Chemical Equilibrium

The contents of this presentation is made to provide a brief idea about the topics, details will be discussed in the classes.
Contents have been collected from multiple textbooks and internet.

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Reversible Reactions

- *Some reactions are **ONE WAY** or **IRREVERSIBLE** reactions because the products do not combine to form the reactants, the reaction goes to completion until there is supply of the reactants.*

$$CH_4\,(g) + 3\,O_2\,(g) \longrightarrow CO_2\,(g) + 2\,H_2O\,(g)$$

$A + B \longrightarrow C + D$	*Forward reaction*
$C + D \longrightarrow A + B$	*Backward reaction*
$A + B \rightleftharpoons C + D$	*Reversible reaction*

- *Many reactions, however, are **REVERSIBLE**, which means, the reaction goes in both directions.*
- *Such reactions do not go to completion, reactants are not fully converted into products. At any time of reactions, one will find a mixture of reactants and products.*
- *Reaction from the reactant side is called the **FORWARD REACTION**, and that from the product side is called the **REVERSE REACTION**.*

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Reversible Reactions

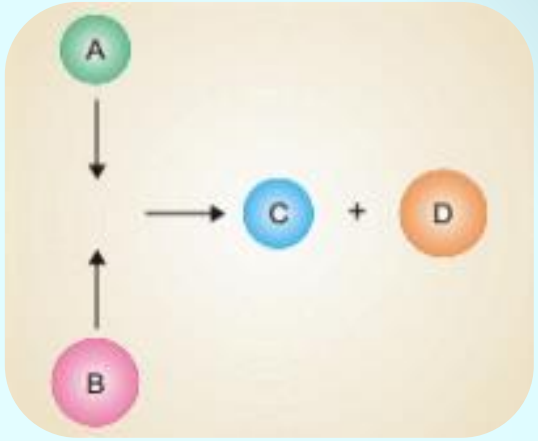
- *A reaction which can go in the forward and backward direction simultaneously is called a **REVERSIBLE REACTION**.*

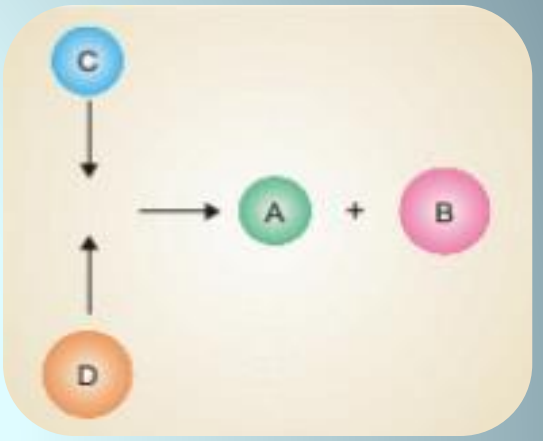
Examples:

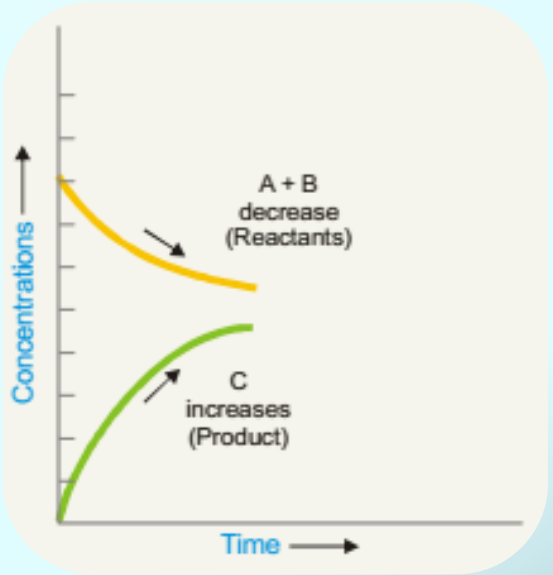
(i) $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

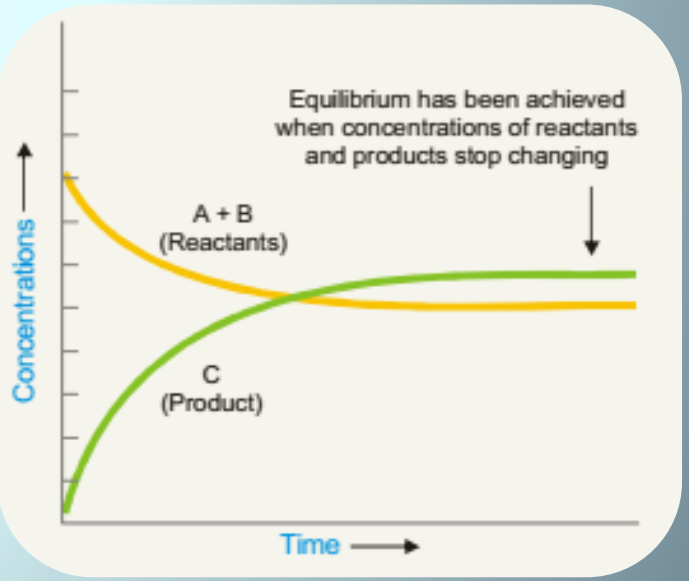
(ii) $N_2O_4(g) \rightleftharpoons 2NO_2(g)$

(iii) $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$









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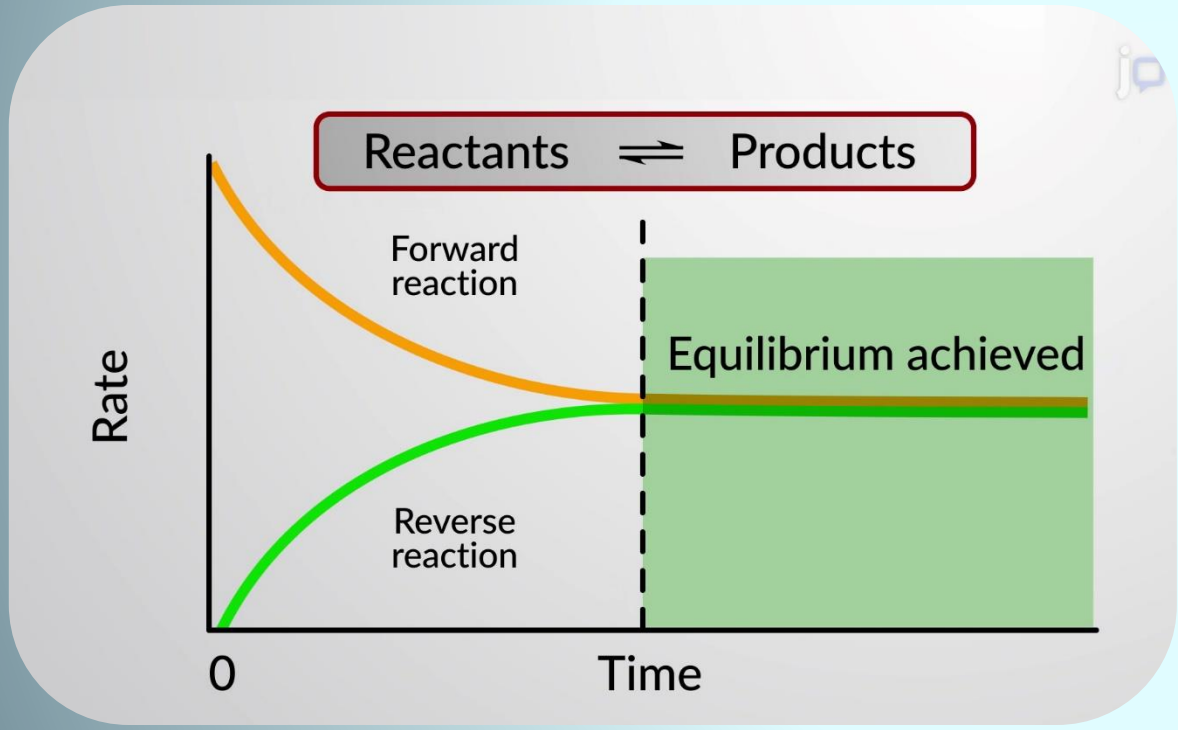
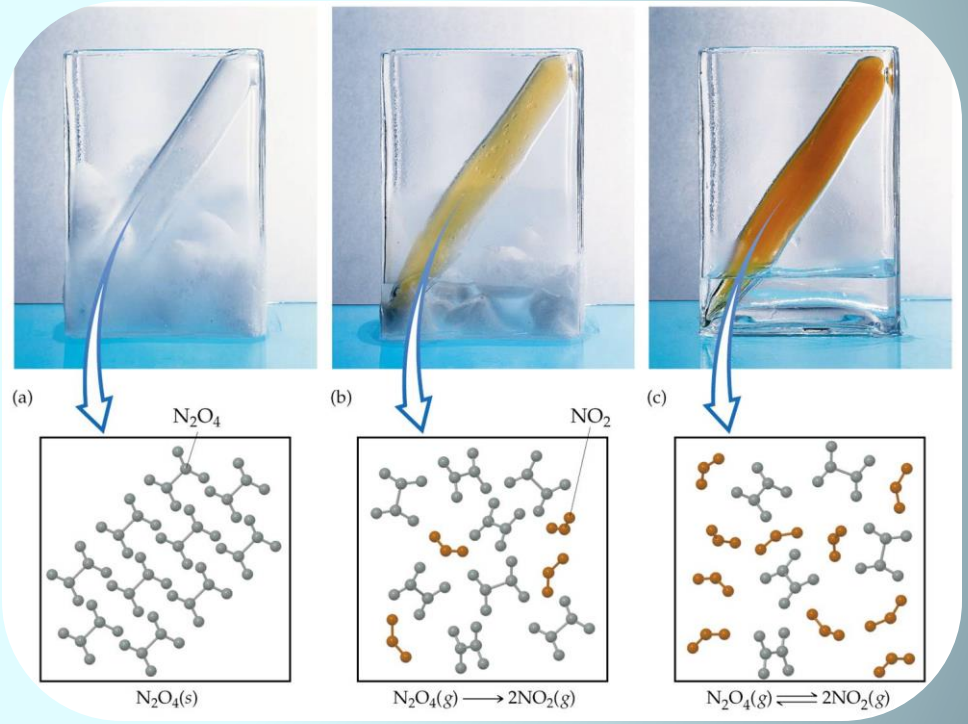
Chemical Equilibrium

- ***CHEMICAL EQUILIBRIUM** may be defined as the state of a reversible reaction when the two opposing reactions occur at the same rate and the concentrations of reactants and products do not change with time.*





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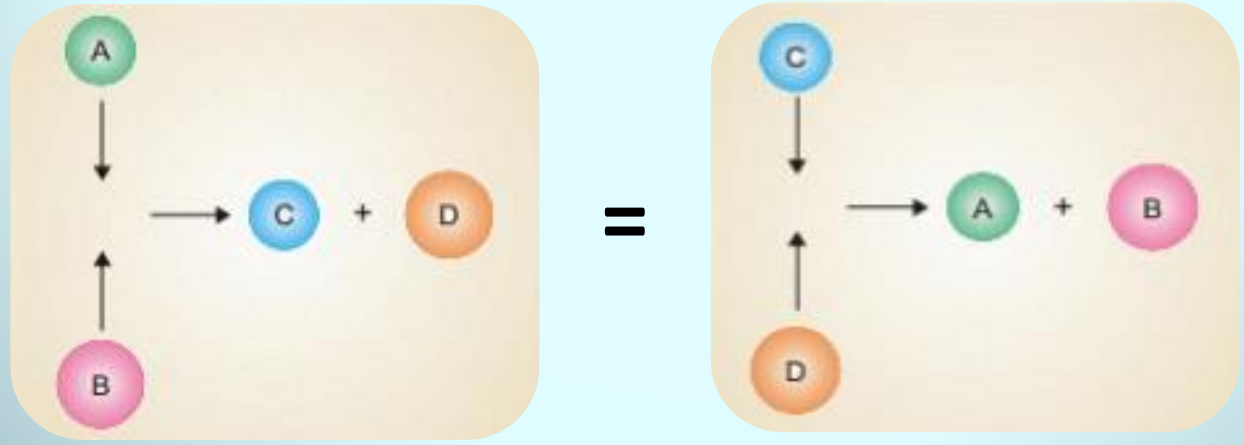
Chemical Equilibrium is Dynamic Equilibrium

- ***Once the reaction attains equilibrium, the concentration of the reactants and the products remain constant with time.***
- ***Apparently, the equilibrium appears to be dead.***
- ***Actually, the forward and reverse reactions take place simultaneously in opposite direction and therefore, the concentrations remain unchanged.***

$$A + B \rightleftharpoons C + D$$



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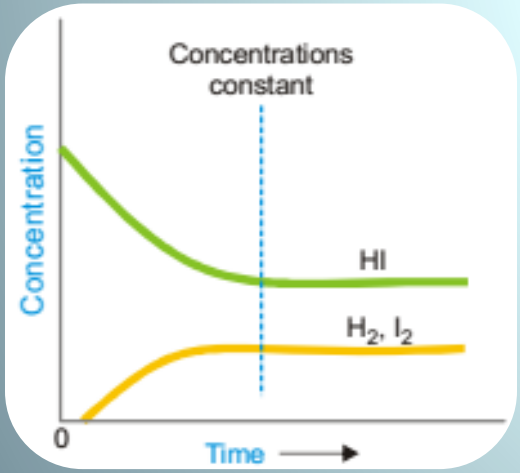
Characteristics of Chemical Equilibrium

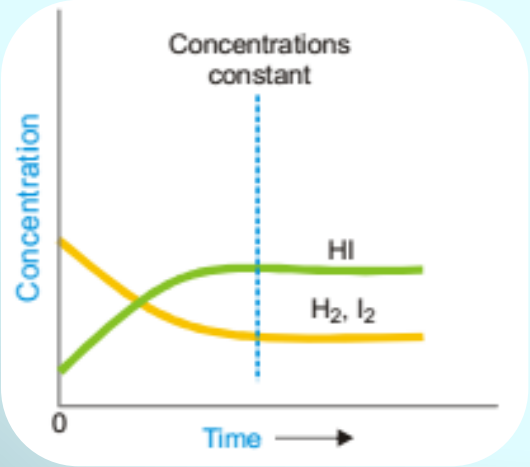
❑ *Concentrations are constant*

- ***When a chemical equilibrium is established in a closed vessel at constant temperature, concentrations of the species in the reaction mixture become constant.***

❑ *Equilibrium can be initiated from either side*

- ***The state of equilibrium of a reversible reaction can be approached whether we start with reactants or products.***





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

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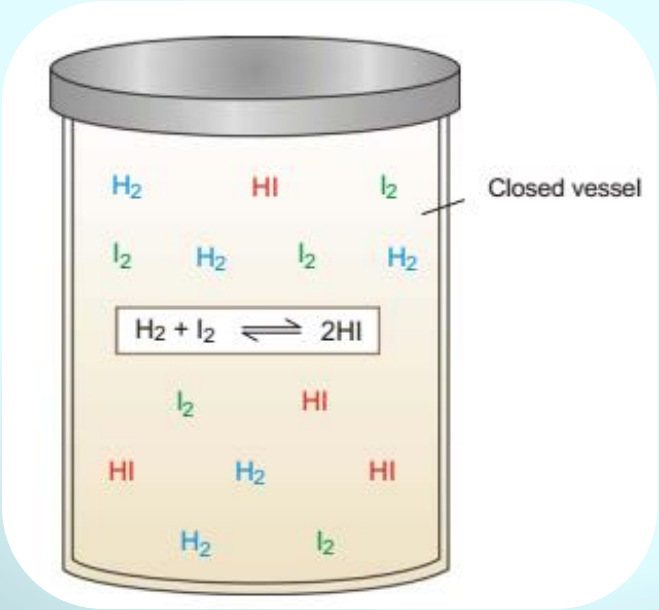
Characteristics of Chemical Equilibrium

❑ *Equilibrium cannot be attained in an open vessel*

- ***The equilibrium can be established only if the reaction vessel is closed and no part of the reactants or products is allowed to escape out.***
- ***In an open vessel, the gaseous reactants and/or products may escape into the atmosphere leaving behind no possibility of attaining equilibrium.***



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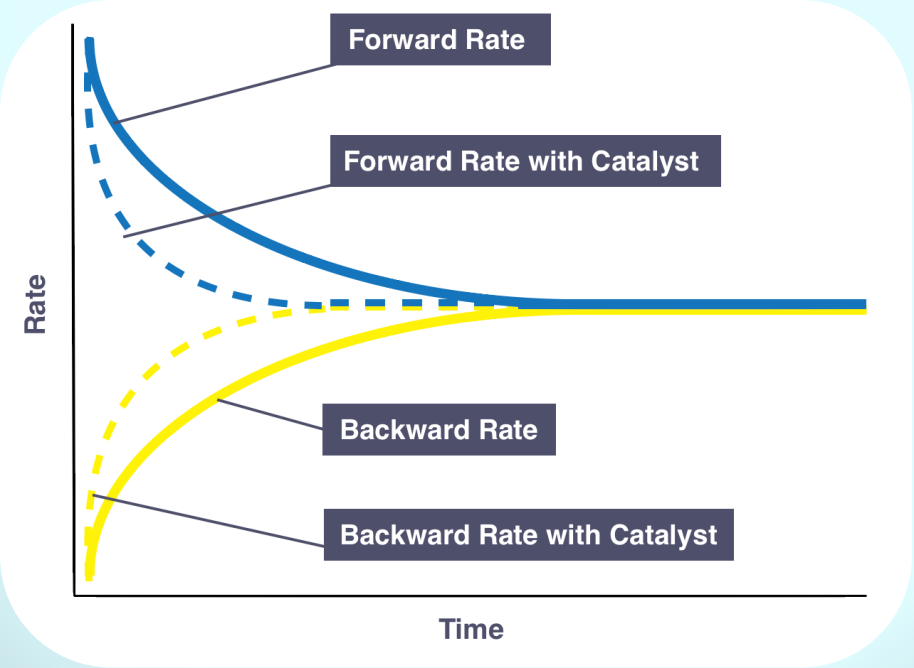
Characteristics of Chemical Equilibrium

❑ *A catalyst cannot change the equilibrium point*

- ***When a catalyst is added to a system in equilibrium, it speeds up the rate of both the forward and the reverse reaction to an equal extent.***



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Law of Mass Action and Equilibrium Constant

- ***Law of Mass Action:*** *The rate of a chemical reaction is proportional to the active masses of the reactants.*

$$A + B \rightleftharpoons C + D$$

Rate of forward reaction $\propto [A][B] = k_1 [A][B]$

And rate of forward reaction $\propto [C][D] = k_2 [C][D]$

At equilibrium, the rate of forward reaction = rate of backward reaction

Therefore, $k_1 [A][B] = k_2 [C][D]$

$$\frac{k_1}{k_2} = \frac{[C][D]}{[A][B]}$$

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

- *At any specific temperature, k_1/k_2 is constant since both k_1 and k_2 are constants.*
- *The ratio k_2/k_2 is called* **EQUILIBRIUM CONSTANT** *and represented by K_c.*
- *The subscript 'c' indicates that the value is in terms of concentration of reactants and products.*

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Law of Mass Action and Equilibrium Constant

- *A general reaction may be written as -*

$$aA + bB \rightleftharpoons cC + dD$$

Where a, b, c and d are numerical quotient of the substance A, B, C and D respectively.

The expression for the equilibrium constant is therefore,

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

Example: $CH_4\,(g) + H_2O\,(g) \rightleftharpoons CO\,(g) + 3H_2\,(g)$

Expression for equilibrium constant, $K_c = \frac{[CO]\,[H_2]^3}{[CH_4]\,[H_2O]}$

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Equilibrium Constant in Terms of Partial Pressure

- *A general reaction may be written as -*

$$aA + bB \rightleftharpoons cC + dD$$

- *The expression for equilibrium constant in terms of partial pressure is,*

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

p_A, p_B, p_C and p_D are the partial pressure for the substances A, B, C and D respectively. Partial pressures are expressed in atmosphere.

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Relation Between K_C and K_P

- *The expression for equilibrium constant in terms of partial pressure is,*

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

From ideal gas equation, the partial pressure-

$p = (n/V)\,RT$; *where* n/V *is the molar concentration*

Thus, the partial pressures of the individual gases A, B, C and D are-

$p_A = [A]\,RT$; $p_B = [B]\,RT$; $p_C = [C]\,RT$; $p_D = [D]\,RT$

Therefore, $K_p = \frac{[C]^c(RT)^c\,[D]^d(RT)^d}{[A]^a(RT)^a\,[B]^b(RT)^b}$; *or,* $K_p = \frac{[C]^c\,[D]^d\,(RT)^{c+d}}{[A]^a\,[B]^b(RT)^{a+b}}$

or, $K_p = Kc \times (RT)^{(c+d)-(a+b)}$

or, $K_p = Kc \times (RT)^{\Delta n}$

where $\Delta n = (c+d) - (a+b)$, *ther difference in the sums of the coefficients for the products and reactions.*

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Units of Equilibrium Constants, K_C and K_P

❑ *When the number of moles of reactants and products are equal*

- ***In the equilibrium expression of these reactions, the concentration or pressure terms in the numerator and denominator exactly cancel out. Thus Kc or Kp for such a reaction is without units.***

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

$$K_c = \frac{[HI]2}{[H_2][I_2]} = \frac{(\frac{mol}{L})^2}{(\frac{mol}{L})(\frac{mol}{L})} \qquad \textbf{[no unit]}$$

$$K_p = \frac{(pHI)^2}{(PH_{2)}\,(PI_{2)}} = \frac{(atm)^2}{(atm)\,(atm)} \qquad \textbf{[no unit]}$$

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Units of Equilibrium Constants, K_C and K_P

❑ *When the number of moles of reactants and products are unequal*

- ***In such reactions K_c will have units (mol/litre)^n and K_p will have units (atm)^n, where n is equal to the total number of moles of products minus the total number of moles of reactants.***

$$N_2O_4\,(g) \rightleftharpoons 2NO_2\,(g)$$

$$PCl_5\,(g) \rightleftharpoons PCl_3(g) + Cl_2\,(g)$$

- ***Units??***

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Predicting the Direction of a Reaction

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

- K_c for the above equilibrium is 54.3 at 430 °C.
- Suppose that in a certain experiment we place 0.243 mole of H_2, 0.146 mole of I_2, and 1.98 moles of HI all in a 1.00-L container at 430°C.
- Which direction will the reaction go? **Forward or backward?**
- Inserting the values in K_c equation -

$$\frac{[HI]_0^2}{[H_2]_0\,[I_2]_0} = \frac{(1.98)^2}{(0.243)(0.146)} = 111$$

- Where the subscript 0 indicates the initial concentrations. Because the value is greater than K_c, instead of equilibrium constant, it is called **Reaction Quotient (Q_c).**
- The direction of the reaction can be determined by comparing the values of Q_c and K_c.

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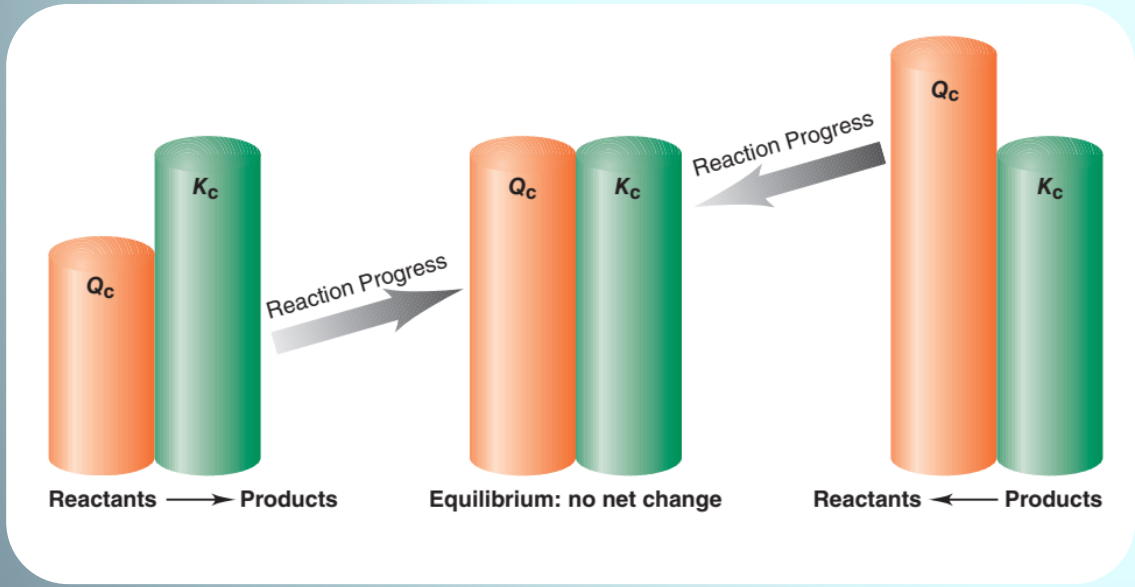
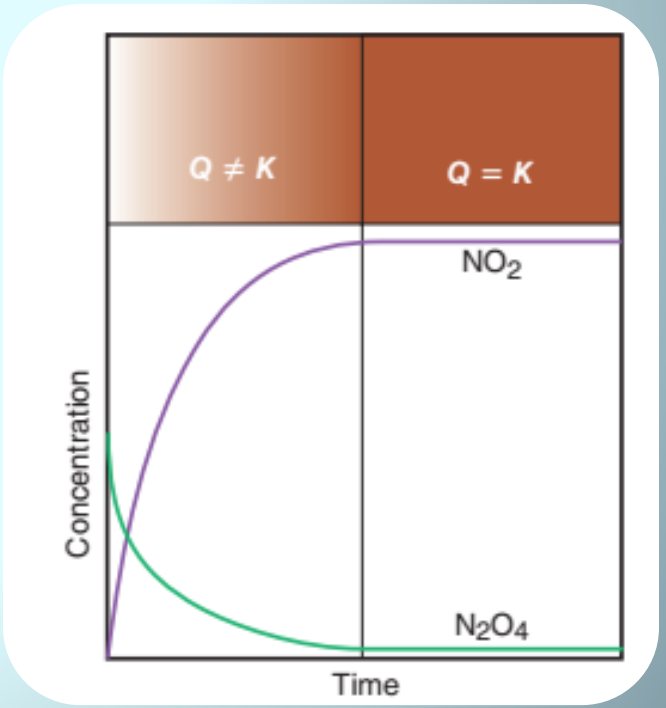
Predicting the Direction of a Reaction

- ***$Q_c < K_c$; the ratio of initial concentration of products to reactants is too small, reaction must proceed from left to right to achieve equilibrium.***
- ***$Q_c > K_c$; the ratio of initial concentration of products to reactants is too large, reaction must proceed from right to left to achieve equilibrium.***
- ***$Q_c = K_c$; the reaction is in equilibrium.***





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Sample Problems

- ***Write the expression of K_c and K_p for the following reactions. What would be their units? What would be the relation between K_c and K_p?***
  - $N_2O_5\,(g) \rightleftharpoons NO_2\,(g) + O_2\,(g)$
  - $N_2O_4\,(g) \rightleftharpoons 2NO_2\,(g)$
  - $2NOCl\,(g) \rightleftharpoons 2NO\,(g) + Cl_2\,(g)$
  - $3C_2H_2\,(g) \rightleftharpoons C_6H_6\,(g)$

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Sample Problems

- ***The value of K_p at 25 ^oC for the following reaction is 1.9 x 10^3 atm^{-1}. Calculate the value of K_c at the same temperature.***
  - ***$2NOCl\ (g) \rightleftharpoons 2NO\ (g) + Cl_2\ (g)$***

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

Here,

$$T = 25 + 273 = 298\ \text{K}$$
$$R = 0.0821$$
$$\Delta n = 2 - (2 + 1) = -1$$
$$K_p = 1.9 \times 10^3$$

Substituting these values in the general expression

$$K_c = \frac{1.9 \times 10^3}{(0.0821 \times 298)^{-1}}$$
$$= 4.6 \times 10^4$$

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Sample Problems

- ***Some nitrogen and hydrogen gases are pumped into an empty five-litre glass bulb at 500°C. When equilibrium is established, 3.00 moles of N_2, 2.10 moles of H_2 and 0.298 mole of NH_3 are found to be present. Find the value of K_c for the reaction at 500 °C.***

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

The equilibrium concentrations are obtained by dividing the number of moles of each reactant and product by the volume, 5.00 litres. Thus,

$$[N_2] = 3.00\ \text{mole}/5.00\ \text{L} = 0.600\ \text{M}$$
$$[H_2] = 2.10\ \text{mole}/5.00\ \text{L} = 0.420\ \text{M}$$
$$[NH_3] = 0.298\ \text{mole}/5.00\ \text{L} = 0.0596\ \text{M}$$

Substituting these concentrations (not number of moles) in the equilibrium constant expression, we get the value of K_c.

$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{(0.0596)^2}{(0.600)(0.420)^3} = 0.080$$

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Sample Problems

- ***At a certain temperature, 0.100 mole of H_2 and 0.100 mole of I_2 were placed in a one-litre flask. The purple colour of iodine vapour was used to monitor the reaction. After a time, the equilibrium was established and it was found that the concentration of I_2 decreased to 0.020 mole/litre. Calculate the value of K_c for the reaction at the given temperature.***

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

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Sample Problems

- ***At a certain temperature, K_c for the following reaction is 4. If the equilibrium concentration of C_2H_2 is 0.5 mole/litre, what is the concentration of C_6H_6?***

$$3C_2H_2\,(g) \rightleftharpoons C_6H_6\,(g)$$

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Sample Problems

- ***At 60°C and a total pressure of 1 atmosphere dinitrogen tetroxide, N_2O_4, is 50% dissociated into nitrogen dioxide, NO_2. Calculate the value of K_p at this temperature.***

$$N_2O_4\,(g) \rightleftharpoons 2NO_2\,(g)$$

	N_2O_4	$\rightleftharpoons$	$2NO_2$
moles at equilibrium :	$(1-x)$		$2x$

Since N_2O_4 is 50% dissociated, $x = 0.5$ mole and the equilibrium mixture contains

$NO_2 = 2x = 2 \times 0.5 = 1$ mole

$N_2O_4 = (1-x) = (1-0.5) = 0.5$ mole

That is, the moles of N_2O_4 and NO_2 are present in the ratio 1 : 2

$\therefore$ The partial pressure of $N_2O_4 = \frac{1}{3}$ atm

The partial pressure of $NO_2 = \frac{2}{3}$ atm

Substituting these values in the equilibrium constant expression, we have

$$K_p = \frac{(p_{NO_2})^2}{p_{N_2O_4}} = \frac{(2/3)^2}{1/3} = \frac{4}{3} = \mathbf{1.33}$$

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Thermodynamic Derivation of Law of Chemical Equilibrium

- *Lets consider a general reaction –*

$$aA + bB + \ldots \rightleftharpoons cC + dD + \ldots.$$

The free energy of a substance in a mixture is related to its activity by expression-

$$G = G^o + RT \ln a$$

Where, G^o is the free energy of the pure substance in standard state of unit activity, R is gas constant and T is the absolute temperature.

- *For 'a' mole of substance A, we can write the equation-*

$$aG_A = a(G_A^o + RT \ln a_A)$$

Similarly, $bG_B = b(G_B^o + RT \ln a_B)$

$$cG_C = c(G_C^o + RT \ln a_C)$$

$$dG_D = d(G_D^o + RT \ln a_D)$$

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Thermodynamic Derivation of Law of Chemical Equilibrium

- *The change in free energy for the reaction is given by,*

$$\Delta G = G_{products} - G_{reactants}$$

$$= (c\,G_C + d\,G_D + ...) - (a\,G_A + b\,G_B + ...)$$

$$= [c\{G_C^o + RT\ln a_C\} + d\{G_D^o + RT\ln a_D\} + ...] - [a\{G_A^o + RT\ln a_A\} + b\{G_B^o + RT\ln a_B\} + ...]$$

$$= [\{cG_C^o + dG_D^o + ...\} - \{aG_A^o + bG_B^o + ...\}] + RT\ln \frac{a_C^c + a_D^d + ...}{a_A^a + a_B^c + ...}$$

$$\Delta G = \Delta G^o + RT\ln \frac{a_C^c + a_D^d + ...}{a_A^a + a_B^b + ...}$$

The equation is known as van't Hoff reaction isotherm.

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Thermodynamic Derivation of Law of Chemical Equilibrium

At equilibrium, $\Delta G = 0$;

Therefore, $\Delta G^o = -RT \ln \frac{a_C^c + a_D^d + \ldots}{a_A^a + a_B^b + \ldots}$

ΔG^o is the change in free energy of the reaction in the standard state and is constant at a given temperature.

$\frac{a_C^c + a_D^d + \ldots}{a_A^a + a_B^b + \ldots}$ *= a constant = K; the equilibrium constant*

Hence, $\Delta G^o = -RT \ln K = -2.303\, RT \log K$

Condition-1: if $\Delta G^o < 0$; $\log K > 0$; $K > 1$; the reaction proceeds spontaneously in the forward direction.

Condition-2: if $\Delta G^o > 0$; $\log K < 0$; $K < 1$; the reaction proceeds spontaneously in the backward direction.

Condition-3: if $\Delta G^o = 0$; $\log K = 0$; $K = 1$; the reaction is at equilibrium

Temperature Dependence of Equilibrium Constant

The dependence of the equilibrium constant on temperature can be determined thermodynamically using the following relation-

$$\Delta G^o = -RT \ln K_P$$

Differentiating the equation with respect to temperature at constant pressure, we get-

$$\left(\frac{\delta(\Delta G^o)}{\delta T}\right)_P = -R \ln K_P - RT \left(\frac{\delta \ln K_P)}{\delta T}\right)_P$$

Multiplying both sides by T, we get-

$$T\left(\frac{\delta(\Delta G^o)}{\delta T}\right)_P = -RT \ln K_P - RT^2 \left(\frac{\delta \ln KP)}{\delta T}\right)_P$$

Or,

$$T\left(\frac{\delta(\Delta G^o)}{\delta T}\right)_P = \Delta G^o - RT^2 \left(\frac{\delta \ln KP)}{\delta T}\right)_P \quad \text{..... (i)}$$

From Gibbs-Helmholts equation, we know-

$$\Delta G^o = \Delta H^o - T \left(\frac{\delta (\Delta G^o))}{\delta T}\right)_P \; ; \quad \text{or, } T\left(\frac{\delta(\Delta G^o)}{\delta T}\right)_P = \Delta G^o - \Delta H^o \quad \text{..... (ii)}$$

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Temperature Dependence of Equilibrium Constant

Comparing equation (i) and (ii)

$$\Delta H^o = RT^2 \left(\frac{\delta \, ln \, KP)}{\delta T}\right)_P$$

This equation is known as van't Hoff equation, where ΔH^o is the enthalpy change of the reaction at constant pressure when all the reactants and products are in their standard state.

Rearrangement and use of ordinary differential gives,

$$\frac{\Delta H^o}{RT^2} = \frac{d \, (ln \, KP)}{dT} \text{ ---------- (iii)}$$

By integrating the above equation, we get, $ln \, K_P = -\frac{\Delta H^o}{RT} + C$

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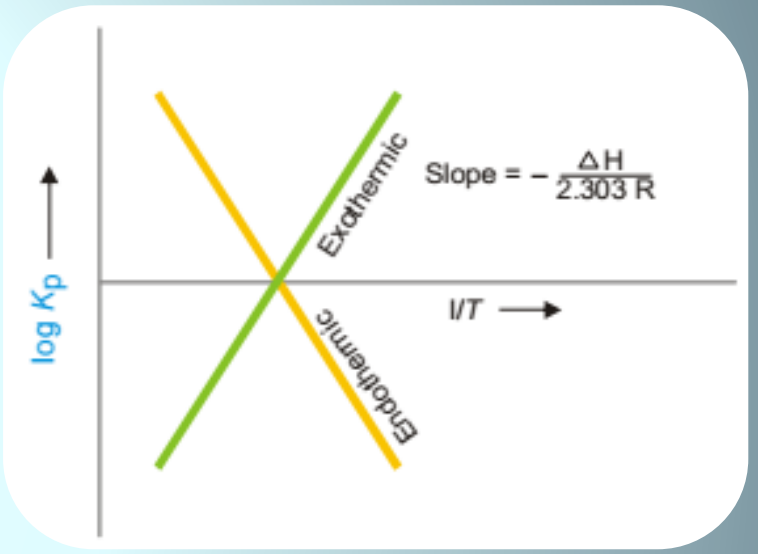
Temperature Dependence of Equilibrium Constant

$$\log K_P = -\frac{\Delta H}{2.303\,RT} + C \ldots\ldots\ldots\ldots \text{(i)} \quad ; \text{where C is a constant of integration.}$$

The plot $\log K_P$ vs $1/T$ is a straight line with slope $-\frac{\Delta H}{2.303\,R}$



(a) For exothermic reaction, ΔH is negative and K_P decreases with increase in temperature.

(b) For endothermic reaction, ΔH is positive and K_P increases with decrease in temperature.

Integrating equation (iii) within limits K_{P1} at temperature T_1 and K_{P2} at temperature T_2.

$$\int_{K_{P1}}^{K_{P2}} d\ln K_P = \int_{T_1}^{T_2} \frac{\Delta H}{RT^2}\,dT \; ; \quad \text{or, } \ln\frac{K_{P2}}{K_{P1}} = -\frac{\Delta H}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right] ; \text{ or } \ln\frac{K_{P2}}{K_{P1}} = \frac{\Delta H}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

$$\text{Or, } \log\frac{K_{P2}}{K_{P1}} = \frac{\Delta H}{2.303\,R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$$

Heat of reaction can be determined from the above equation if the values of equilibrium constants and temperatures are known, and vice-versa.

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Equilibrium in Liquid Systems

The chemical reactions in which all the reactants and products are in liquid phase, are known as liquid equilibria.

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

Lets start with a moles of acetic acid and b moles of ethyl alcohol.

At equilibrium, if x moles of acetic acid reacts with x moles of ethyl alcohol to produce x moles of ester and x moles of water, then the moles of the reactants and products present at equilibrium are-

CH_3COOH = (a – x) moles; C_2H_5OH = (b – x) moles; $CH_3COOC_2H_5$ = x moles; H_2O = x moles

If V litre be the total volume of the reaction system at equilibrium, then-

$[CH_3COOH] = (a - x)/V$; $[C_2H_5OH] = (b - x)/V$; $[CH_3COOC_2H_5] = x/V$; $[H_2O] = x/V$

Then, $K = \dfrac{\left(\frac{x}{V}\right) x \left(\frac{x}{V}\right)}{\left(\frac{a-x}{V}\right) x \left(\frac{b-x}{V}\right)}$; *or,* $K = \dfrac{x^2}{(a-x)(b-x)}$

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Heterogeneous Equilibria

The chemical equilibria in which the reactants and products are not all in the same phase are called heterogeneous equilibria.

$CaCO_3\,(s) \rightleftharpoons CaO\,(s) + CO_2\,(g);$ Then, $K = \frac{[CO_2]\,[CaO]}{[CaCO_3]}$

But $CaCO_3$ and CaO are pure solids. The concentration (moles per unit volume) of a pure solid (or liquid) is fixed and does not vary.

Thus the concentrations of pure solids or liquids are not included in the equilibrium constant expression.

$K_C = [CO_2]$ and $K_P = P_{CO2}$

$2H_2O\,(l) \rightleftharpoons 2H_2\,(g) + O_2\,(g);$ $K = \frac{[H_2]^2\,[O_2]}{[H_2O]^2}$

Ignoring the concentration of liquid water, $K_C = [H_2]^2\,[O_2]$; and $K_P = (P_{H2})^2\,(P_{O2})$

Unit of equilibrium constant for heterogeneous equilibria??

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Le Chatelier's Principle

'When a stress is applied on a system in equilibrium, the system tends to adjust itself so as to reduce the stress.'

Lets discuss the effect of the following factors on equilibrium-

i) Effect of change in concentration of reactants and products

ii) Effect of change in pressure

iii) Effect of change in temperature

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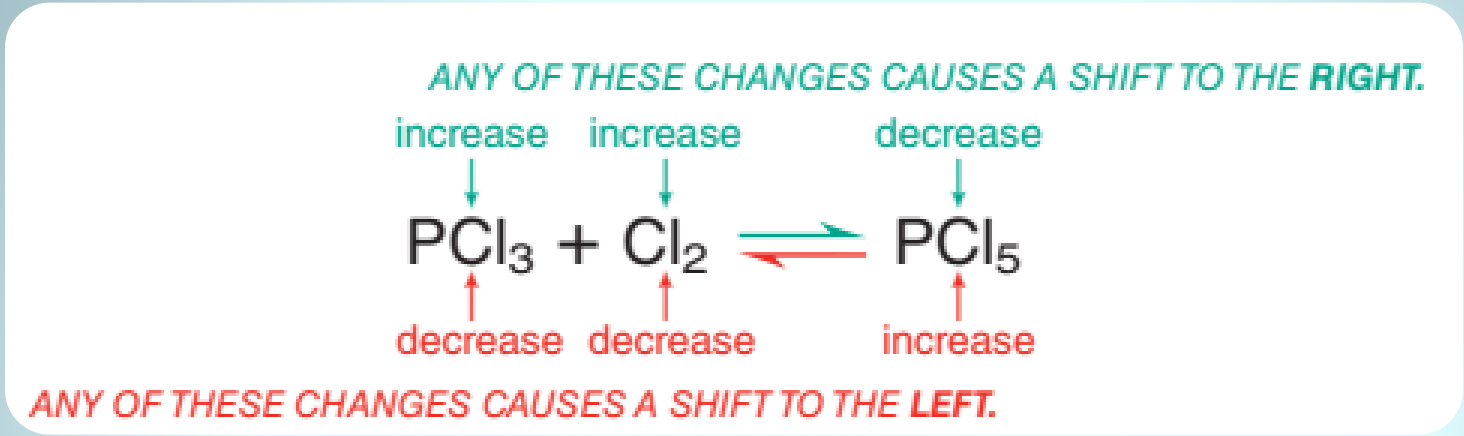
Effect of Change in Concentration of Reactants and Products



Sample Problem:

At 720°C, the equilibrium constant K_c for the reaction $N_2\,(g) + 3H_2\,(g) \rightleftharpoons 2NH_3\,(g)$ is 2.37 x 10^{-3}. In a certain experiment, the equilibrium concentrations are $[N_2]$ = 0.683 M, $[H_2]$ = 8.80 M, and $[NH_3]$ = 1.05 M. Suppose some NH_3 is added to the mixture so that its concentration is increased to 3.65 M. (a) Use Le Châtelier's principle to predict the shift in direction of the net reaction to reach a new equilibrium. (b) Confirm your prediction by calculating the reaction quotient Q_c and comparing its value with K_c.

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Effect of Change in Pressure

The increase of pressure on a chemical equilibrium shifts it in that direction in which the number of molecules decreases and vice-versa.

TABLE 17.1. EFFECT OF PRESSURE ON VARIOUS GASEOUS EQUILIBRIA

System	Pressure increased	Pressure decreased
(1) $N_2O_4 \rightleftharpoons 2NO_2$	←	→
(2) $PCl_5 \rightleftharpoons PCl_3 + Cl_2$	←	→
(3) $2SO_2 + O_2 \rightleftharpoons 2SO_3$	→	←
(4) $N_2 + 3H_2 \rightleftharpoons 2NH_3$	→	←
(5) $H_2 + I_2 \rightleftharpoons 2HI$	No effect	No effect
(6) $N_2 + O_2 \rightleftharpoons 2NO$	No effect	No effect

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Effect of Change in Temperature

The increase of temperature favours the reverse change in an exothermic reaction and the forward change in an endothermic reaction.

TABLE 17.2. THE DIRECTION OF EQUILIBRIUM SHIFT IN SOME REACTIONS ON INCREASE OF TEMPERATURE

Reaction	Equilibrium Shift
$4HCl + O_2 \rightleftharpoons 2H_2O + 2Cl_2 + 284\,kcal$	←
$H_2 + Cl_2 \rightleftharpoons 2HCl + 44.2\,kcal$	←
$CH_4 + 2O_2 \rightleftharpoons CO_2 + 2H_2O + 212.8\,kcal$	←
$2CO_2 + 135.2\ kcal \rightleftharpoons 2CO + O_2$	→
$N_2O_4 + 14\,kcal \rightleftharpoons 2NO_2$	→
$H_2 + I_2 + 12.4\,kcal \rightleftharpoons 2HI$	→

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