

1. Details of Module and its structure

Module Detail	
Subject Name	Chemistry
Course Name	Chemistry 01 (Class XI, Semester 01)
Module Name/Title	Equilibrium: Part 2
Module Id	kech_10702
Pre-requisites	Various types of equilibrium, equilibrium constant K_c , law of chemical equilibrium
Objectives	After going through this module, the learner will be able to: <ul style="list-style-type: none">• Establish a relationship between K_p and K_c• Appreciate characteristics of equilibrium constant• Apply the concept of equilibrium constant to predict the extent and direction of a reaction• Explain various factors that affect the equilibrium state of a reaction
Keywords	Homogeneous and heterogeneous equilibria, K_p and K_c , reaction quotient, Gibbs free energy, equilibrium constant, factors affecting equilibria.

2. Development Team

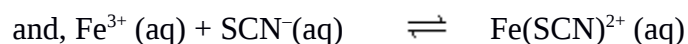
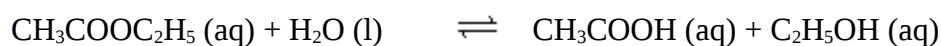
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1. Homogeneous Equilibria

In a homogeneous system, all the reactants and products are in the same phase. For example, in the gaseous reaction, $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$, reactants and products are in the homogeneous phase. Similarly, for the reactions,



all the reactants and products are in homogeneous solution phase. We shall now consider equilibrium constant for some homogeneous reactions.

2. Equilibrium Constant in Gaseous Systems - Deriving relation Between K_p and K_c

So far we have expressed equilibrium constant of the reactions in terms of molar concentration of the reactants and products, and used symbol, K_c for it. For reactions involving gases, however, it is usually more convenient to express the equilibrium constant in terms of partial pressure.

The ideal gas equation is written as,

$$pV = nRT$$

$$\Rightarrow p = \frac{n}{V}RT$$

where n/V is concentration c , expressed in mol/m^3 in SI units. If c is in mol/L or mol/dm^3 and p is in bar, then

$$p = cRT$$

We can also write $p = [\text{gas}]RT$ where $[\text{gas}]$ means concentration of the gas and $R = 0.0831$ bar litre/mol K.

Thus, we see that at constant temperature, the pressure of the gas is proportional to its concentration i.e.,

$$p \propto [\text{gas}]$$

For a reaction in equilibrium, for example: $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$

we can write either

(1)

$$\text{Further, since } p_{\text{HI}} = [\text{HI}(\text{g})]RT$$

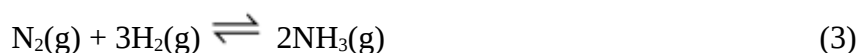
$$p_{\text{I}_2} = [\text{I}_2(\text{g})]RT$$

$$p_{\text{H}_2} = [\text{H}_2(\text{g})]RT$$

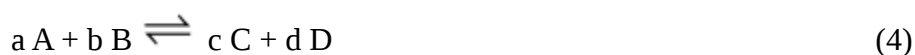
Therefore,

$$\begin{aligned} K_p &= \frac{(p_{\text{HI}})^2}{(p_{\text{H}_2})(p_{\text{I}_2})} = \frac{[\text{HI}(\text{g})]^2 [RT]^2}{[\text{H}_2(\text{g})]RT \cdot [\text{I}_2(\text{g})]RT} \\ &= \frac{[\text{HI}(\text{g})]^2}{[\text{H}_2(\text{g})][\text{I}_2(\text{g})]} = K_c \end{aligned} \quad (2)$$

In this example, $K_p = K_c$ i.e., both equilibrium constants are equal. However, this is not always the case. For example, in reaction for the formation of ammonia by Haber's process



Similarly, for a general reaction



where $\Delta n = (\text{number of moles of gaseous products}) - (\text{number of moles of gaseous reactants})$ in the balanced chemical equation.

(It is necessary that while calculating the value of K_p , pressure should be expressed in bar as standard state is 1bar). We know, 1pascal, Pa=1Nm⁻², and 1bar = 10⁵ Pa

Problem 1

PCl₅, PCl₃ and Cl₂ are at equilibrium at 500 K and having concentration 1.59M PCl₃, 1.59M Cl₂ and 1.41 M PCl₅. Calculate K_c for the reaction, $\text{PCl}_5 \rightleftharpoons \text{PCl}_3 + \text{Cl}_2$

Solution:

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

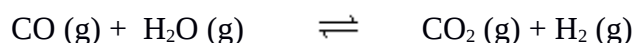
$$K_c = [\text{PCl}_3] [\text{Cl}_2] / [\text{PCl}_5] = (1.59)^2 / 1.41 = \mathbf{1.79}$$

Problem 2

The value of $K_c = 4.24$ at 800K for the reaction, $\text{CO (g)} + \text{H}_2\text{O (g)} \rightleftharpoons \text{CO}_2 \text{(g)} + \text{H}_2 \text{(g)}$
Calculate equilibrium concentrations of CO₂, H₂, CO and H₂O at 800 K, if only CO and H₂O are present initially at concentration of 0.10M each.

Solution:

For the reaction,



Initial concentration:

$$0.1\text{M} \quad 0.1\text{M} \qquad \qquad 0 \qquad 0$$

Let x mole per litre of each of the product be formed.

At equilibrium:

$$(0.1-x) \text{ M} \quad (0.1-x) \text{ M} \qquad \qquad x \text{ M} \quad x \text{ M}$$

where x is the amount of CO₂ and H₂ at equilibrium.

Hence, equilibrium constant can be written as,

$$K_c = x^2 / (0.1-x)^2 = 4.24 ; \quad x^2 = 4.24(0.01 + x^2 - 0.2x)$$

$$x^2 = 0.0424 + 4.24x^2 - 0.848x$$

$$3.24x^2 - 0.848x + 0.0424 = 0$$

$$a = 3.24, \quad b = -0.848, \quad c = 0.0424$$

(for quadratic equation $ax^2 + bx + c = 0$,

$$x = \frac{(-b \pm \sqrt{b^2 - 4ac})}{2a}$$

$$x = 0.848 \pm \sqrt{(0.848)^2 - 4(3.24)(0.0424)} / (3.24 \times 2)$$

$$x = (0.848 \pm 0.4118) / 6.48$$

$$x_1 = (0.848 - 0.4118) / 6.48 = 0.067$$

$$x_2 = (0.848 + 0.4118) / 6.48 = 0.194$$

The value 0.194 should be neglected because it will give concentration of the reactant which is more than initial concentration.

Hence the equilibrium concentrations are,

$$[\text{CO}_2] = [\text{H}_2] = x = 0.067 \text{ M}$$

$$[\text{CO}] = [\text{H}_2\text{O}] = 0.1 - 0.067 = 0.033 \text{ M}$$

Problem 3

For the equilibrium, $2\text{NOCl}(\text{g}) \rightleftharpoons 2\text{NO}(\text{g}) + \text{Cl}_2(\text{g})$

the value of the equilibrium constant, K_c is 3.75×10^{-6} at 1069 K. Calculate the K_p for the reaction at this temperature.

Solution:

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

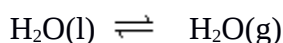
For the above reaction,

$$\Delta n = (2+1) - 2 = 1$$

$$K_p = 3.75 \times 10^{-6} (0.0831 \times 1069) K_p = 0.033$$

3. Heterogeneous Equilibria

Equilibrium in a system having more than one phase is called heterogeneous equilibrium. The equilibrium between water vapour and liquid water in a closed container is an example of heterogeneous equilibrium.



In this example, there is a gas phase and a liquid phase. In the same way, equilibrium between a solid and its saturated solution, $\text{Ca}(\text{OH})_2(s) + (\text{aq}) \rightleftharpoons \text{Ca}^{2+}(\text{aq}) + 2\text{OH}^-(\text{aq})$ is a heterogeneous equilibrium.

Heterogeneous equilibria often involve pure solids or liquids. We can simplify equilibrium expressions for the heterogeneous equilibria involving a pure liquid or a pure solid, as the molar concentration of a pure solid or liquid is constant (i.e., independent of the amount present). In other words if a substance 'X' is involved, then $[\text{X}(s)]$ and $[\text{X}(l)]$ are constant, whatever be the amount of 'X' is taken. Contrary to this, $[\text{X}(g)]$ and $[\text{X}(aq)]$ will vary as the amount of X in a given volume varies. Let us take the thermal dissociation of calcium carbonate which is an interesting and important example of heterogeneous chemical equilibrium

Δ



On the basis of the stoichiometric equation, we can write,

Since $[\text{CaCO}_3(s)]$ and $[\text{CaO}(s)]$ are both constant, therefore modified equilibrium constant for the thermal decomposition of calcium carbonate will be

$$K_c = \frac{[\text{CO}_2(g)]}{1} \quad (6)$$

$$\text{or } K_p = p_{\text{CO}_2} \quad (7)$$

p

This shows that at a particular temperature, there is a constant concentration or pressure of CO₂ in equilibrium with CaO(s) and CaCO₃(s). Experimentally it has been found that at 1100 K, the pressure of CO₂ in equilibrium with CaCO₃(s) and CaO(s), is 2.0 × 10⁵ Pa. Therefore, equilibrium constant at 1100K for the above reaction is:

$$K_p \approx p_{\text{CO}_2} \approx 2 \times 10^5 \text{ Pa} / 10^5 \text{ Pa} \approx 2.00$$

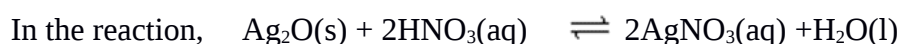
Similarly, in the equilibrium between nickel, carbon monoxide and nickel carbonyl (used in the purification of nickel),



the equilibrium constant is written as

$$K_c = \frac{[\text{Ni(CO)}_4]}{[\text{CO}]^4}$$

It must be remembered that in heterogeneous equilibrium pure solids or liquids must be present (however small it may be) for the equilibrium to exist, but their concentrations or partial pressures do not appear in the expression of the equilibrium constant.

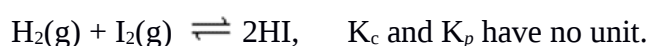


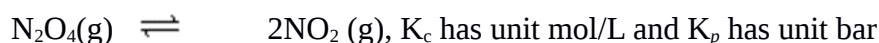
$$K_c = \frac{[\text{AgNO}_3]^2}{[\text{HNO}_3]^2}$$

Units of Equilibrium Constant

The value of equilibrium constant K_c can be calculated by substituting the concentration terms in mol/L and for K_p partial pressure is substituted in Pa, kPa, bar or atm. This results in units of equilibrium constant based on molarity or pressure, unless the exponents of both the numerator and denominator are same.

For the reactions,

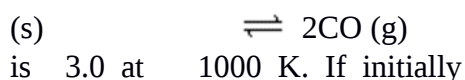




Equilibrium constants can also be expressed as dimensionless quantities if the standard state of reactants and products are specified. For a pure gas, the standard state is 1 bar. Therefore, a pressure of 4 bar in standard state can be expressed as $4 \text{ bar}/1 \text{ bar} = 4$, which is a dimensionless number. Standard state (c_0) for a solute is 1 molar solution and all concentrations can be measured with respect to it. The numerical value of equilibrium constant depends on the standard state chosen. Thus, in this system both K_p and K_c are dimensionless quantities but have different numerical values due to different standard states.

Problem 4

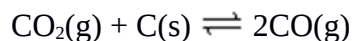
The value of K_p for the reaction,
 $\text{CO}_2(\text{g}) + \text{C}$



$p_{\text{CO}_2} = 0.48 \text{ bar}$ and $p_{\text{CO}} = 0 \text{ bar}$ and pure graphite is present, calculate the equilibrium partial pressures of CO and CO_2 .

Solution

For the reaction, let 'x' be the amount of CO_2 reacted, then



Initial pressure: 0.48 bar 0

At equilibrium:

(0.48 - x) bar 2x bar

$$K_p = \frac{p_{\text{CO}}^2}{p_{\text{CO}_2}}$$

$$K_p = (2x)^2 / (0.48 - x) = 3$$

$$4x^2 = 3(0.48 - x)$$

$$4x^2 = 1.44 - x$$

$$4x^2 + 3x - 1.44 = 0$$

$$a = 4, b = 3, c = -1.44$$

$$x = \frac{(-b \pm \sqrt{b^2 - 4ac})}{2a}$$

$$= [-3 \pm \sqrt{(3)^2 - 4(4)(-1.44)}] / 2 \times 4$$

$$= (-3 \pm 5.66) / 8$$

$$= (-3 + 5.66) / 8 \text{ (as value of } x \text{ cannot be negative hence we neglect that value)}$$

$$x = 2.66 / 8 = 0.33$$

The equilibrium partial pressures are,

$$p_{\text{CO}} = 2x = 2 \times 0.33 = 0.66 \text{ bar}$$

$$p_{\text{CO}_2} = 0.48 - x = 0.48 - 0.33 = 0.15 \text{ bar}$$

4. Applications of Equilibrium Constants

Before considering the applications of equilibrium constants, let us summarise the important features of equilibrium constants as follows:

1. Equilibrium constant is applicable only when concentrations of the reactants and products have attained their equilibrium state.
2. The value of equilibrium constant is independent of initial concentrations of the reactants and products.
3. Equilibrium constant is temperature dependent having one unique value for a particular reaction represented by a balanced equation at a given temperature.

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- The equilibrium constant for the reverse reaction is equal to the inverse of the equilibrium constant for the forward reaction.
 - 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.

Let us consider the applications of equilibrium constant to:

- predict the extent of a reaction on the basis of its magnitude,
- predict the direction of the reaction, and
- calculate equilibrium concentrations.

Predicting the Extent of a Reaction

The numerical value of the equilibrium constant for a reaction indicates the extent of the reaction. But it is important to note that an equilibrium constant does not give any information about the rate at which the equilibrium is reached. The magnitude of K_c or K_p is directly proportional to the concentrations of products (as these appear in the numerator of equilibrium constant expression) and inversely proportional to the concentrations of the reactants (these appear in the denominator). This implies that a high value of K is suggestive of a high concentration of products and vice-versa.

We can make the following generalisations concerning the composition of equilibrium mixtures:

- If $K_c > 10^3$, products predominate over reactants, i.e., if K_c is very large, the reaction proceeds nearly to completion. Consider the following examples:

(a) The reaction of H_2 with O_2 at 500 K has a very large equilibrium constant, $K_c = 2.4 \times 10^{47}$

(b) $H_2(g) + Cl_2(g) \rightleftharpoons 2HCl(g)$ at 300K has $K_c = 4.0 \times 10^{31}$

(c) $H_2(g) + Br_2(g) \rightleftharpoons 2HBr(g)$ at 300 K, $K_c = 5.4 \times 10^{18}$

- If $K_c < 10^{-3}$, reactants predominate over products, i.e., if K_c is very small, the reaction proceeds rarely. Consider the following examples:

(a) The decomposition of H_2O into H_2 and O_2 at 500 K has a very small equilibrium constant, $K_c = 4.1 \times 10^{-48}$

(b) $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{NO}(\text{g})$, at 298 K has $K_c = 4.8 \times 10^{-31}$.

- If K_c is in the range of 10^{-3} to 10^3 , appreciable concentrations of both reactants and products are present. Consider the following examples:

(a) For reaction of H_2 with I_2 to give HI , $K_c = 57.0$ at 700K.

(b) Also, gas phase decomposition of N_2O_4 to NO_2 is another reaction with a value of $K_c = 4.64 \times 10^{-3}$ at 25°C which is neither too small nor too large. Hence, equilibrium mixtures contain appreciable concentrations of both N_2O_4 and NO_2 . These generalisations are illustrated in Fig. 1

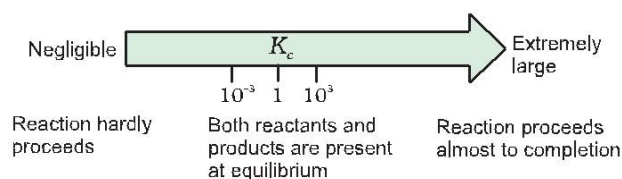
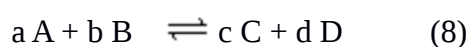


Fig. 1 Dependence of extent of reaction on K_c

Predicting the Direction of the Reaction

The equilibrium constant helps in predicting the direction in which a given reaction will proceed at any stage. For this purpose, we calculate the **reaction quotient Q**. The reaction quotient, Q (Q_c with molar concentrations and Q_p with partial pressures) is defined in the same way as the equilibrium constant K_c except that the concentrations in Q_c are not necessarily equilibrium values. For a general reaction:



$$Q = \frac{[\text{C}]^c[\text{D}]^d}{[\text{A}]^a[\text{B}]^b} \quad (9)$$

c

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 proceed in the direction of the products (forward reaction).

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

Consider the gaseous reaction of H_2 with I_2 ,



Suppose we have molar concentrations, $[H_2]_t = 0.10M$, $[I_2]_t = 0.20 M$ and $[HI]_t = 0.40 M$. (the subscript t on the concentration symbols means that the concentrations were measured at some arbitrary time t, not necessarily at equilibrium).

Thus, the reaction quotient, Q_c at this stage of the reaction is given by,

$$\begin{aligned} Q_c &= \frac{[HI]_t^2}{[H_2]_t [I_2]_t} = \frac{(0.40)^2}{(0.10) \times (0.20)} \\ &= 8.0 \end{aligned}$$

Now, in this case, Q_c (8.0) does not equal K_c (57.0) and so the mixture of $H_2(g)$, $I_2(g)$ and $HI(g)$ is not at equilibrium; that is, more $H_2(g)$ and $I_2(g)$ will react to form more $HI(g)$ and their concentrations will decrease till $Q_c = K_c$.

The reaction quotient, Q_c is useful in predicting the direction of reaction by comparing the values of Q_c and K_c .

Thus, we can make the following generalisations concerning the direction of the reaction (Fig. 2) :

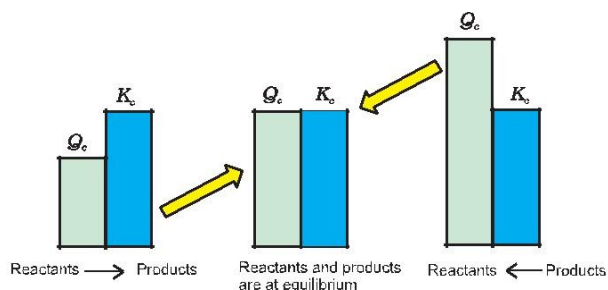


Fig. 2 Predicting the direction of the reaction

- If $Q_c < K_c$, net reaction goes from left to right
- If $Q_c > K_c$, net reaction goes from right to left.
- If $Q_c = K_c$, no net reaction occurs.

Problem 5

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

Solution:

For the reaction, the reaction quotient Q_c is given by,

$$Q_c = [B][C] / [A]^2$$

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

$Q_c = (3 \times 10^{-4})(3 \times 10^{-4}) / (3 \times 10^{-4})^2 = 1$ as $Q_c > K_c$ so the reaction will proceed in the reverse direction

Calculating Equilibrium Concentrations

In case of a problem in which we know the initial concentrations but do not know any of the equilibrium concentrations, the following three steps shall be followed:

Step 1. Write the balanced equation for the reaction.

Step 2. Under the balanced equation, make a table that lists for each substance involved in the reaction:

- (a) the initial concentration,
- (b) the change in concentration on going to equilibrium, and
- (c) the equilibrium concentration.

In constructing the table, define x as the concentration (mol/L) of one of the substances that reacts on going to equilibrium, then use the stoichiometry of the reaction to determine the concentrations of the other substances in terms of x .

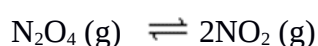
Step 3. Substitute the equilibrium concentrations into the equilibrium equation for the reaction and solve for x . If you are to solve a quadratic equation choose the mathematical solution that makes chemical sense.

Step 4. Calculate the equilibrium concentrations from the calculated value of x .

Step 5. Check your results by substituting them into the equilibrium equation.

Problem 6

13.8g of N_2O_4 was placed in a 1L reaction vessel at 400K and allowed to attain equilibrium



The total pressure at equilibrium was found to be 9.15 bar. Calculate K_c , K_p and partial pressure at equilibrium.

Solution:

We know that $pV = nRT$

Total volume (V) = 1 L

Molecular mass of $N_2O_4 = 92$ g

Number of moles of the gas (n) = $13.8g/92$ g = 0.15

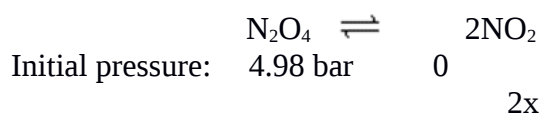
Gas constant (R) = 0.083 bar L mol⁻¹K⁻¹

Temperature (T) = 400 K

$$pV = nRT$$

$$p \times 1L = 0.15 \text{ mol} \times 0.083 \text{ bar L mol}^{-1}\text{K}^{-1} \times 400 \text{ K}$$

$$p = 4.98 \text{ bar}$$



At equilibrium: (4.98 - x) bar bar

Hence,

$$P_{\text{total}} \text{ at equilibrium} = p_{N_2O_4} + p_{NO_2}$$

$$9.15 = (4.98 - x) + 2x$$

$$9.15 = 4.98 + x$$

$$x = 9.15 - 4.98 = 4.17 \text{ bar}$$

Partial pressures at equilibrium are,

$$p_{N_2O_4} = 4.98 - 4.17 = 0.81 \text{ bar}$$

$$p_{NO_2} = 2x = 2 \times 4.17 = 8.34 \text{ bar}$$

$$K_p = \frac{p_{\text{NO}_2}^2}{p_{\text{N}_2\text{O}_4}}$$

$$= \frac{(8.34)^2}{0.81} = 85.87$$

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

$$85.87 = K_c (0.083 \times 400)^1$$

$$K_c = 2.586 = 2.6$$

5. Relationship Between Equilibrium Constant K , Reaction Quotient Q and Gibbs Energy G

The value of K_c for a reaction does not depend on the rate of the reaction. However, as you have studied in Unit on Thermodynamics, it is directly related to the thermodynamics of the reaction and in particular, to the change in Gibbs energy, ΔG . If,

- ΔG is negative, then the reaction is spontaneous and proceeds in the forward direction.
- ΔG is positive, then the reaction is considered non-spontaneous. Instead, as reverse reaction would have a negative ΔG , the products of the forward reaction shall be converted to the reactants.
- ΔG is 0, the reaction has achieved equilibrium; at this point, there is no longer any free energy left to drive the reaction.

A mathematical expression of this thermodynamic view of equilibrium can be described by the following equation:

$$\Delta G = \Delta G^0 + RT \ln Q \quad (10)$$

where, G^0 is standard Gibbs energy.

At equilibrium, when $\Delta G = 0$ and $Q = K_c$, the equation (7.21) becomes,

$$\Delta G = \Delta G^0 + RT \ln K = 0$$

$$\Delta G^0 = -RT \ln K \quad (11)$$

$$\ln K = -\Delta G^0 / RT$$

Taking antilog of both sides, we get,

$$K = e^{-\Delta G^0 / RT}$$

$$(12)$$

Hence, using the equation (12), the reaction spontaneity can be interpreted in terms of the value of

ΔG^0 .

- If $\Delta G^0 < 0$, then $-\Delta G^0/RT$ is positive, and $e^{-\Delta G^0/RT} > 1$, making $K > 1$, which implies a spontaneous reaction or the reaction which proceeds in the forward direction to such an extent that the products are present predominantly.
- If $\Delta G^0 > 0$, then $-\Delta G^0/RT$ is negative, and $e^{-\Delta G^0/RT} < 1$, that is, $K < 1$, which implies a non-spontaneous reaction or a reaction which proceeds in the forward direction to such a small degree that only a very minute quantity of product is formed.

6. Factors Affecting Equilibria

One of the principal goals of chemical synthesis is to maximise the conversion of the reactants to products while minimizing the expenditure of energy. This implies maximum yield of products at mild temperature and pressure conditions. If it does not happen, then the experimental conditions need to be adjusted. For example, in the Haber process for the synthesis of ammonia from N_2 and H_2 , the choice of experimental conditions is of real economic importance. Annual world production of ammonia is about hundred million tons, primarily for use as fertilizers.

Equilibrium constant, K_c is independent of initial concentrations. But if a system at equilibrium is subjected to a change in the concentration of one or more of the reacting substances, then the system is no longer at equilibrium; and net reaction takes place in some direction until the system returns to equilibrium once again. Similarly, a change in temperature or pressure of the system may also alter the equilibrium. In order to decide what course the reaction adopts and make a qualitative prediction about the effect of a change in conditions on equilibrium we use

Le Chatelier's principle. It states that a **change in any of the factors that determine the equilibrium conditions of a system will cause the system to change in such a manner so as to reduce or to counteract the effect of the change.** This is applicable to all physical and chemical equilibria.

We shall now be discussing factors which can influence the equilibrium.

Effect of Concentration Change

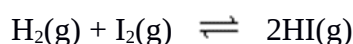
In general, when equilibrium is disturbed by the addition/removal of any reactant/ products, Le Chatelier's principle predicts that:

- The concentration stress of an added reactant/product is relieved by net reaction in the direction that consumes the added substance.
- The concentration stress of a removed reactant/product is relieved by net reaction in the direction that replenishes the removed substance.

or in other words,

“When the concentration of any of the reactants or products in a reaction at equilibrium is changed, the composition of the equilibrium mixture changes so as to minimize the effect of concentration changes”.

Let us take the reaction,



If H_2 is added to the reaction mixture at equilibrium, then the equilibrium of the reaction is disturbed. In order to restore it, the reaction proceeds in a direction wherein H_2 is consumed, i.e., more of H_2 and I_2 react to form HI and finally the equilibrium shifts in right (forward) direction (Fig.3). This is in accordance with the Le Chatelier’s principle which implies that in case of addition of a reactant/product, a new equilibrium will be set up in which the concentration of the reactant/product should be less than what it was after the addition but more than what it was in the original mixture.

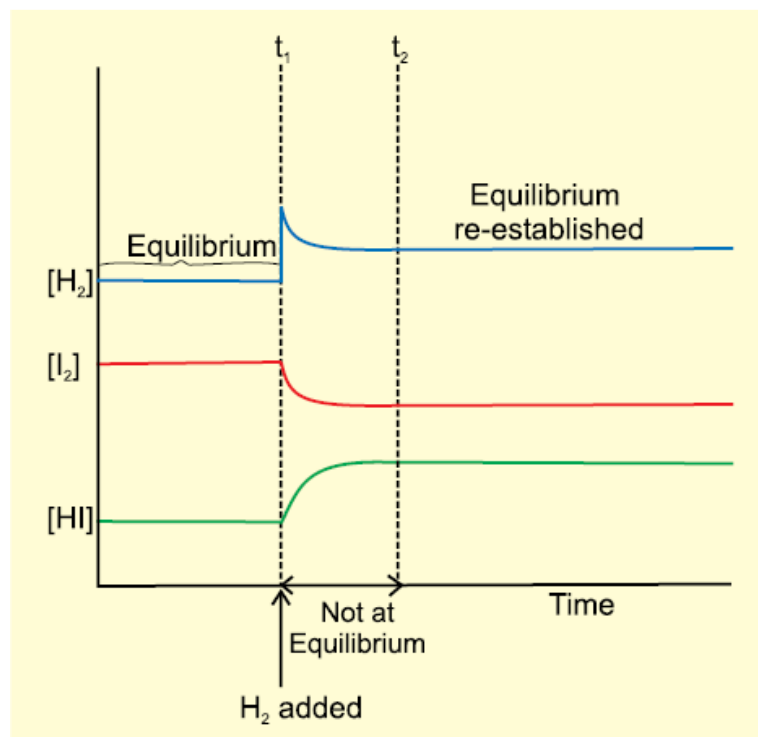


Fig. 3 Effect of addition of H_2 on change of concentration for the reactants and products in the reaction, $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$

The same point can be explained in terms of the reaction quotient, Q_c ,

$$Q_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]}$$

Addition of hydrogen at equilibrium results in value of Q_c being less than K_c . Thus, in order to attain equilibrium again reaction moves in the forward direction. Similarly, we can say that removal of a product also boosts the forward reaction and increases the concentration of the products and this has great commercial application in cases of reactions, where the product is a gas or a volatile substance. In case of manufacture of ammonia, ammonia is liquified and removed from the reaction mixture so that reaction keeps moving in forward direction. Similarly, in the large scale production of CaO (used as important building material) from CaCO_3 , constant removal of CO_2 from the kiln drives the reaction to completion. It should be remembered that continuous removal of a product maintains Q_c at a value less than K_c and reaction continues to move in the forward direction.

Effect of Concentration - An experiment

This can be demonstrated by the following reaction:



$$K_c = \frac{[\text{Fe}(\text{SCN})^{2+}(\text{aq})]}{[\text{Fe}^{3+}(\text{aq})][\text{SCN}^{-}(\text{aq})]} \quad (14)$$

A reddish colour appears on adding two drops of 0.002 M potassium thiocyanate solution to 1 mL of 0.2 M iron(III) nitrate solution due to the formation of $[\text{Fe}(\text{SCN})]^{2+}$. The intensity of the red colour becomes constant on attaining equilibrium. This equilibrium can be shifted in either forward or reverse directions depending on our choice of adding a reactant or a product. The equilibrium can be shifted in the opposite direction by adding reagents that remove Fe^{3+} or SCN^{-} ions. For example, oxalic acid ($\text{H}_2\text{C}_2\text{O}_4$), reacts with Fe^{3+} ions to form the stable complex ion $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$, thus decreasing the concentration of free $\text{Fe}^{3+}(\text{aq})$. In accordance with the Le

Chatelier's principle, the concentration stress of removed Fe^{3+} is relieved by dissociation of $[\text{Fe}(\text{SCN})]^{2+}$ to

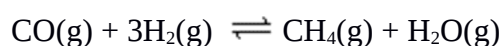
replenish the Fe^{3+} ions. Because the concentration of $[\text{Fe}(\text{SCN})]^{2+}$ decreases, the intensity of red colour decreases.

Addition of aq. HgCl_2 also decreases red colour because Hg^{2+} reacts with SCN^- ions to form stable complex ion $[\text{Hg}(\text{SCN})_4]^{2-}$. Removal of free SCN^- (aq) shifts the equilibrium in equation (13) from right to left to replenish SCN^- ions. Addition of potassium thiocyanate on the other hand increases the colour intensity of the solution as it shift the equilibrium to right.

Effect of Pressure Change

A pressure change obtained by changing the volume can affect the yield of products in case of a gaseous reaction where the total number of moles of gaseous reactants and total number of moles of gaseous products are different. In applying Le Chatelier's principle to a heterogeneous equilibrium the effect of pressure changes on solids and liquids can be ignored because the volume (and concentration) of a solution/liquid is nearly independent of pressure.

Consider the reaction,



Here, 4 mol of gaseous reactants ($\text{CO} + 3\text{H}_2$) become 2 mol of gaseous products ($\text{CH}_4 + \text{H}_2\text{O}$). Suppose equilibrium mixture (for above reaction) kept in a cylinder fitted with a piston at constant temperature is compressed to one half of its original volume. Then, total pressure will be doubled (according to $pV = \text{constant}$). The partial pressure and therefore, concentration of reactants and products have changed and the mixture is no longer at equilibrium. The direction in which the reaction goes to re-establish equilibrium can be predicted by applying the Le Chatelier's principle. Since pressure has doubled, the equilibrium now shifts in the forward direction, a direction in which the number of moles of the gas or pressure decreases (we know pressure is proportional to moles of the gas). This can also be understood by using reaction quotient, Q_c . Let $[\text{CO}]$, $[\text{H}_2]$, $[\text{CH}_4]$ and $[\text{H}_2\text{O}]$ be the molar concentrations at equilibrium for methanation reaction. When volume of the reaction mixture is halved, the partial pressure and the concentration are doubled. We obtain the reaction quotient by replacing each equilibrium concentration by double its value.

$$Q_c = \frac{[\text{CH}_4(\text{g})][\text{H}_2\text{O}(\text{g})]}{[\text{CO}(\text{g})][\text{H}_2(\text{g})]^3}$$

As $Q_c < K_c$, the reaction proceeds in the forward direction.

In reaction $\text{C}(\text{s}) + \text{CO}_2(\text{g}) \rightleftharpoons 2\text{CO}(\text{g})$, when pressure is increased, the reaction goes in the reverse direction because the number of moles of gas increases in the forward direction.

Effect of Inert Gas Addition

If the volume is kept constant and an inert gas such as argon is added which does not take part in the reaction, the equilibrium remains undisturbed. It is because the addition of an inert gas at constant volume does not change the partial pressures or the molar concentrations of the substance involved in the reaction. The reaction quotient changes only if the added gas is a reactant or product involved in the reaction.

Effect of Temperature Change

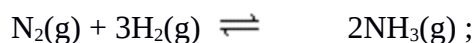
Whenever an equilibrium is disturbed by a change in the concentration, pressure or volume, the composition of the equilibrium mixture changes because the reaction quotient, Q_c no longer equals the equilibrium constant, K_c . However, when a change in temperature occurs, the value of equilibrium constant, K_c is changed.

In general, the temperature dependence of the equilibrium constant depends on the sign of ΔH for the reaction.

- The equilibrium constant for an exothermic reaction (negative ΔH) decreases as the temperature increases.
- The equilibrium constant for an endothermic reaction (positive ΔH) increases as the temperature increases.

Temperature changes affect the equilibrium constant and rates of reactions.

Production of ammonia according to the reaction,

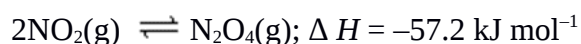


$$\Delta H = -92.38 \text{ kJ mol}^{-1}$$

is an exothermic process. According to Le Chatelier's principle, raising the temperature shifts the equilibrium to left and decreases the equilibrium concentration of ammonia. In other words, low temperature is favourable for high yield of ammonia, but practically very low temperatures slow down the reaction and thus a catalyst is used.

Effect of Temperature - An experiment

Effect of temperature on equilibrium can be demonstrated by taking NO_2 gas (brown in colour) which dimerises into N_2O_4 gas (colourless).



NO_2 gas prepared by addition of Cu turnings to conc. HNO_3 is collected in two 5 mL test tubes (ensuring same intensity of colour of gas in each tube) and stopper sealed with araldite. Three 250 mL beakers 1, 2 and 3 containing freezing mixture, water at room temperature and hot water (363K), respectively, are taken (Fig. 4). Both the test tubes are placed in beaker 2 for 8-10 minutes. After this one is placed in beaker 1 and the other in beaker 3. The effect of temperature on direction of reaction is depicted very well in this experiment. At low temperatures in beaker 1, the forward reaction of formation of N_2O_4 is preferred, as reaction is exothermic, and thus, intensity of brown colour due to NO_2 decreases. While in beaker 3, high temperature favours the reverse reaction of formation of NO_2 and thus, the brown colour intensifies.

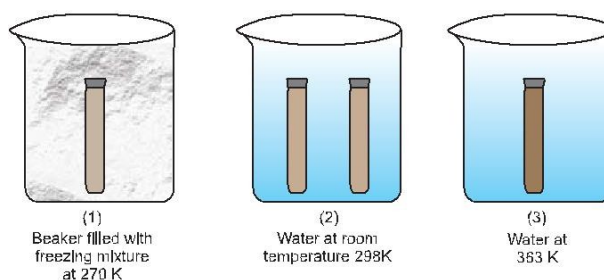
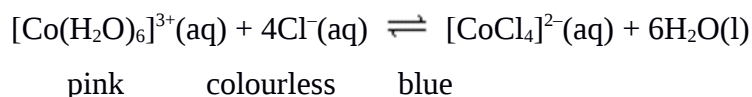


Fig.4 Effect of temperature on equilibrium for the reaction, $2\text{NO}_2(\text{g}) \rightleftharpoons \text{N}_2\text{O}_4(\text{g})$

Effect of temperature can also be seen in an endothermic reaction,



At room temperature, the equilibrium mixture is blue due to $[\text{CoCl}_4]^{2-}$. When cooled in a freezing mixture, the colour of the mixture turns pink due to $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$.

Effect of a Catalyst

A catalyst increases the rate of the chemical reaction by making available a new low energy pathway for the conversion of reactants to products. It increases the rate of forward and reverse reactions that pass through the same transition state and does not affect equilibrium. Catalyst lowers the activation energy for the forward and reverse reactions by exactly the same amount. Catalyst does not affect the equilibrium composition of a reaction mixture. It does not appear in the balanced chemical equation or in the equilibrium constant expression.

Let us consider the formation of NH_3 from dinitrogen and dihydrogen which is highly exothermic reaction and proceeds with decrease in total number of moles formed as compared to the reactants. Equilibrium constant decreases with increase in temperature. At low temperature rate decreases and it takes long time to reach at equilibrium, whereas high temperatures give satisfactory rates but poor yields.

German chemist, Fritz Haber discovered that a catalyst consisting of iron catalyse the reaction to occur at a satisfactory rate at temperatures, where the equilibrium concentration of NH_3 is reasonably favourable. Since the number of moles formed in the reaction is less than those of reactants, the yield of NH_3 can be improved by increasing the pressure.

Optimum conditions of temperature and pressure for the synthesis of NH_3 using catalyst are around 500°C and 200 atm.

Similarly, in manufacture of sulphuric acid by contact process,



though the value of K is suggestive of reaction going to completion, but practically the oxidation of SO_2 to SO_3 is very slow. Thus, platinum or divanadium penta-oxide (V_2O_5) is used as catalyst to increase the rate of the reaction.

Note: If a reaction has an exceedingly small K , a catalyst would be of little help.

7. Summary

Equilibrium constant has a constant value at a fixed temperature and at this stage all the macroscopic properties such as concentration, pressure, etc. become constant.

Le Chatelier's principle states that the change in any factor such as temperature, pressure, concentration, etc. will cause the equilibrium to shift in such a direction so as to reduce or counteract the effect of the change. It can be used to study the effect of various factors such as temperature, concentration, pressure, catalyst and inert gases on the direction of equilibrium and to control the yield of products by controlling these factors. **Catalyst** does not effect the equilibrium composition of a reaction mixture but increases the rate of chemical reaction by making available a new lower energy pathway for conversion of reactants to products and vice-versa. Addition of inert gas at constant volume has no effect but at constant pressure the reaction moves in the direction with higher number of gaseous moles.