16 At 46°C , K_p for the reaction $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$ is 0.667 atm. Compute the percent dissociation of N_2O_4 at 46°C at a total pressure of 380 Torr.

- Q.17 When 36.8g $\text{N}_2\text{O}_4(\text{g})$ is introduced into a 1.0-litre flask at 27°C . The following equilibrium reaction occurs : $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$; $K_p = 0.1642 \text{ atm}$.
- Calculate K_c of the equilibrium reaction.
 - What are the number of moles of N_2O_4 and NO_2 at equilibrium?
 - What is the total gas pressure in the flask at equilibrium?
 - What is the percent dissociation of N_2O_4 ?
- Q.18 At some temperature and under a pressure of 4 atm, PCl_5 is 10% dissociated. Calculate the pressure at which PCl_5 will be 20% dissociated, temperature remaining same.
- Q.19 In a mixture of N_2 and H_2 in the ratio of 1:3 at 64 atmospheric pressure and 300°C , the percentage of ammonia under equilibrium is 33.33 by volume. Calculate the equilibrium constant of the reaction using the equation. $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$.

- Q.20 The system $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$ maintained in a closed vessel at 60°C & a pressure of 5 atm has an average (i.e. observed) molecular weight of 69, calculate K_p . At what pressure at the same temperature would the observed molecular weight be (230/3)?
- Q.21 The vapour density of N_2O_4 at a certain temperature is 30. Calculate the percentage dissociation of N_2O_4 at this temperature. $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$.
- Q.22 In the esterification $\text{C}_2\text{H}_5\text{OH}(\text{l}) + \text{CH}_3\text{COOH}(\text{l}) \rightleftharpoons \text{CH}_3\text{COOC}_2\text{H}_5(\text{l}) + \text{H}_2\text{O}(\text{l})$ an equimolar mixture of alcohol and acid taken initially yields under equilibrium, the water with mole fraction = 0.333. Calculate the equilibrium constant.

Heterogeneous equilibrium

- Q.23 Solid Ammonium carbamate dissociates as: $\text{NH}_2\text{COONH}_4(\text{s}) \rightleftharpoons 2\text{NH}_3(\text{g}) + \text{CO}_2(\text{g})$. In a closed vessel solid ammonium carbamate is in equilibrium with its dissociation products. At equilibrium, ammonia is added such that the partial pressure of NH_3 at new equilibrium now equals the original total pressure. Calculate the ratio of total pressure at new equilibrium to that of original total pressure.
- Q.24 A sample of $\text{CaCO}_3(\text{s})$ is introduced into a sealed container of volume 0.821 litre & heated to 1000K until equilibrium is reached. The equilibrium constant for the reaction $\text{CaCO}_3(\text{s}) \rightleftharpoons \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$ is $4 \times 10^{-2} \text{ atm}$ at this temperature. Calculate the mass of CaO present at equilibrium.
- Q.25 Anhydrous calcium chloride is often used as a desiccant. In the presence of excess of CaCl_2 , the amount of the water taken up is governed by $K_p = 6.4 \times 10^{85}$ for the following reaction at room temperature, $\text{CaCl}_2(\text{s}) + 6\text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{CaCl}_2 \cdot 6\text{H}_2\text{O}(\text{s})$. What is the equilibrium vapour pressure of water in a closed vessel that contains $\text{CaCl}_2(\text{s})$?
- Q.26 20.0 grams of $\text{CaCO}_3(\text{s})$ were placed in a closed vessel, heated & maintained at 727°C under equilibrium $\text{CaCO}_3(\text{s}) \rightleftharpoons \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$ and it is found that 75% of CaCO_3 was decomposed. What is the value of K_p ? The volume of the container was 15 litres.

Changes in concentration at equilibrium Le Chatelier's principle

- Q.27 Suggest four ways in which the concentration of hydrazine, N_2H_4 , could be increased in an equilibrium described by the equation
- $$\text{N}_2(\text{g}) + 2\text{H}_2(\text{g}) \rightleftharpoons \text{N}_2\text{H}_4(\text{g}) \quad \Delta H = 95 \text{ kJ}$$

Q.28 How will an increase in temperature affect each of the following equilibria? An increase in pressure?

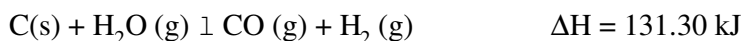
- (a) $2\text{NH}_3(\text{g}) \rightleftharpoons \text{N}_2(\text{g}) + 3\text{H}_2(\text{g})$ $\Delta\text{H} = 92 \text{ kJ}$
 (b) $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{NO}(\text{g})$ $\Delta\text{H} = 181 \text{ kJ}$
 (c) $2\text{O}_3(\text{g}) \rightleftharpoons 3\text{O}_2(\text{g})$ $\Delta\text{H} = -285 \text{ kJ}$
 (d) $\text{CaO}(\text{s}) + \text{CO}_2(\text{g}) \rightleftharpoons \text{CaCO}_3(\text{s})$ $\Delta\text{H} = -176 \text{ kJ}$

Q.29(a) Methanol, a liquid fuel that could possibly replace gasoline, can be prepared from water gas and additional hydrogen at high temperature and pressure in the presence of a suitable catalyst. Write the expression for the equilibrium constant for the reversible reaction.



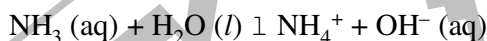
- (b) Assume that equilibrium has been established and predict how the concentration of H_2 , CO and CH_3OH will differ at a new equilibrium if (1) more H_2 is added. (2) CO is removed. (3) CH_3OH is added. (4) the pressure on the system is increased. (5) the temperature of the system is increased. (6) more catalyst is added.

Q.30(a) Water gas, a mixture of H_2 and CO , is an important industrial fuel produced by the reaction of steam with red-hot coke, essentially pure carbon. Write the expression for the equilibrium constant for the reversible reaction.



- (b) Assume that equilibrium has been established and predict how the concentration of each reactant and product will differ at a new equilibrium if (1) more C is added. (2) H_2O is removed. (3) CO is added. (4) the pressure on the system is increased. (5) the temperature of the system is increased.

Q.31 Ammonia is a weak base that reacts with water according to the equation



Will any of the following increase the percent of ammonia that is converted to the ammonium ion in water? (a) Addition of NaOH . (b) Addition of HCl . (c) Addition of NH_4Cl .

Q.32 Suggest two ways in which the equilibrium concentration of Ag^+ can be reduced in a solution of Na^+ , Cl^- , Ag^+ and NO_3^- , in contact with solid AgCl .



Q.33 Additional solid silver sulfate, a slightly soluble solid, is added to a solution of silver ion and sulfate ion in equilibrium with solid silver sulfate. Which of the following will occur? (a) The Ag^+ and SO_4^{2-} concentration will not change. (b) The added silver sulfate will dissolve. (c) Additional silver sulfate will form and precipitate from solution as Ag^+ ions and SO_4^{2-} ions combine. (d) The Ag^+ ion concentration will increase and the SO_4^{2-} ion concentration will decrease.

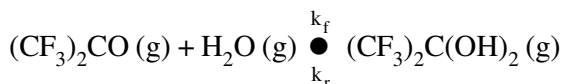
Kinetics and equilibrium constant

Q.34 Consider a general, single-step reaction of the type $\text{A} + \text{B} \rightleftharpoons \text{C}$. Show that the equilibrium constant is equal to the ratio of the rate constant for the forward and reverse reaction, $K_c = k_f/k_r$.

Q.35 Which of the following relative values of k_f and k_r results in an equilibrium mixture that contains large amounts of reactants and small amounts of product?

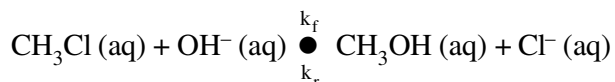
- (a) $k_f > k_r$ (b) $k_f = k_r$ (c) $k_f < k_r$

Q.36 Consider the gas-phase hydration of hexafluoroacetone, $(\text{CF}_3)_2\text{CO}$:



At 76°C , the forward and reverse rate constants are $k_f = 0.13 \text{ M}^{-1}\text{s}^{-1}$ and $k_r = 6.02 \times 10^{-4}\text{s}^{-1}$. What is the value of the equilibrium constant K_c ?

Q.37 Consider the reaction of chloromethane with OH^- in aqueous solution

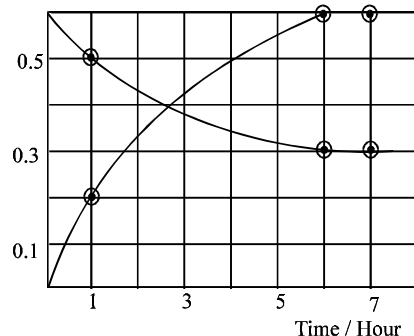


At 25°C , the rate constant for the forward reaction is $6 \times 10^{-6} \text{ M}^{-1}\text{s}^{-1}$, and the equilibrium constant K_c is 1×10^{16} . Calculate the rate constant for the reverse reaction at 25°C .

Q.38 The progress of the reaction

A \rightarrow nB with time, is presented in figure. Determine

- the value of n.
- the equilibrium constant k.
- the initial rate of conversion of A.



Temperature dependence of equilibrium constant

Q.39 Listed in the table are forward and reverse rate constants for the reaction $2\text{NO}(\text{g}) \rightleftharpoons \text{N}_2(\text{g}) + \text{O}_2(\text{g})$

Temperature (K)	$k_f (\text{M}^{-1}\text{s}^{-1})$	$k_r (\text{M}^{-1}\text{s}^{-1})$
1400	0.29	1.1×10^{-6}
1500	1.3	1.4×10^{-5}

Is the reaction endothermic or exothermic? Explain in terms of kinetics.

Q.40 Forward and reverse rate constant for the reaction $\text{CO}_2(\text{g}) + \text{N}_2(\text{g}) \rightleftharpoons \text{CO}(\text{g}) + \text{N}_2\text{O}(\text{g})$ exhibit the following temperature dependence.

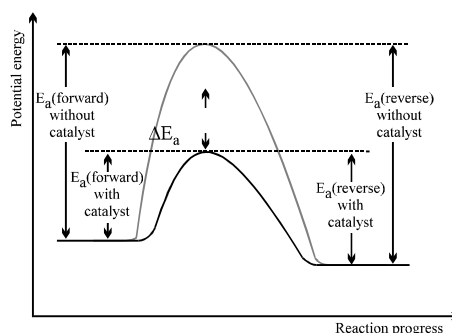
Temperature (K)	$k_f (\text{M}^{-1}\text{s}^{-1})$	$k_r (\text{M}^{-1}\text{s}^{-1})$
1200	9.1×10^{-11}	1.5×10^5
1500	2.7×10^{-9}	2.6×10^5

Is the reaction endothermic or exothermic? Explain in terms of kinetics.

Q.41 The equilibrium constant K_p for the reaction $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$ is 3.81×10^2 at 600 K and 2.69×10^3 at 700 K. Calculate $\Delta_f H$.

Q.42 As shown in figure a catalyst lowers the activation energy for the forward and reverse reactions by the same amount, ΔE_a .

- Apply the Arrhenius equation, $K = Ae^{-E_a/RT}$ to the forward and reverse reactions, and show that a catalyst increases the rates of both reactions by the same factor.
- Use the relation between the equilibrium constant and the forward and reverse rate constants, $K_c = k_f/k_r$, to show that a catalyst does not affect the value of the equilibrium constant.



Temperature dependence of equilibrium constant

Q.43 Variation of equilibrium constant 'K' with temperature 'T' is given by equation

$$\log K = \log A - \frac{\Delta H^\circ}{2.303RT}$$

A graph between $\log K$ and $1/T$ was a straight line with slope of 0.5 and intercept 10. Calculate

- ΔH°
- Pre exponential factor
- Equilibrium constant at 298 K
- Equilibrium constant at 798 K assuming ΔH° to be independent of temperature.

Q.44 Rate of disappearance of the reactant A at two different temperature is given by A \perp B

$$\frac{-d[A]}{dt} = (2 \times 10^{-2} \text{ S}^{-1}) [A] - 4 \times 10^{-3} \text{ S}^{-1} [B]; 300\text{K}$$

$$\frac{-d[A]}{dt} = (4 \times 10^{-2} \text{ S}^{-1}) [A] - 16 \times 10^{-4} [B]; 400\text{K}$$

Calculate heat of reaction in the given temperature range. When equilibrium is set up.

Q.45 The K_p for reaction $A + B \rightleftharpoons C + D$ is 1.34 at 60°C and 6.64 at 100°C . Determine the free energy change of this reaction at each temperature and ΔH° for the reaction over this range of temperature?

Equilibrium expressions and equilibrium constants

Q.46 If $K_c = 7.5 \times 10^{-9}$ at 1000 K for the reaction $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{NO}(\text{g})$, what is K_c at 1000 K for the reaction $2\text{NO}(\text{g}) \rightleftharpoons \text{N}_2(\text{g}) + \text{O}_2(\text{g})$?

Q.47 An equilibrium mixture of PCl_5 , PCl_3 and Cl_2 at a certain temperature contains $8.3 \times 10^{-3} \text{ M PCl}_5$, $1.5 \times 10^{-2} \text{ M PCl}_3$, and $3.2 \times 10^{-2} \text{ M Cl}_2$. Calculate the equilibrium constant K_c for the reaction $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$.

Q.48 A sample of HI ($9.30 \times 10^{-3} \text{ mol}$) was placed in an empty 2.00 L container at 1000 K. After equilibrium was reached, the concentration of I_2 was $6.29 \times 10^{-4} \text{ M}$. Calculate the value of K_c at 1000 K for the reaction $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$.

Q.49 The vapour pressure of water at 25°C is 0.0313 atm. Calculate the values of K_p and K_c at 25°C for the equilibrium $\text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_2\text{O}(\text{g})$.

Q.50 For each of the following equilibria, write the equilibrium constant expression for K_c . Where appropriate, also write the equilibrium constant expression for K_p .

- | | |
|-------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------|
| (a) $\text{Fe}_2\text{O}_3(\text{s}) + 3\text{CO}(\text{g}) \rightleftharpoons 2\text{Fe}(\text{l}) + 3\text{CO}_2(\text{g})$ | (b) $4\text{Fe}(\text{s}) + 3\text{O}_2(\text{g}) \rightleftharpoons 2\text{Fe}_2\text{O}_3(\text{s})$ |
| (c) $\text{BaSO}_4(\text{s}) \rightleftharpoons \text{BaO}(\text{s}) + \text{SO}_3(\text{g})$ | (d) $\text{BaSO}_4(\text{s}) \rightleftharpoons \text{Ba}^{2+}(\text{aq}) + \text{SO}_4^{2-}(\text{aq})$ |

General problems

Q.51 When 0.5 mol of N_2O_4 is placed in a 4.00 L reaction vessel and heated at 400 K, 79.3% of the N_2O_4 decomposes to NO_2 .

Calculate K_c and K_p at 400 K for the reaction $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$

Q.52 What concentration of NH_3 is in equilibrium with $1.0 \times 10^{-3} \text{ M N}_2$ and $2.0 \times 10^{-3} \text{ M H}_2$ at 700K? At this temperature $K_c = 0.291$ for the reaction $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$.

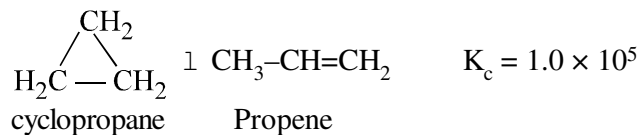
Q.53 At 100 K, the value of K_c for the reaction $\text{C}(\text{s}) + \text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{CO}(\text{g}) + \text{H}_2(\text{g})$ is 3.0×10^{-2} . Calculate the equilibrium concentrations of H_2O , CO_2 , and H_2 in the reaction mixture obtained by heating 6.0 mol of steam and an excess of solid carbon in a 5.0 L container. What is the molar composition of the equilibrium mixture?

Q.54 When 1.0 mol of PCl_5 is introduced into a 5.0 L container at 500 K, 78.5 % of the PCl_5 dissociates to give an equilibrium mixture of PCl_5 , PCl_3 , and Cl_2 .



- (a) Calculate the values of K_c and K_p .
 (b) If the initial concentrations in a particular mixture of reactants and products are $[\text{PCl}_5] = 0.5 \text{ M}$, $[\text{PCl}_3] = 0.15 \text{ M}$, and $[\text{Cl}_2] = 0.6 \text{ M}$, in which direction does the reaction proceed to reach equilibrium? What are the concentrations when the mixture reaches equilibrium?

Q.55 The equilibrium constant K_c for the gas-phase thermal decomposition of cyclopropane to propene is 1.0×10^5 at 500 K.



- (a) What is the value of K_p at 500 K?
 (b) What is the equilibrium partial pressure of cyclopropane at 500 K when the partial pressure of propene is 5.0 atm?
 (c) Can you alter the ratio of the two concentrations at equilibrium by adding cyclopropane or by decreasing the volume of the container? Explain.
 (d) Which has the larger rate constant, the forward reaction or the reverse reaction?
 (e) Why is cyclopropane so reactive?

Thermodynamic and equilibrium constant

Q.56 α -D-Glucose undergoes mutarotation to β -D-Glucose in aqueous solution. If at 298 K there is 60% conversion. Calculate ΔG° of the reaction.



Q.57 For the reaction at 298 K
 $\text{A}(\text{g}) + \text{B}(\text{g}) \rightleftharpoons \text{C}(\text{g}) + \text{D}(\text{g})$
 $\Delta H^\circ = -29.8 \text{ kcal}$; $\Delta S^\circ = -0.1 \text{ kcal / K}$
 Calculate ΔG° and K .

Q.58 The equilibrium constant of the reaction $2\text{C}_3\text{H}_6(\text{g}) \rightleftharpoons \text{C}_2\text{H}_4(\text{g}) + \text{C}_4\text{H}_8(\text{g})$ is found to fit the expression

$$\ln K = -1.04 - \frac{1088 \text{ K}}{T}$$

Calculate the standard reaction enthalpy and entropy at 400 K.

PROFICIENCY TEST

1. K for the reaction $2A + B \rightleftharpoons 2C$ is 1.5×10^{12} . This indicates that at equilibrium the concentration of _____ would be maximum.
2. The reaction $N_2 + O_2 \rightleftharpoons 2NO - \text{Heat}$, would be favoured by _____ temperature.
3. K for the reaction $X_2 + Y_2 \rightleftharpoons 2XY$ is 100 K. For reaction $XY \rightleftharpoons \frac{1}{2}X_2 + \frac{1}{2}Y_2$ would be _____.
4. Compared to K for the dissociation, $2H_2S \rightleftharpoons 2H^+ + 2HS^-$, then K' for the $H^+ + HS^- \rightleftharpoons H_2S$ would have _____.
5. The equilibrium constant for a reaction decreases with increase in temperature, the reaction must be _____.
6. For the reaction, $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$, K_p and K_c are related as _____.
7. For the reactions, $N_2O_4(g) \rightleftharpoons 2NO_2(g)$, at equilibrium, increase in pressure shifts the equilibrium in _____ direction.
8. ΔG° is related to K by the relation _____.
9. Vant Hoff's equation is _____.
10. When the reaction is at equilibrium, the value of ΔG is _____.
11. Dimensions of equilibrium constant, K_c for the reaction $2NH_3 \rightleftharpoons N_2 + 3H_2$, are _____.
12. The value of K for a reaction can be changed by changing _____.
13. The law of mass action was proposed by _____.
14. The degree of dissociation of PCl_5 [$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$], _____ with increase in pressure at equilibrium.
15. If concentration quotient, Q is greater than K_c , the net reaction is taking place in _____ direction.
16. The reaction, $N_2 + 3H_2 \rightleftharpoons 2NH_3$ would be favoured by _____ pressure.
17. K_p is related to K_c as _____.
18. Solubility of a gas in water _____ with increase in temperature.
19. Introduction of inert gas at constant volume to a gaseous reaction at equilibrium results in formation of _____ product.
20. The product is more stable than reactants in reaction having _____ K.
21. Van't Hoff's equation gives the quantitative relation between change in value of K with change in temperature.

22. The larger value of K indicates that the product is more stable relative to reactants.
23. The value of equilibrium constant changes with change in the initial concentration of the reactants.
24. Extent of a reaction can always be increased by increasing the temperature.
25. K_p is related to K_c as $K_p = K_c (RT)^{\Delta n}$.
26. Introduction of inert gas at a gaseous reaction ($\Delta n_g \neq 0$) at equilibrium keeping pressure constant has no effect on equilibrium state.
27. For the reaction, $N_2O_4(g) \rightleftharpoons 2NO_2(g)$, $K_p = K_c (RT)$.
28. For a reaction the value of Q greater than K indicates that the net reaction is proceeding in backward direction.
29. Solubilities of all solids in water increase with increase in temperature.
30. Dissolution of all gases in water is accompanied by evolution of heat.
31. For the reaction, $N_2 + 3H_2 \rightleftharpoons 2NH_3$, the equilibrium expression may be written as $K = \frac{[NH_3]^2}{[N_2][H_2]^3}$.
32. For the reaction, $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$, $K_p = P_{CO_2}$.
33. A catalyst increases the value of the equilibrium constant for a reaction.
34. If concentration quotient of reaction is less than K, the net reaction is proceeding in the backward direction.
35. In case of endothermic reactions, the equilibrium shifts in backward direction on increasing the temperature.
36. The value of K increases with increase in pressure.
37. For the reaction, $H_2 + I_2 \rightleftharpoons 2HI$, the equilibrium constant, K is dimensionless.
38. The reaction $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$, $\Delta H = -X \text{ kJ}$, is favoured by high pressure and high temperature.
39. A very high value of K indicates that at equilibrium most of the reactants are converted into products.
40. The value of K for the reaction, $N_2 + 2H_2 \rightleftharpoons 2NH_3$, can be increased by applying high pressure or by using a catalyst.

EXERCISE II

- Q.1 At high temperatures phosgene, COCl_2 decompose to give CO & Cl_2 . In a typical experiment 9.9×10^{-4} kg of COCl_2 is injected into a flask of volume 0.4105 dm^3 at 1000 K . When equilibrium is established it is found that the total pressure in the flask is 3.039×10^5 pascals. Calculate the equilibrium constant (K_p) for this reaction at 1000 K .
- Q.2 2 moles of A & 3 moles of B are mixed in 1 litre vessel and the reaction is carried at 400°C according to the equation; $\text{A} + \text{B} \rightleftharpoons 2\text{C}$. The equilibrium constant of the reaction is 4. Find the number of moles of C at equilibrium.
- Q.3 $2 \text{NOBr}(\text{g}) \rightleftharpoons 2 \text{NO}(\text{g}) + \text{Br}_2(\text{g})$. If nitrosyl bromide (NOBr) is 33.33% dissociated at 25°C & a total pressure of 0.28 atm . Calculate K_p for the dissociation at this temperature.
- Q.4 At 90°C , the following equilibrium is established :
 $\text{H}_2(\text{g}) + \text{S}(\text{s}) \rightleftharpoons \text{H}_2\text{S}(\text{g}) \quad K_p = 6.8 \times 10^{-2}$
If 0.2 mol of hydrogen and 1.0 mol of sulphur are heated to 90°C in a 1.0 litre vessel, what will be the partial pressure of H_2S at equilibrium?
- Q.5 The equilibrium constant for the reaction is 9.40 at 900°C $\text{S}_2(\text{g}) + \text{C}(\text{s}) \rightleftharpoons \text{CS}_2(\text{g})$. Calculate the pressure of two gases at equilibrium, when 1.42 atm of S_2 and excess of $\text{C}(\text{s})$ come to equilibrium.
- Q.6 A mixture of 2 moles of CH_4 & 34 gms of H_2S was placed in an evacuated container, which was then heated to & maintained at 727°C . When equilibrium was established in the gaseous reaction $\text{CH}_4 + 2 \text{H}_2\text{S} \rightleftharpoons \text{CS}_2 + 4 \text{H}_2$ the total pressure in the container was 0.92 atm & the partial pressure of hydrogen was 0.2 atm . What was the volume of the container ?
- Q.7 At 817°C , K_p for the reaction between pure CO_2 and excess hot graphite to form $2\text{CO}(\text{g})$ is 10 atm .
(a) What is the analysis of the gases at equilibrium at 817°C & a total pressure of 4.0 atm ? What is the partial pressure of CO_2 at equilibrium ?
(b) At what total pressure will the gas mixture analyze 6% , CO_2 by volume ?
- Q.8 The equilibrium mixture $\text{SO}_2 + \text{NO}_2 \rightleftharpoons \text{SO}_3 + \text{NO}$ was found to contain 0.6 mol of SO_3 , 0.40 mol of NO , 0.8 mol of SO_2 & 0.1 mol of NO_2 in a 1L vessel. One mole of NO was then forced into the reaction vessel with V & T constant. Calculate the amounts of each gas in the new equilibrium mixture.
- Q.9 For the reaction $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$, equilibrium mixture contains NO_2 at $P = 1.1 \text{ atm}$ & N_2O_4 at $P = 0.28 \text{ atm}$ at 350 K . The volume of the container is doubled. Calculate the equilibrium pressures of the two gases when the system reaches new equilibrium.
- Q.10 In the preceding problem, calculate the degree of dissociation, α at both pressures corresponding to mean molar masses of 65 & 76.667 . Use data from the preceding problem.
- Q.11 PCl_5 dissociates according to the reaction $\text{PCl}_5 \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$. At 523 K , $K_p = 1.78 \text{ atm}$. Find the density of the equilibrium mixture at a total pressure of 1 atm .
- Q.12 The reaction $3/2\text{H}_2(\text{g}) + 1/2 \text{N}_2(\text{g}) \rightleftharpoons \text{NH}_3(\text{g})$ was carried out at $T = 620 \text{ K}$ & $P = 10 \text{ atm}$ with an initial mixture of $\text{H}_2 : \text{N}_2 = 3 : 1$, the mixture at equilibrium contained 7.35% NH_3 . Find K_p and K_c .

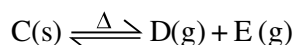
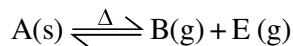
- Q.13 For the reaction $\text{SO}_2(\text{g}) + 1/2 \text{O}_2(\text{g}) \rightleftharpoons \text{SO}_3(\text{g})$ $\Delta H^\circ_{298} = -98.32 \text{ kJ/mole}$, $\Delta S^\circ_{298} = -95.0 \text{ J/K/mole}$. Find the K_p for this reaction at 298 K.
- Q.14 The following data for the equilibrium composition of the reaction
 $2\text{Na}(\text{g}) \rightleftharpoons \text{Na}_2(\text{g})$
 at 1.013 MPa pressure and 1482.53 K have been obtained.
 mass % Na (monomer gas) = 71.3
 mass % Na_2 (dimer gas) = 28.7
 Calculate the equilibrium constant K_p .
- Q.15 The degree of dissociation of HI at a particular temperature is 0.8. Find the volume of 1.5M sodium thiosulphate solution required to react completely with the iodine present at equilibrium in acidic conditions, when 0.135 mol each of H_2 and I_2 are heated at 440 K in a closed vessel of capacity 2.0 L.
- Q.16 A reaction system in equilibrium according to the equation $2 \text{SO}_2 + \text{O}_2 \rightleftharpoons 2 \text{SO}_3$ in 1 litre reaction vessel at a given temperature was found to contain 0.11 mol of SO_2 , 0.12 mol of SO_3 and 0.05 mol of O_2 . Another 1 litre reaction vessel contains 64 g of SO_2 at the same temperature. What mass of O_2 must be added to this vessel in order that at equilibrium half of SO_2 is oxidised to SO_3 ?
- Q.17 A mixture of hydrogen & iodine in the mole ratio 1.5 : 1 is maintained at 450°C. After the attainment of equilibrium $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2 \text{HI}(\text{g})$, it is found on analysis that the mole ratio of I_2 to HI is 1 : 18. Calculate the equilibrium constant & the number of moles of each species present under equilibrium, if initially, 127 grams of iodine were taken.
- Q.18 In a closed container nitrogen and hydrogen mixture initially in a mole ratio of 1:4 reached equilibrium. It is found that the half hydrogen is converted to ammonia. If the original pressure was 180 atm, what will be the partial pressure of ammonia at equilibrium. (There is no change in temperature)
- Q.19 The equilibrium constant for the reaction $\text{CO}(\text{g}) + \text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{CO}_2(\text{g}) + \text{H}_2(\text{g})$ is 7.3 at 450°C & 1atm pressure. The initial concentration of water gas [$\text{CO} + \text{H}_2$] & steam are 2 moles & 5 moles respectively. Find the number of moles of CO , H_2 , CO_2 & H_2O (vapour) at equilibrium.
- Q.20 At 1200°C, the following equilibrium is established between chlorine atoms & molecule:
 $\text{Cl}_2(\text{g}) \rightleftharpoons 2\text{Cl}(\text{g})$
 The composition of the equilibrium mixture may be determined by measuring the rate of effusion of the mixture through a pin hole. It is found that at 1200°C and 1 atm pressure the mixture effuses 1.16 times as fast as krypton effuses under the same condition. Calculate the equilibrium constant K_c .
- Q.21 Two solids X and Y dissociate into gaseous products at a certain temperature as follows:
 $\text{X}(\text{s}) \rightleftharpoons \text{A}(\text{g}) + \text{C}(\text{g})$, and $\text{Y}(\text{s}) \rightleftharpoons \text{B}(\text{g}) + \text{C}(\text{g})$. At a given temperature, pressure over excess solid X is 40 mm and total pressure over solid Y is 60 mm. Calculate:
 (a) the values of K_p for two reactions (in mm)
 (b) the ratio of moles of A and B in the vapour state over a mixture of X and Y.
 (c) the total pressure of gases over a mixture of X and Y.
- Q.22 SO_3 decomposes at a temperature of 1000 K and at a total pressure of 1.642 atm. At equilibrium, the density of mixture is found to be 1.28 g/l in a vessel of 90 liters. Find the degree of dissociation of SO_3 for $\text{SO}_3 \rightleftharpoons \text{SO}_2 + 1/2 \text{O}_2$.

Q.23 Consider the equilibrium: $P(g) + 2Q(g) \rightleftharpoons R(g)$. When the reaction is carried out at a certain temperature, the equilibrium concentration of P and Q are 3M and 4M respectively. When the volume of the vessel is doubled and the equilibrium is allowed to be reestablished, the concentration of Q is found to be 3M. Find (A) K_c (B) concentration of R at two equilibrium stages.

Q.24 When PCl_5 is heated, it dissociates into PCl_3 and Cl_2 . The vapor density of the gaseous mixture at $200^\circ C$ and $250^\circ C$ is 70.2 and 57.9 respectively. Find the % dissociation of PCl_5 at $200^\circ C$ and $250^\circ C$.

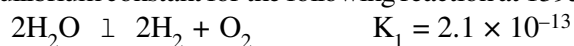
Q.25 The density of an equilibrium mixture of N_2O_4 and NO_2 at 101.32 KPa is 3.62 g dm^{-3} at 288 K and 1.84 g dm^{-3} at 348K. What is the heat of the reaction for $N_2O_4 \rightleftharpoons 2NO_2(g)$.

Q.26 Two solid compounds A & C dissociates into gaseous product at temperature as follows



At $20^\circ C$ pressure over excess solid A is 50atm & that over excess solid C is 68atm. Find the total pressure of gases over the solid mixture.

Q.27 The equilibrium constant for the following reaction at 1395 K.



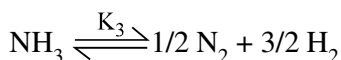
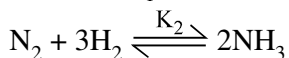
Calculate the value of K for the reaction : $H_2 + CO_2 \rightleftharpoons CO + H_2O$

Q.28 A saturated solution of iodine in water contains $0.33 \text{ g I}_2 / \text{L}$. More than this can dissolve in a KI solution because of the following equilibrium: $I_2(aq) + I^-(aq) \rightleftharpoons I_3^-(aq)$. A 0.10 M KI solution (0.10 M I^-) actually dissolves 12.5 g of iodine/L, most of which is converted to I_3^- . Assuming that the concentration of I_2 in all saturated solutions is the same, calculate the equilibrium constant for the above reaction. What is the effect of adding water to a clear saturated of I_2 in the KI solution ?

Q.29 The equilibrium p-Xyloquinone + methylene white \rightleftharpoons p-Xylohydroquinone + methylene blue may be studied conveniently by observing the difference in color methylene white and methylene blue. One mmol of methylene blue was added to 1L of solution that was 0.24 M in p-Xylohydroquinone and 0.012 M in p-Xyloquinone. It was then found that 4% of the added methylene blue was reduced to methylene white. What is the equilibrium constant of the above reaction? The equation is balanced with one mole each of 4 substances.

Q.30 A mixture of N_2 & H_2 are in equilibrium at 600 K at a total pressure of 80 atm . If the initial ratio of N_2 and H_2 are 3:1 and at equilibrium NH_3 is 10% by volume. Calculate K_p of reaction at given temperature.

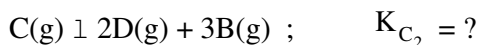
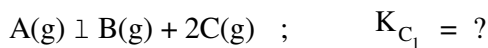
Q.31 ΔG° (298 K) for the reaction $1/2 N_2 + 3/2 H_2 \xrightleftharpoons{K_1} NH_3$ is $-16.5 \text{ kJ mol}^{-1}$. Find the equilibrium constant (K_1) at $25^\circ C$. What will be the equilibrium constants K_2 and K_3 for the following reactions:



Q.32 A certain gas A polymerizes to a small extent at a given temperature & pressure, $nA \rightleftharpoons A_n$. Show that the gas obeys the approx. equation $\frac{PV}{RT} = \left[1 - \frac{(n-1)K_c}{V^{n-1}} \right]$ where $K_c = \frac{[A_n]}{[A]^n}$ & V is the volume of the container. Assume that initially one mole of A was taken in the container.

Q.33 10^{-3} mol of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ is introduced in a 1.9 L vessel maintained at a constant temperature of 27°C containing moist air at relative humidity of 12.5%. What is the final molar composition of solid mixture? For $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}(s) \rightleftharpoons \text{CuSO}_4(s) + 5\text{H}_2\text{O}(g)$, $K_p(\text{atm}) = 10^{-10}$. Take vapor pressure of water at 27°C as 28 torrs.

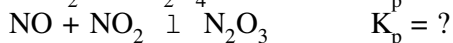
Q.34 When 1 mol of $\text{A}(g)$ is introduced in a closed 1L vessel maintained at constant temperature, the following equilibria are established.



The pressure at equilibrium is $\left(\frac{13}{6}\right)$ times the initial pressure.

Calculate K_{C_1} & K_{C_2} if $\frac{[\text{C}]_{\text{eq}}}{[\text{A}]_{\text{eq}}} = \frac{4}{9}$.

Q.35 When NO & NO_2 are mixed, the following equilibria are readily obtained;

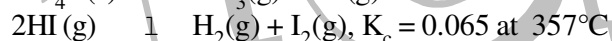


In an experiment when NO & NO_2 are mixed in the ratio of 1 : 2, the total final pressure was 5.05 atm & the partial pressure of N_2O_4 was 1.7 atm. Calculate

(a) the equilibrium partial pressure of NO .

(b) K_p for $\text{NO} + \text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_3$

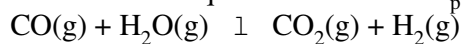
Q.36 Solid NH_4I on rapid heating in a closed vessel at 357°C develops a constant pressure of 275 mm Hg owing to partial decomposition of NH_4I into NH_3 and HI but the pressure gradually increases further (when the excess solid residue remains in the vessel) owing to the dissociation of HI . Calculate the final pressure developed at equilibrium.



Q.37 Given are the following standard free energies of formation at 298K.

	$\text{CO}(g)$	$\text{CO}_2(g)$	$\text{H}_2\text{O}(g)$	$\text{H}_2\text{O}(l)$
$\Delta_f G^\circ / \text{kJ mol}^{-1}$	-137.17	-394.36	-228.57	-237.13

(a) Find $\Delta_r G^\circ$ and the standard equilibrium constant K_p^0 at 298 K for the reaction



(b) If CO , CO_2 and H_2 are mixed so that the partial pressure of each is 101.325 kPa and the mixture is brought into contact with excess of liquid water, what will be the partial pressure of each gas when equilibrium is attained at 298K. The volume available to the gases is constant.

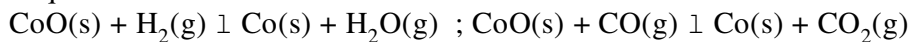
Q.38 For the reaction



K_p^0 is 0.05 and $\Delta_f G^\circ$ is $22.384 \text{ kJ mol}^{-1}$ at 900 K. If an initial mixture comprising 20 mol of C_2H_6 and 80 mol of N_2 (inert) is passed over a dehydrogenation catalyst at 900K, what is the equilibrium percentage composition of the effluent gas mixture? The total pressure is kept at 0.5 bar. Given : $\Delta_r S^\circ = 135.143 \text{ J K}^{-1} \text{ mol}^{-1}$ at 300K. Calculate $\Delta_r G^\circ$ at 300K. (Assume $\Delta_r C_p = 0$)

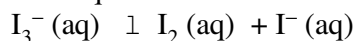
Q.39(a) The equilibrium $\text{H}_2(\text{g}) + \text{CO}_2(\text{g}) \rightleftharpoons \text{H}_2\text{O}(\text{g}) + \text{CO}(\text{g})$ is established in an evacuated vessel at 723 K starting with 0.1 mole of H_2 & 0.2 mole of CO_2 . If the equilibrium mixture contains 10 mole per cent of water vapour, calculate K_p , given that the equilibrium pressure is 0.5 atm. Calculate the partial pressures of the component species & the volume of the container.

(b) If now, into the flask (mentioned in the preceding problem), solid CoO & solid Co are introduced two new equilibria are established.



The new equilibrium mixture contains 30 mole percent of water vapour. Calculate the equilibrium constants for the new equilibria.

Q.40 Some iodine is dissolved in an aqueous solution of KI of concentration 0.102 mole/l, and the solution is then shaken with equal volume of CCl_4 until equilibrium is reached (at 15°C). The total amount of iodine (present as I_3^- (aq) or as I_2 (aq)) at equilibrium is found to be 0.048 mol/l in the aqueous layer and 0.085 mol/l in the CCl_4 layer. The distribution coefficient of iodine between CCl_4 and water is 85. Calculate the equilibrium constant at 15°C for the reaction:



EXERCISE III

- Q.1 Consider following reactions in equilibrium with equilibrium concentration 0.01 M of every species
(I) $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$ (II) $2\text{HI}(\text{g}) \rightleftharpoons \text{H}_2(\text{g}) + \text{I}_2(\text{g})$
(III) $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$
Extent of the reactions taking place is:
(A) $\text{I} > \text{II} > \text{III}$ (B) $\text{I} < \text{II} < \text{III}$ (C) $\text{II} < \text{III} < \text{I}$ (D) $\text{III} < \text{I} < \text{II}$
- Q.2 For the reaction $3\text{A}(\text{g}) + \text{B}(\text{g}) \rightleftharpoons 2\text{C}(\text{g})$ at a given temperature, $K_c = 9.0$. What must be the volume of the flask, if a mixture of 2.0 mol each of A, B and C exist in equilibrium?
(A) 6L (B) 9L (C) 36 L (D) None of these
- Q.3 Sulfide ion in alkaline solution reacts with solid sulfur to form polysulfide ions having formulas S_2^{2-} , S_3^{2-} , S_4^{2-} and so on. The equilibrium constant for the formation of S_2^{2-} is 12 (K_1) & for the formation of S_3^{2-} is 132 (K_2), both from S and S^{2-} . What is the equilibrium constant for the formation of S_3^{2-} from S_2^{2-} and S?
(A) 11 (B) 12 (C) 132 (D) None of these
- Q.4 For the following gases equilibrium. $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$
 K_p is found to be equal to K_c . This is attained when
(A) 0°C (B) 273 K (C) 1 K (D) 12.19 K
- Q.5 1 mole N_2 and 3 mol H_2 are placed in a closed container at a pressure of 4 atm. The pressure falls to 3 atm at the same temperature when the following equilibrium is attained.
 $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$. The equilibrium constant K_p for dissociation of NH_3 is:
(A) $\frac{1}{0.5} \times (1.5)^3 \text{ atm}^{-2}$ (B) $0.5 \times (1.5)^3 \text{ atm}^2$ (C) $\frac{0.5 \times (1.5)^3}{3 \times 3} \text{ atm}^2$ (D) $\frac{3 \times 3}{0.5 \times (1.5)^3} \text{ atm}^{-2}$
- Q.6 One mole of $\text{N}_2\text{O}_4(\text{g})$ at 300 K is left in a closed container under one atm. It is heated to 600 K when 20 % by mass of $\text{N}_2\text{O}_4(\text{g})$ decomposes to $\text{NO}_2(\text{g})$. The resultant pressure is :
(A) 1.2 atm (B) 2.4 atm (C) 2.0 atm (D) 1.0 atm
- Q.7 For the reaction : $2\text{HI}(\text{g}) \rightleftharpoons \text{H}_2(\text{g}) + \text{I}_2(\text{g})$, the degree of dissociated (α) of $\text{HI}(\text{g})$ is related to equilibrium constant K_p by the expression
(A) $\frac{1+2\sqrt{K_p}}{2}$ (B) $\sqrt{\frac{1+2K_p}{2}}$ (C) $\sqrt{\frac{2K_p}{1+2K_p}}$ (D) $\frac{2\sqrt{K_p}}{1+2\sqrt{K_p}}$
- Q.8 The vapour density of N_2O_4 at a certain temperature is 30. What is the % dissociation of N_2O_4 at this temperature?
(A) 53.3% (B) 106.6% (C) 26.7% (D) None
- Q.9 For the reaction $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$, the forward reaction at constant temperature is favoured by
(A) introducing an inert gas at constant volume
(B) introducing chlorine gas at constant volume
(C) introducing an inert gas at constant pressure
(D) increasing the volume of the container
(E) introducing PCl_5 at constant volume.

- Q.10 When N_2O_5 is heated at temp. T, it dissociates as $\text{N}_2\text{O}_5 \rightleftharpoons \text{N}_2\text{O}_3 + \text{O}_2$, $K_c = 2.5$. At the same time N_2O_3 also decomposes as : $\text{N}_2\text{O}_3 \rightleftharpoons \text{N}_2\text{O} + \text{O}_2$. If initially 4.0 moles of N_2O_5 are taken in 1.0 litre flask and allowed to attain equilibrium, concentration of O_2 was formed to be 2.5 M. Equilibrium concentration of N_2O is
 (A) 1.0 (B) 1.5 (C) 2.166 (D) 0.334
- Q.11 Densities of diamond and graphite are 3.5 and 2.3 gm/mL.
 $\text{C (diamond)} \rightleftharpoons \text{C (graphite)}$ $\Delta_f H = -1.9 \text{ kJ/mole}$
 favourable conditions for formation of diamond are
 (A) high pressure and low temperature (B) low pressure and high temperature
 (C) high pressure and high temperature (D) low pressure and low temperature
- Q.12 When NaNO_3 is heated in a closed vessel, oxygen is liberated and NaNO_2 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
- Q.13 The equilibrium $\text{SO}_2\text{Cl}_2(\text{g}) \rightleftharpoons \text{SO}_2(\text{g}) + \text{Cl}_2(\text{g})$ is attained at 25°C in a closed rigid container and an inert gas, helium is introduced. Which of the following statements is/are correct.
 (A) concentrations of SO_2 , Cl_2 and SO_2Cl_2 do not change
 (B) more chlorine is formed
 (C) concentration of SO_2 is reduced
 (D) more SO_2Cl_2 is formed
- Q.14 For the gas phase reaction, $\text{C}_2\text{H}_4 + \text{H}_2 \rightleftharpoons \text{C}_2\text{H}_6$ ($\Delta H = -32.7 \text{ kcal}$), carried out in a closed 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) adding some C_2H_6
- Q.15 An exothermic reaction is represented by the graph :
- (A)

(B)

(C)

(D)
- Q.16 The correct relationship between free energy change in a reaction and the corresponding equilibrium constant K is
 (A) $-\Delta G^\circ = RT \ln K$ (B) $\Delta G = RT \ln K$ (C) $-\Delta G = RT \ln K$ (D) $\Delta G^\circ = RT \ln K$
- Q.17 The value of ΔG_f° of gaseous mercury is 31 K J/mole. At what total external pressure mercury start boiling at 25°C . [$R = 8.3$]
 (A) $10^{-5.44}$ (B) $10^{-12.5}$ (C) $10^{-6.52}$ (D) $10^{-3.12}$

- Q.18 What is $\Delta_r G$ (KJ/mole) for synthesis of ammonia at 298 K at following sets of partial pressure:
 $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$; $\Delta_r G^\circ = -33$ KJ/mole. [Take $R = 8.3$ J/K mole, $\log 2 = 0.3$; $\log 3 = 0.48$]
- | | | | |
|----------------|-------|-------|--------|
| Gas | N_2 | H_2 | NH_3 |
| Pressure (atm) | 1 | 3 | 0.02 |
- (A) + 6.5 (B) - 6.5 (C) + 60.5 (D) - 60.5
- Q.19 In a 7.0 L evacuated chamber, 0.50 mol H_2 and 0.50 mol I_2 react at $427^\circ C$.
 $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$. At the given temperature, $K_c = 49$ for the reaction.
- (i) What is the value of K_p ?
 (A) 7 (B) 49 (C) 24.5 (D) None
- (ii) What is the total pressure (atm) in the chamber?
 (A) 83.14 (B) 831.4 (C) 8.21 (D) None
- (iii) How many moles of the iodine remain unreacted at equilibrium?
 (A) 0.388 (B) 0.112 (C) 0.25 (D) 0.125
- (iv) What is the partial pressure (atm) of HI in the equilibrium mixture?
 (A) 6.385 (B) 12.77 (C) 40.768 (D) 646.58
- Q.20 Equilibrium constants are given (in atm) for the following reactions at $0^\circ C$:
 $SrCl_2 \cdot 6H_2O(s) \rightleftharpoons SrCl_2 \cdot 2H_2O(s) + 4H_2O(g)$ $K_p = 5 \times 10^{-12}$
 $Na_2HPO_4 \cdot 12H_2O(s) \rightleftharpoons Na_2HPO_4 \cdot 7H_2O(s) + 5H_2O(g)$ $K_p = 2.43 \times 10^{-13}$
 $Na_2SO_4 \cdot 10H_2O(s) \rightleftharpoons Na_2SO_4(s) + 10H_2O(g)$ $K_p = 1.024 \times 10^{-27}$
 The vapor pressure of water at $0^\circ C$ is 4.56 torr.
- (i) Which is the most effective drying agent at $0^\circ C$?
 (A) $SrCl_2 \cdot 2H_2O$ (B) $Na_2HPO_4 \cdot 7H_2O$ (C) Na_2SO_4 (D) all equally
- (ii) At what relative humidities will $Na_2SO_4 \cdot 10H_2O$ be efflorescent when exposed to air at $0^\circ C$?
 (A) above 33.33% (B) below 33.33% (C) above 66.66% (D) below 66.66%
- (iii) At what relative humidities will Na_2SO_4 be deliquescent (i.e. absorb moisture) when exposed to the air at $0^\circ C$?
 (A) above 33.33% (B) below 33.33% (C) above 66.66% (D) below 66.66%

EXERCISE IV

Q.1 A sample of air consisting of N_2 and O_2 was heated to 2500K until the equilibrium $N_2(g) + O_2(g) \rightleftharpoons 2NO$ was established with an equilibrium constant $K_c = 2.1 \times 10^{-3}$. At equilibrium, the mol% of NO was 1.8. Estimate the initial composition of air in mol fraction of N_2 and O_2 .

[JEE 1997]

Q.2 For the reaction $CO(g) + H_2O \rightleftharpoons CO_2(g) + H_2(g)$ at a given temperature the equilibrium amount of $CO_2(g)$ can be increased by :

- (A) adding a suitable catalyst (B) adding an inert gas
(C) decreasing the volume of the container (D) increasing the amount of $CO(g)$.

[JEE 1998]

Q.3 For the reaction, $N_2O_5(g) = 2NO_2(g) + 0.5 O_2(g)$, calculate the mole fraction of $N_2O_5(g)$ decomposed at a constant volume & temperature, if the initial pressure is 600 mm Hg & the pressure at any time is 960 mm Hg. Assume ideal gas behaviour .

[JEE 1998]

Q.4 The degree of dissociation is 0.4 at 400K & 1.0 atm for the gaseous reaction $PCl_5 \rightleftharpoons PCl_3 + Cl_2(g)$. Assuming ideal behaviour of all gases. Calculate the density of equilibrium mixture at 400K & 1.0 atm pressure.

[JEE 1999]

Q.5 When 3.06g of solid NH_4HS is introduced into a two litre evacuated flask at $27^\circ C$, 30% of the solid decomposes into gaseous ammonia and hydrogen sulphide.

- (i) Calculate K_c & K_p for the reaction at $27^\circ C$.
(ii) What would happen to the equilibrium when more solid NH_4HS is introduced into the flask?

[JEE 2000]

Q.6 When 1-pentyne (A) is treated with 4N alcoholic KOH at $175^\circ C$, it is converted slowly into an equilibrium mixture of 1.3% 1-pentyne (A), 95.2% 2-pentyne (B) & 3.5% of 1, 2,-pentadiene (C). The equilibrium was maintained at $175^\circ C$. Calculate ΔG° for the following equilibria.

$$B = A$$

$$\Delta G_1^\circ = ?$$

$$B = C$$

$$\Delta G_2^\circ = ?$$

From the calculated value of ΔG_1° & ΔG_2° indicate the order of stability of A, B & C. Write a reasonable reaction mechanism sharing all intermediate leading to A, B & C.

[JEE 2001]

Q.7 $N_2O_4(g) \rightleftharpoons 2NO_2(g)$
This reaction is carried out at 298 K and 20 bar. 5 mol each of N_2O_4 and NO_2 are taken initially.

$$\text{Given: } \Delta G_{N_2O_4}^\circ = 100 \text{ kJ mol}^{-1}; \Delta G_{NO_2}^\circ = 50 \text{ kJ mol}^{-1}$$

- (i) Find ΔG for reaction at 298 K under given condition.
(ii) Find the direction in which the reaction proceeds to achieve equilibrium.

[JEE 2004]

Q.8 $N_2 + 3H_2 \rightleftharpoons 2NH_3$

Which is correct statement if N_2 is added at equilibrium condition?

- (A) The equilibrium will shift to forward direction because according to II law of thermodynamics the entropy must increases in the direction of spontaneous reaction.
(B) The condition for equilibrium is $G_{N_2} + 3G_{H_2} = 2G_{NH_3}$ where G is Gibbs free energy per mole of the gaseous species measured at that partial pressure. The condition of equilibrium is unaffected by the use of catalyst, which increases the rate of both the forward and backward reactions to the same extent.
(C) The catalyst will increase the rate of forward reaction by α and that of backward reaction by β .
(D) Catalyst will not alter the rate of either of the reaction.

[JEE 2006]

ANSWER KEY
EXERCISE I

- Q.1 (a) 25, shifts left, (b) 0.22, shifts right, (c) ∞ , shifts left, (d) 1, shifts right, (e) 0, shift right, (f) 4, shifts left
- Q.2 (a) $K = [\text{Ag}^+][\text{Cl}^-]$ is less than 1. AgCl is insoluble thus the concentration of ions are much less than 1 M
(b) $K = 1/[\text{Pb}^{2+}][\text{Cl}^-]^2$ is greater than one because PbCl₂ is insoluble and formation of the solid will reduce the concentration of ions to a low level
- Q.4 K about 10 Q.6p (a) incomplete (b) almost complete Q.7 c Q.8 $\sim 9 \times 10^{-32}$ mol/L
- Q.9 The reaction is not an equilibrium because $Q_c > K_c$. The reaction will proceed from right to left to reach equilibrium
- Q.11 5.9×10^{-3} M Q.12 $[\text{NO}] = 0.056$ M, $[\text{N}_2] = [\text{O}_2] = 1.37$ M
- Q.13 $[\text{PCl}_3] = [\text{Cl}_2] = 0.071$ M, $[\text{PCl}_5] = 0.089$
- Q.14 $P_{\text{ClF}} = P_{\text{F}_2} = 0.389$ atm, $P_{\text{ClF}_3} = 1.08$ atm
- Q.15 $K_p = 0.4$, $a \sim 0.1$ Q.16 50%
- Q.17 (a) 6.667×10^{-3} mol L⁻¹; (b) $n(\text{N}_2\text{O}_4) = 0.374$ mol; $n(\text{NO}_2) = 0.052$ mol ;
(c) 10.49 atm (d) 6.44 %
- Q.18 0.97 atm Q.19 $K_p = 1.3 \times 10^{-3}$ atm⁻²
- Q.20 $K_p = 2.5$ atm, $P = 15$ atm Q.21 53.33%
- Q.22 $K = 4$ Q.23 31/27 Q.24 22.4 mg
- Q.25 $P_{\text{H}_2\text{O}} = 5 \times 10^{-15}$ atm Q.26 0.821 atm
- Q.27 add N₂, add H₂, increase the pressure, heat the reaction
- Q.28 (a) shift right, shift left, (b) shift right, no effect, (c) shift left, shift left, (d) shift left, shift right
- Q.29 (a) $K = [\text{CH}_3\text{OH}]/[\text{H}_2]^2[\text{CO}]$,
(b) 1. [H₂] increase, [CO] decrease, [CH₃OH] increase; 2. [H₂] increase, [CO] decrease, [CH₃OH] decrease; 3. [H₂] increase, [CO] increase, [CH₃OH] increase; 4. [H₂] increase, [CO] increase, [CH₃OH] increase; 5. [H₂] increase, [CO] increase, [CH₃OH] decrease; 6. no change
- Q.30 (a) $K = [\text{CO}][\text{H}_2]/[\text{H}_2\text{O}]$;
(b) in each of the following cases the mass of carbon will change, but its concentration (activity) will not change. 1. [H₂O] no change, [CO] no change, [H₂] no change; 2. [H₂O] decrease, [CO] decrease, [H₂] decrease; 3. [H₂O] increase, [CO] increase, [H₂] decrease; 4. [H₂O] increase, [CO] increase, [H₂] increase; 5. [H₂O] decrease, [CO] increase, [H₂] increase
- Q.31 b
- Q.32 Add NaCl or some other salt that produces Cl⁻ in the solution. Cool the solution.
- Q.33 a
- Q.34 $k_f [\text{A}][\text{B}] = k_r [\text{C}]$; $\frac{k_f}{k_r} = \frac{[\text{C}]}{[\text{A}][\text{B}]} = K_c$ Q.36 216
- Q.38 (i) 2; (ii) 1.2 mol/L; (iii) 0.1 moles/hr
- Q.39 k_r increase more than k_f , this means that E_a (reverse) is greater than E_a (forward). The reaction is exothermic when E_a (reverse) > E_a (forward).
- Q.43 (a) -9.574 J/mol, (b) $A = 10^{10}$, (c) 9.96×10^9 , (d) 9.98×10^9
- Q.44 16.06 kJ Q.45 -810 J/mol; -5872 J/mol and 41.3 kJ/mol
- Q.46 1.3×10^8 Q.47 0.058
- Q.48 29.0 Q.49 $K_p = 0.0313$ atm, $K_c = 1.28 \times 10^{-3}$
- Q.50 (a) $K_c = \frac{[\text{CO}_2]^3}{[\text{CO}]^3}$, $K_p = \frac{(P_{\text{CO}_2})^3}{(P_{\text{CO}})^3}$, (b) $K_c = \frac{1}{[\text{O}_2]^3}$, $K_p = \frac{1}{(P_{\text{O}_2})^3}$, (c) $K_c = [\text{SO}_3]$, $K_p = P_{\text{SO}_3}$
 $K_c = [\text{Ba}^{2+}][\text{SO}_4^{2-}]$

- Q.51 $K_c = 1.51k$ $K_p = 49.6$ Q.52 $1.5 \times 10^{-6} M$
 Q.53 $[CO] = [H_2] = 0.18 M$; $[H_2O] = 1.02 M$
 Q.54 (a) $K_c = 0.573$ and $K_p = 23.5$; (b) to the right, $[PCl_5] = 0.365 M$; $[PCl_3] = 0.285 M$; $[Cl_2] = 0.735 M$
 Q.56 $-1.005 kJ/mol$ Q.57 $\Delta G^\circ = 0$; $K = 1$
 Q.58 $\Delta H^\circ = 9.04 kJ/mol$; $\Delta S^\circ = -8.64 J/mol^{-1}K^{-1}$

PROFICIENCY TEST

- | | | | |
|----------------------------------------------------------------------------------------------------|------------------------|---------------------------------|---------------------------------|
| 1. C | 2. high | 3. $\frac{1}{10}$ | 4. $\frac{1}{\sqrt{K}}$ |
| 5. exothermic | 6. $K_p = K_c (RT)$ | 7. backward | 8. $\Delta G^\circ = -RT \ln K$ |
| 9. $\log \frac{K_2}{K_1} = \frac{\Delta H^\circ}{2.303R} \left[\frac{T_2 - T_1}{T_2 T_1} \right]$ | 10. zero | 11. mol^2L^{-2} | |
| 12. temperature | 13. Guldberg and Waage | 14. decreases | |
| 15. backward | 16. high | 17. $K_p = K_c (RT)^{\Delta n}$ | |
| 18. decreases | 19. same amount of | 20. larger value of | |
| 21. T | 22. T | 23. F | 24. F |
| 25. T | 26. F | 27. T | 28. T |
| 29. F | 30. T | 31. T | 32. T |
| 33. F | 34. F | 35. F | 36. F |
| 37. T | 38. F | 39. T | 40. F |

EXERCISE II

- Q.1 $K_p (atm) = 1.13$ Q.3 $K_p = 0.01 atm$ Q.4 $0.379 atm$
 Q.2 2.4 mole
 Q.5 $P_{CS_2} = 1.284 atm$, $P_{S_2} = 0.1365 atm$
 Q.6 300L
 Q.7 (i) $x_{CO} = 0.765$, $x_{CO_2} = 0.235$; $p(CO_2) = 0.938 atm$ (ii) $P_{Total} = 0.68 atm$
 Q.8 ($K_c = 3$), $n_{SO_2} = 0.92$, $n_{SO_3} = 0.48$, $n_{NO} = 1.28$, $n_{NO_2} = 0.22$
 Q.9 $P_{NO_2} = 0.64 atm$, $P_{N_2O_4} = 0.095 atm$ Q.10 $\alpha = 0.415$ and 0.2
 Q.11 2.7 g/lit Q.12 $K_c = 1.337$, $K_p = 0.0263$ Q.13 $K_p = 1.862 \times 10^{12} atm^{-1/2}$
 Q.14 $p_{Na} = 0.843 MPa$; $p_{Na_2} = 0.170 MPa$; $k_p = 0.239$ Q.15 $V = 144 mL$
 Q.16 9.34 g Q.17 $K_c = 54$, $n_{HI} = 0.9 mol$, $n_{I_2} = 0.05 mol$, $n_{H_2} = 0.3 mol$
 Q.18 48 atm Q.19 $n_{CO_2} = 0.938$, $n_{H_2} = 1.938$, $n_{CO} = 0.062$, $n_{H_2O(g)} = 4.062$
 Q.20 6.71×10^{-4} Q.21 (a) $400mm^2$, $900mm^2$ (b) 4: 9, (c) $72.15 mm Hg$
 Q.22 $\alpha = 0.5$
 Q.23 $K_c = 1/12$, $[R] = 4$ (initial), $= 1.5$ (final) Q.24 dissociation = 48.5%, 80.05%
 Q.25 $\Delta_r H = 75.5 kJ mol^{-1}$ Q.26 Total pressure = 84.34 atm
 Q.27 $K = 2.58$ Q.28 $K = 707.2$, backward reaction is favoured
 Q.29 $K_c = 480$ Q.30 1.32×10^{-3}
 Q.31 $K_A = 779.4$, $K_B = 6.074 \times 10^5$; $K_c = 1.283 \times 10^{-3}$
 Q.32 To be proved Q.33 $CuSO_4 \cdot 5H_2O = 9.2 \times 10^{-4} mol$, $CuSO_4 = 8 \times 10^{-5} moles$
 Q.34 $k_{C_1} = 0.111$; $k_{C_2} = 0.14$ Q.35 (a) 1.05 atm, (b) $3.43 atm^{-1}$ Q.36 314.1 atm

