Chapter- 7: Equilibrium

1. Equilibrium State: It is represents the state of a process in which the properties like temperature, pressure etc do not show any change with the passage of time.

i) Homogeneous Equilibria: In a Homogeneous Equilibrium system, all the reactants and products are in the same phase. For example, in the gaseous reaction, $N_2 (g) + 3H_2 (g) \rightleftharpoons 2NH_3 (g)$, reactants and products are in the homogeneous phase.

ii) Heterogeneous Equilibrium System: When equilibrium in a system having more than one phase is called heterogeneous equilibrium system. The equilibrium between water vapor and liquid water in a closed container is an example of heterogeneous equilibrium. For example

$$H_2O (l) \rightleftharpoons H_2O (g)$$

$$CaCO_3 (s) \rightleftharpoons CaO (s) + CO_2 (g)$$

2. Equilibrium in physical processes: Physical equilibrium is defined as the equilibrium which develops between different phases or physical properties. In these processes, there is no change in chemical composition. The following are some examples of Physical Equilibrium:

i) Solid-Liquid Equilibrium
ii) Liquid-Gas Equilibrium
iii) Solid-Vapor Equilibrium

i) Solid-Liquid Equilibrium: Consider ice and water in a perfectly insulated thermos flask at 0°C in an open atmosphere. There will be no change in the level of water and quantity of ice, which implies that the rate of transfer of molecules from water to ice is equal to the rate of transfer of molecules from ice to water. Hence, we can conclude that this system is in steady state. This can be represented by the following equation:

$$H_2O (s) \rightleftharpoons H_2O (l)$$

Rate of melting = Rate of freezing

ii) Liquid-Gas Equilibrium: Take distilled water in a closed container and start heating, the water converts to vapour. After a certain time, we will observe that the level of water becomes constant implying that there is no more conversion of water to vapour and vice-versa. We can technically say that the rate of evaporation (liquid to vapour) is equal to the rate of condensation (vapour to liquid) thus achieving steady state. This equation can be represented by the following equation:

$$H_2O (l) \rightleftharpoons H_2O (g)$$

Rate of evaporation = Rate of condensation

iii) Solid-Vapor Equilibrium: This kind of equilibrium can exist only in case of sublimates (solid directly converts to vapour). Consider heating of solid iodine in a closed container, slowly the vessel is filled with violet coloured vapour and the intensity of color increases with time. After a certain time, the intensity of color doesn’t change with time. This implies steady state is attained where the rate of sublimation of solid iodine is equal to the rate of deposition of iodine vapour.

$$I_2 (s) \rightleftharpoons I_2 (vap)$$

$$\text{Camphor (s)} \rightleftharpoons \text{Camphor (vap)}$$

Rate of sublimation = Rate of deposition

3. Equilibrium involving Dissolution of Solid or Gases in Liquids:

i) Solids in liquids: During dissolving sugar in water, we observe that after adding certain quantity, the added sugar gets deposited. We call a solution saturated when the solution cannot dissolve any more solute in it, at a given temperature. In a saturated solution, a dynamic equilibrium exists between solute molecules in the solid state and in the solution at given temperature. The increase in temperature increases the solubility of the solution i.e. solubility depends on temperature.

$$\text{Sugar (solution)} \rightleftharpoons \text{sugar (solid)}$$

Rate of dissolution of sugar = Rate of crystallization of sugar

ii) Gases in Liquids: When the gas fizzing out from the cold drink at room temperature is more than the drink that is refrigerated. This happens because the solubility of carbon dioxide at different pressures.

The relation between the quantity of gas dissolved can be given by **Henry's Law**. This law states that the mass of a gas dissolved in the given amount of solvent at any temperature is proportional to the pressure of the gas above the solvent. The solubility of gases decreases with increase in temperature.

$$[\text{Mass of the gas}] \ \alpha \ [\text{pressure of the gas}]$$

$$m \ \alpha \ p$$

$$m = kHp$$

Where kH is the proportionality constant, called Henry's law constant and depends on the temperature.

4. General Characteristics of Equilibria involving Physical Process: from NCERT pg- 189

5. Equilibrium in chemical processes (Dynamic Equilibrium): Chemical equilibrium is a state in which the rate of the forward reaction equals the rate of the backward reaction. In other words, there is no net change in concentrations of reactants and products. This kind of equilibrium is also called dynamic equilibrium. Equilibrium is possible only in a closed system at a given temperature. A mixture of reactants and products in the equilibrium state is called an equilibrium mixture.

6. Law of chemical equilibrium and equilibrium constant: Guldberg and Waage (Norwegian Chemists) worked on so many equilibrium reactions and postulated a generalization called the Law of Mass action, which is based on the Molecular Collision theory. According to it "the rate of a chemical reaction is proportional to the active masses of the reactants". By the term `active mass', it is meant the molar concentration i.e., number of moles per litre.

Let us suppose a simple reversible reaction: $A + B \rightleftharpoons C + D$
According to the law of mass action,
Rate of forward reaction = $K_f [A] [B]$
Where K_f is the rate constant for the forward reaction and [A] and [B] are molar concentrations of the products A and B respectively.
Rate of backward reaction = $K_b [C] [D]$
Where K_b is the rate constant for the backward reaction and [C] and [D] are molar concentrations of the products C and D respectively.

At equilibrium, the rate of two opposing reactions becomes equal, so
Rate of forward reaction = Rate of backward reaction
$K_f [A] [B] = K_b [C] [D]$
$K_f / K_b = [C] [D] / [A] [B]$

At any specific temperature, the ratio K_f / K_b is called equilibrium constant and is represented by the symbol Kc. The subscript `c' indicates that the value is in terms of concentration of reactants and products. The equation (1) may be written as

$$K_c = \frac{[C]\ [D]}{[A]\ [B]}$$

This equation is known as the equilibrium constant expression or equilibrium law.
For a general reaction: $aA + bB \rightleftharpoons cC + dD$
The equilibrium constant will be given as

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

Where a, b, c and d are numerical quotients of the substance A, B, C and D respectively. The general definition of the equilibrium constant may thus be stated as:
The product of the equilibrium concentrations of the products divided by the product of the equilibrium concentrations of the reactants, with each concentration term raised to a power equal to the coefficient of the substance in the balanced equation.
For Example, consider the equilibrium constant expression for the reaction
$N_2 (g) + 3H_2 (g) \rightleftharpoons 2NH_3 (g)$
$Kc = [NH_3]^2 / [N_2] [H_2]^3$
The equilibrium constant for the reverse reaction $2NH_3 (g) \rightleftharpoons N_2 (g) + 3H_2 (g)$
$K'c = [N_2] [H_2]^3 / [NH_3]^2$
So $K'c = 1/ Kc$
The equilibrium constant for the reaction $naA + nbB \rightleftharpoons ncC + ndD$
$K''c = Kc^n$

7. Equilibrium Constant Expression in Gaseous System or in Homogeneous system (Relationship between Kp and Kc):

For a general equilibrium reaction: $aA + bB \rightleftharpoons cC + dD$

The equilibrium constant will be given as

$$Kc = \frac{[C]^c\,[D]^d}{[A]^a\,[B]^b} \quad \text{------ (1)}$$

Where a, b, c and d are numerical quotients of the substance A, B, C and D respectively. If the equilibrium involves gaseous species, then the concentrations may be expressed in terms of partial pressures of the gaseous substance. So the equilibrium constant in terms of partial pressures may be given as:

$$Kp = \frac{p_C{}^c\, p_D{}^d}{p_A{}^a\, p_B{}^b} \quad \text{--------- (2)}$$

Where p_A, p_B, p_C and p_D represents the partial pressures of the substance A, B, C and D respectively. If gases are assumed to be ideal, then according to ideal gas equation:

$$Pv = nRT$$

$$P = nRT / V$$

Where p is the pressure in Pa, n is the amount of gas in moles, V is the Volume in m^3 and T is the temperature in Kelvin.

Hence $n/V = C$ (concentration in mole/m^3)

The $p = CRT$ or [gas] RT

Here $R = 0.0831$ bar litre $mol^{-1}\,K^{-1}$

Therefore, at constant temp, the pressure of the gas P is proportional to its concentration C, i.e

$p \,\alpha\, C$

While, $p = CRT$

Hence, $p_A = [A]\,RT$, where [A] is the molar concentration of A, Similarly

$p_B = [B]\,RT$

$p_C = [C]\,RT$

$p_D = [D]\,RT$

Substituting these values in expression for Kp i.e. in equation (2)

$$Kp = \frac{p_C{}^c\, p_D{}^d}{p_A{}^a\, p_B{}^b} = \frac{[C]^c\,[D]^d\,[RT]^{(c+d)}}{[A]^a\,[B]^b\,[RT]^{(a+b)}}$$

$$Kp = \frac{[C]^c\,[D]^d}{[A]^a\,[B]^b}\,[RT]^{(c+d)-(a+b)}$$

$$Kp = \frac{[C]^c\,[D]^d}{[A]^a\,[B]^b}\,[RT]^{\Delta n}$$

$$Kp = Kc\,(RT)^{\Delta n}$$

Where Δn = (c + d) – (a + b) i.e. number of moles of gaseous products – number of moles of gaseous reactants in the balanced chemical reaction.

For example in equilibrium reaction: $H_2 (g) + I_2 (g) \rightleftharpoons 2HI (g)$

$Kp = Kc$

$N_2 (g) + 3H_2 (g) \rightleftharpoons 2NH_3 (g)$

$Kp = Kc (RT)^{-2}$

Note: During calculation the value of Kp, pressure should be expressed in bar.

1 pascal (Pa) = $1Nm^{-2}$ and 1 bar= 10^5Pa

8. Equilibrium constant expression in Heterogeneous system: Heterogeneous equilibrium reaction composed of a variety of phases like solid (s), liquid (l), gas (g) and aqueous (aq). During expression of equilibrium constant for heterogeneous equilibrium reactions, we cannot consider the liquid and solid phase of reactant and product because they cannot change their concentration because they are pure substances.

For Example i) $CaCO_3 (s) \rightleftharpoons CaO (s) + CO_2 (g)$

$Kc = [CO_2]$

$Kp = p_{CO_2}$

Example ii) $Ni (s) + 4CO (g) \rightleftharpoons Ni(CO)_4 (g)$

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

Example iii) $Ag_2O + 2H_2O (aq) \rightleftharpoons 2AgNO_3 (aq) + H_2O(l)$

$$Kc = \frac{[AgNO_3]^2}{[HNO_3]^2}$$

9. Characteristics of Equilibrium Constant

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.
4) The equilibrium constant for the reverse reaction is equal to the inverse of the equilibrium constant for the forward reaction.
5) 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.

10. Applications of equilibrium constant:

1) Predict the extent of a reaction on the basis of its magnitude.
2) Predict the direction of the reaction
3) Calculate equilibrium concentrations.

1) Predict the extent of a reaction on the basis of its magnitude: Kc can be used to predict the extent of a reaction, i.e. the degree of disappearance of the reactants.

If Kc > 10^3 (very large) the products predominate over reactants leading to near completion of the forward reaction. The reverse reaction is negligible.

If Kc< 10^{-3} (very low), the reaction proceeds very rarely. Here the reactants dominate over the products, backward reaction is more prevalent.

If 10^{-3}<Kc< 10^3, there will be an appreciable amount of both products and reactants.

2) Predict the direction of the reaction: Equilibrium constant can be used to predict the direction of the reaction when a reaction has reached equilibrium. If a reaction is not at equilibrium, we can use the reaction quotient (Q). Reaction quotient (Qc expressed in terms of concentrations or Qp in terms of partial pressures) similar to the equilibrium constant except that the conditions are not at equilibrium, i.e. reaction quotient is ratio of concentration of products raised to their respective stoichiometric coefficients to concentration of reactants raised to their respective stoichiometric coefficients at any time in the reaction.

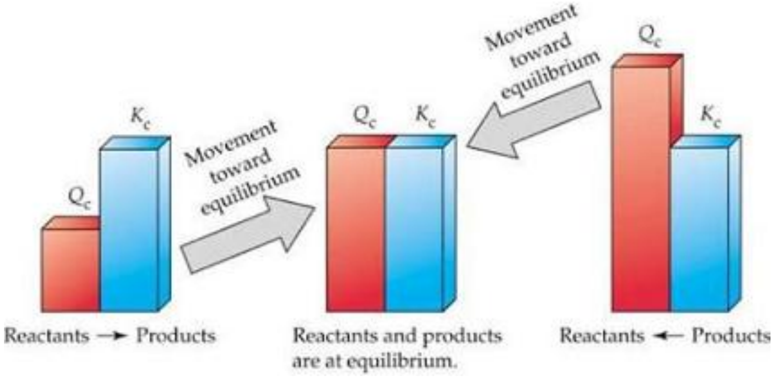
For a balanced reaction, a A + b B ⇌ c C + d D

Reaction quotient (Qc or Qp) is given as:

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

$$Q_p = \frac{p_C^c\, p_D^d}{p_A^a\, p_B^b}$$

Qc > Kc The result will move backwards i.e. in the direction of reactants (reverse reaction).
Qc < Kc The reaction will move forward i.e. in the directions of products (forward reaction).
Qc = Kc The reaction is at equilibrium.



If we know the equilibrium constant for a reaction, and also know about all the concentrations, we can predict the direction of the reaction will proceed.

Example 1: If 1.0 x 10^{-2} moles of hydrogen gas and 1.0 x 10^{-2} moles of iodine gas are placed in a 1-liter flask at 448°C with 2.0 x 10^{-3} moles of HI, while equilibrium value is 50.53, will more HI be produced?

Solution: The balanced equation for the reaction is: H_2 (g) +I_2 (g) ⇌2HI (g)

The reaction quotient under these conditions is:

$$Q = \frac{[HI]^2}{[H_2][I_2]}$$

$$Q = \frac{2.0 \cdot 10^{-3}}{(1.0 \cdot 10^{-3})^2} = 0.040$$

This value is smaller than the equilibrium value of 50.53, which tells us there is an excess amount of reactants present. Therefore, the reaction will proceed in the forward direction.

Example 2: If only 1.0 x 10^{-3} moles of H_2 and 1.0 x 10^{-3} moles I_2 had been used, together with 2.0 x 10^{-2} mole of HI, would more HI have been produced spontaneously?

Solution: After resolving, the value of reaction quotient is find out, Q = 400. This value is greater than the equilibrium value so there is now too much of the products for equilibrium to exist. Therefore, the reverse reaction is favored.

3) Calculate equilibrium concentrations: The easiest approach for calculating equilibrium concentrations is to use an ICE Table, which is an organized method to track which quantities are known and which need to be calculated. ICE stands for:

"I" is for the "initial" concentration or the initial amount

"C" is for the "change" in concentration or change in the amount from the initial state to Equilibrium "E" is for the "equilibrium" concentration or amount and represents the expression for the amounts at equilibrium.

Example 1: Hydrogenation of Ethylene For the gaseous hydrogenation reaction below, what is the concentration for each substance at equilibrium?

C_2H_4 (g) + H_2 (g) ⇌ C_2H_6 (g)

with Kc=0.98 characterized from previous experiments and with the following initial concentrations:

$[C_2H_4]_0 = 0.33$

$[H_2]_0 = 0.53$

Solution: First the equilibrium expression is written for this reaction:

Kc=[C_2H_6] / [C_2H_4] [H_2]= 0.98

ICE Table Method:

a) The concentrations for the reactants are added to the "Initial" row of the table. The initial amount of C_2H_6 is not mentioned, so it is given a value of 0. This amount will change over the course of the reaction.

b) The change in the concentrations is added to the table. Because ethane, C_2H_6 is a product, and there cannot have negative concentrations, the reactants must decrease in stoichiometric

intervals. To represent this, a positive or negative "x" is added to each column in the ICE table. The reactant concentrations change by -x, and product concentrations change show by +x.
c) Equilibrium is determined by adding "Initial" and Change" together.

ICE	C_2H_4	H_2	C_2H_6
Initial	0.33	0.53	0
Change	-x	-x	+x
Equilibrium	0.33-x	0.53-x	x

The expressions in the "Equilibrium" row are substituted into the equilibrium constant expression to find calculate the value of x. The equilibrium expression is simplified into a quadratic expression.

11. Relation b/w Equilibrium Constant (K) Reaction Quotient (Q) and Gibbs Energy (G): It can be given as

$$\Delta_r G = \Delta_r G^\circ + RT \ln Q$$

Where $\Delta_r G^\circ$ is change in standard Gibbs energy.
At equilibrium conditions $\Delta_r G = 0$ and Q = Kc then

$$\Delta_r G^\circ + RT \ln K = 0$$

$$\Delta_r G^\circ = -RT \ln K$$

$$\Delta_r G^\circ = -2.303RT \log K$$

$$\ln K = \frac{-\Delta_r G^\circ}{RT}$$

After taking antilog on both side we get,

$$K = e^{-\Delta_r G^\circ / RT}$$

- If ΔG° is negative (< 0) then K will be positive (>1), reaction should be spontaneous and proceeds in the forward direction to extend the products.
- If ΔG° is positive (> 0) then K will be negative (< 1), reaction should be non-spontaneous and proceeds in the forward direction to such a small degree of the products is formed.

12. Factors Affecting Equilibria: One of the major goals of chemical reactions is to extract maximum products from the given reactants and also to minimize the energy expenditure. In other words, we can say that at mild temperature and pressure there should be maximum yield of products. For example, if we take Haber's process in which ammonia is synthesized from N2 and H2, here economic condition should be kept in mind with the experiment. About hundred million tones of ammonia are produced every year for fertilizers and hence, efficiency plays a major role here.

To know about the overall change in the reaction due to effect of a change in the conditions on equilibrium, we use Le Chatelier's principle.

Le Chatelier's Principle: According to this, if there is any change in the factors that affect the equilibrium condition of the system, the system will counteract or reduce the effect of the overall change. This principle is applicable for both physical as well as chemical equilibrium.

1) **Effect of change of concentration:** 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 change. For eg:- H2(g) + I2(g) → 2HI(g)

If H2 is added to the reaction mixture at equilibrium, the equilibrium of the reaction is disturbed. In order to restore it, the reaction proceeds in a direction whereas H2 is consumed i.e more of H2 and I2 react to form HI and finally the equilibrium shifts in forward direction.

2) **Effect of change of pressure**: When the pressure is increased the equilibrium shifts in the direction in which the number of moles of the gas decreases.

Consider the reaction, CO (g) + 3H2 (g) ⇌ CH4 (g) + H2O (g) Here, 4 mol of gaseous reactants (CO + 3H2) become 2 mol of gaseous products (CH4 (g) + H2O).

so by Le Chatelier‘s principle. The increase in pressure will shift the equilibrium in the forward direction, a direction in which the number of moles of the gas or pressure decreases.

3) **Effect of change of Temperature:** When a change in temperature occurs, the value of equilibrium constant changes. 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 (-ve ΔH) decreases as the temperature increases. The equilibrium constant for an endothermic reaction (+ve ΔH) increases as the temperature increases. When the Temperature is increased the equilibrium shifts in the direction in of endothermic reaction.

Consider a reaction N_2 (g) + $3H_2$ (g) → $2NH_3$ (g) ΔH = -92.38Kj/mol

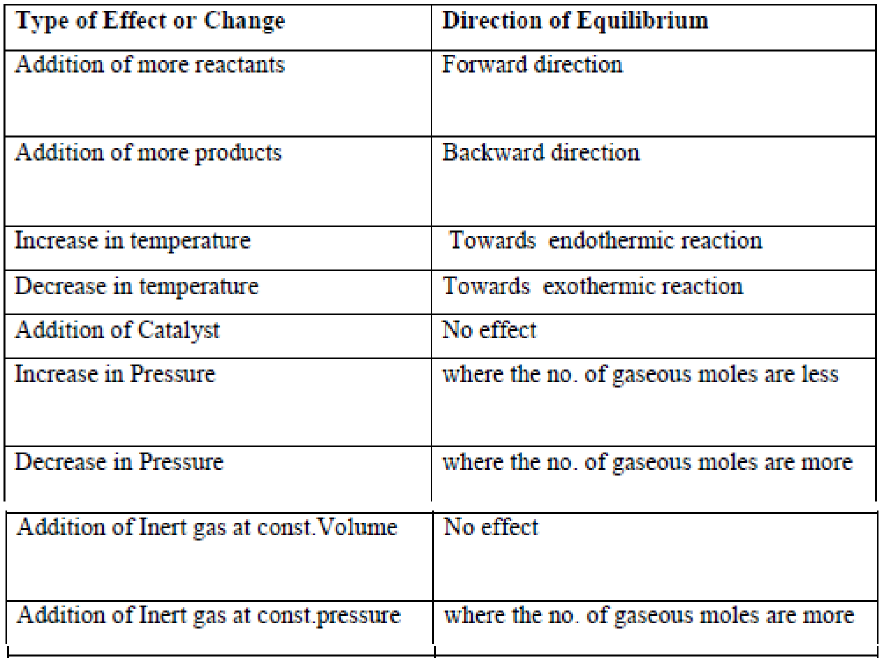
According to Le Chatelier‘s principle, raising the temperature shifts the equilibrium to left (backward direction i.e direction of endothermic reaction) and decreases the equilibrium concentration of ammonia.

4) **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.

5) **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.

Summary of Le Chatelier's Principle:



Type of Effect or Change	Direction of Equilibrium
Addition of more reactants	Forward direction
Addition of more products	Backward direction
Increase in temperature	Towards endothermic reaction
Decrease in temperature	Towards exothermic reaction
Addition of Catalyst	No effect
Increase in Pressure	where the no. of gaseous moles are less
Decrease in Pressure	where the no. of gaseous moles are more
Addition of Inert gas at const.Volume	No effect
Addition of Inert gas at const.pressure	where the no. of gaseous moles are more

7. Equilibrium: Some Important Formulas

1. Equilibrium constant in terms of molar concentration may be given as:

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

2. Equilibrium constant in terms of partial pressures may be given as:

$$Kp = \frac{p_C^{\,c}\,p_D^{\,d}}{p_A^{\,a}\,p_B^{\,b}} \quad \text{---------} \quad (2)$$

3. Relation b/w Kp and Kc: $Kp = Kc\,(RT)^{\Delta n}$

Where $\Delta n = (c + d) - (a + b)$ i.e. number of moles of gaseous products – number of moles of gaseous reactants in the balanced chemical reaction.

4. Equilibrium constant expression in Heterogeneous system: Heterogeneous equilibrium reaction composed of a variety of phases like solid (s), liquid (l), gas (g) and aqueous (aq). During expression of equilibrium constant for heterogeneous equilibrium reactions, we cannot consider the liquid and solid phase of reactant and product because they cannot change their concentration because they are pure substances.

For Example i) $CaCO_3\,(s) \rightleftharpoons CaO\,(s) + CO_2\,(g)$

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$$Kp = p_{CO_2}$$

Example ii) $Ni\,(s) + 4CO\,(g) \rightleftharpoons Ni(CO)_4\,(g)$

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

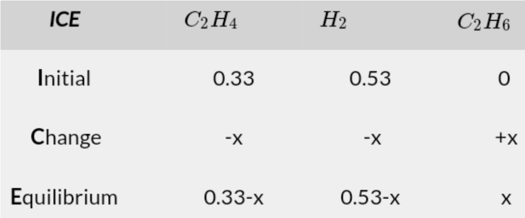
Example iii) $Ag_2O + 2H_2O\,(aq) \rightleftharpoons 2AgNO_3\,(aq) + H_2O\,(l)$

$$Kc = \frac{[AgNO_3]^2}{[HNO_3]^2}$$

5. Predict the direction of the reaction by value of Reaction Quotient (Qc) and Kc:

$Qc > Kc$ The result will move backwards i.e. in the direction of reactants (reverse reaction). $Qc < Kc$ The reaction will move forward i.e. in the directions of products (forward reaction). $Qc = Kc$ The reaction is at equilibrium.

6. ICE table:



ICE	C_2H_4	H_2	C_2H_6
Initial	0.33	0.53	0
Change	-x	-x	+x
Equilibrium	0.33-x	0.53-x	x

7. Relation b/w Equilibrium Constant (Kc) Reaction Quotient (Q) and Gibbs Energy (G):

$$\Delta G = \Delta G^\circ + RT \ln Q$$

Where $\Delta_r G^\circ$ is change in standard Gibbs energy. At equilibrium $\Delta_r G = 0$ and $Q = Kc$ then

$$\Delta G^\circ = -2.303\ RT \log Kc$$

8. Summary of Le Chatelier's Principle:

Type of Effect or Change	**Direction of Equilibrium**
Addition of more reactants	Forward direction
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