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Fundamentals of Chemistry

CHEM 101

Chemical Equilibrium

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Chemical Equilibrium

A reaction which can go in the forward and backward direction simultaneously is called a Reversible reaction.

$$CO_2 + H_2O \rightleftharpoons H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$$

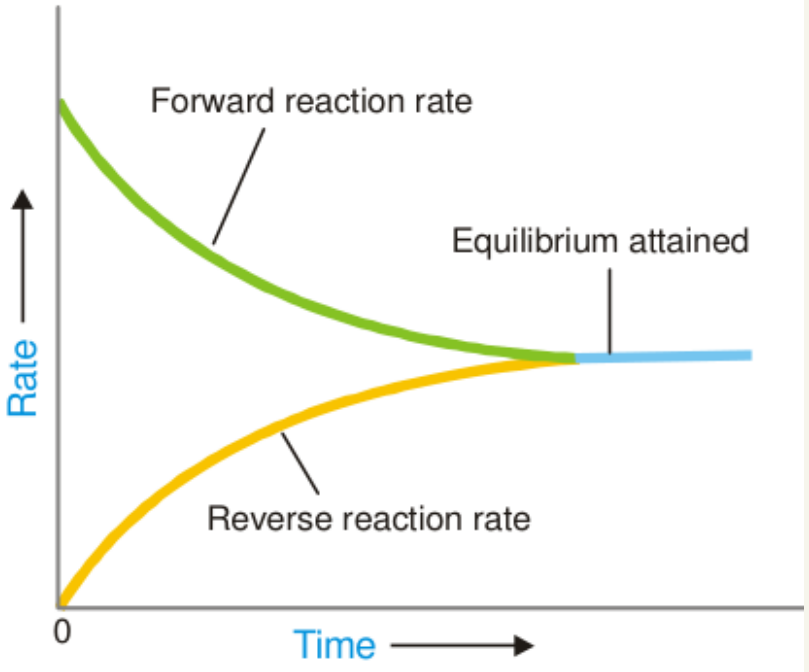
$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

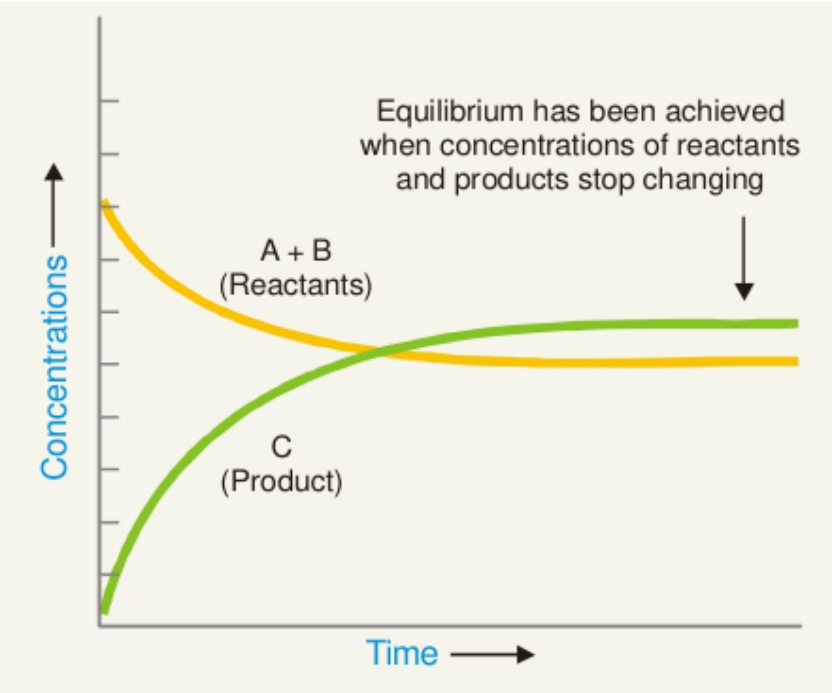
$$CH_3COOH(l) + C_2H_5OH(l) \rightleftharpoons CH_3COOC_2H_5(l) + H_2O(l)$$

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

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

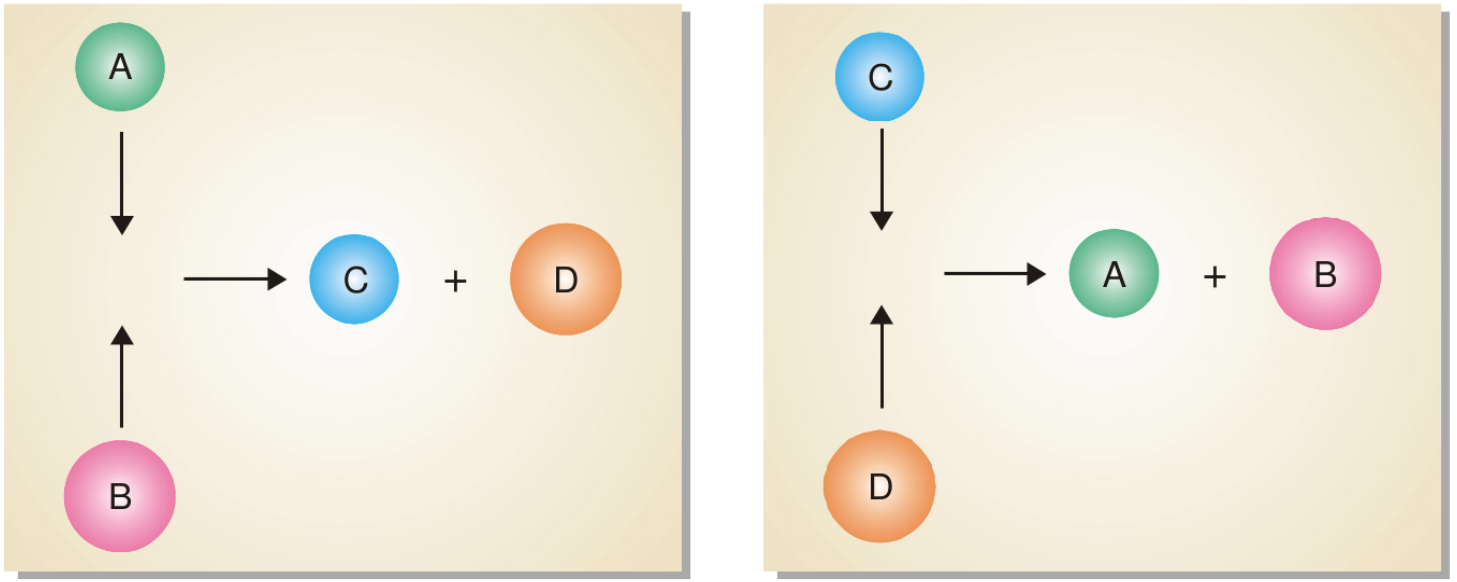
Chemical equilibrium is a state in which the forward and reverse reactions of a chemical reaction occur **at equal rates**, resulting in a **constant concentration** of reactants and products over time.





Chemical Equilibrium is Dynamic Equilibrium

Apparently it appears that the equilibrium is dead. But it is not so. The equilibrium is dynamic. Actually, the forward and the reverse reactions are taking place at equilibrium but the concentrations remain unchanged.

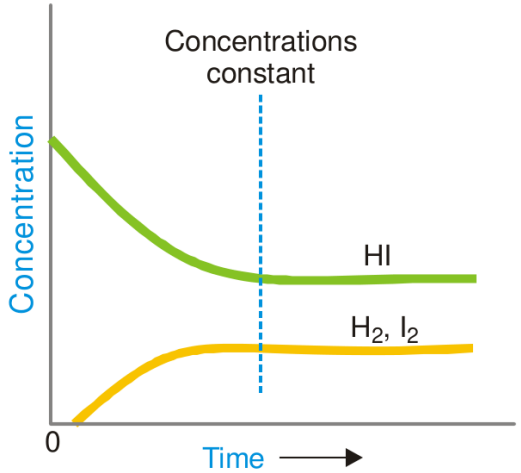


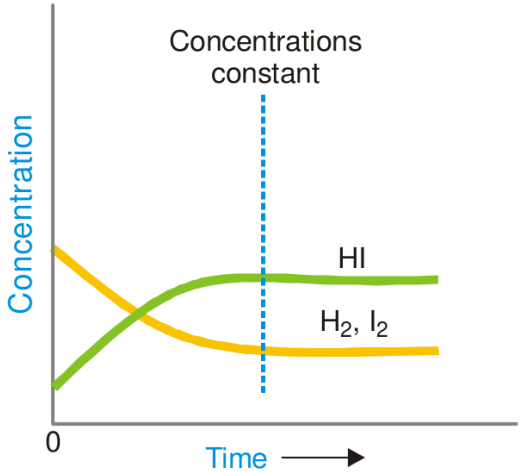
The dynamic nature of chemical equilibrium can be easily understood on the basis of the kinetic molecular model using microscopic reversibility. The molecules of A and B in the equilibrium mixture collide with each other to form C and D. Likewise C and D collide to give back A and B. The collisions of molecules in a closed system is a ceaseless phenomenon.

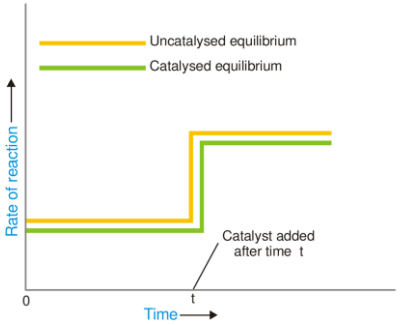
Chemical Equilibrium

Nature/Features of Chemical Equilibrium

- Constancy of concentrations
- Equilibrium can be initiated from either side
- Equilibrium cannot be Attained in an Open Vessel
- A catalyst cannot change the equilibrium point
- Value of Equilibrium Constant does not depend upon the initial concentration of reactants
- At Equilibrium $\Delta G = 0$





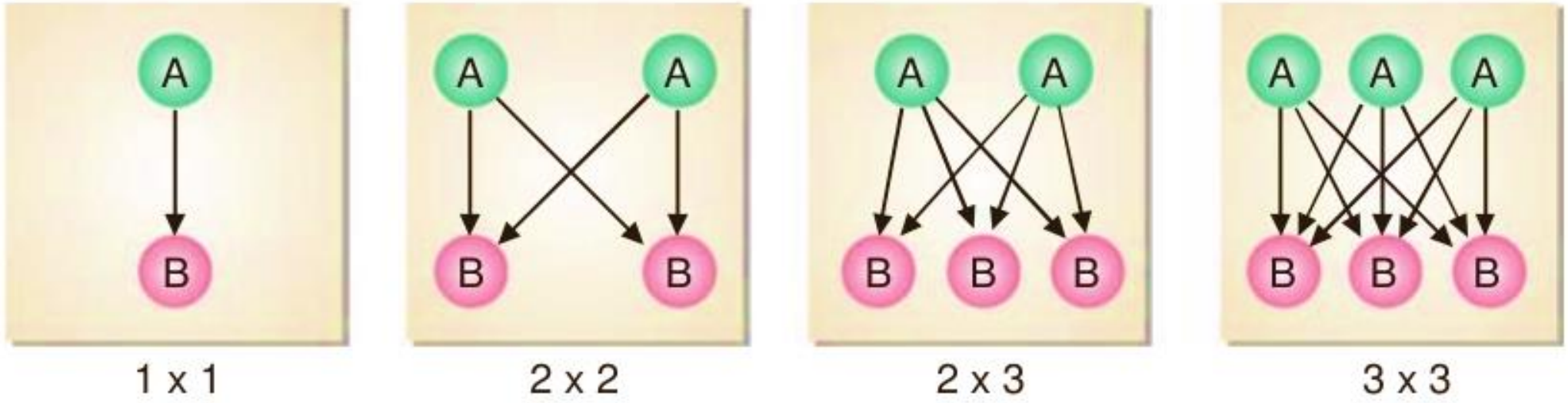


Chemical Equilibrium

LAW OF MASS ACTION

The rate of a chemical reaction is proportional to the active masses of the reactants.

molar concentrations



Here, the possibilities of collisions between the reacting molecules A and B are equal to the product of the number of molecules of each species per unit volume.

Chemical Equilibrium

Since the rate of reaction is determined by molecular impacts, it is proportional to moles per unit volume i.e., molar concentration

$$\text{Rate of reaction} \propto [A]\,[B]$$

$$= k\,[A]\,[B]$$

Equilibrium Constant : Equilibrium Law

Let us consider a general reaction

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

and let [A], [B], [C] and [D] represent the molar concentrations of A, B, C and D at the equilibrium point. According to the Law of Mass action.

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

$$\text{Rate of reverse reaction} \propto [C][D] = k_2 [C][D]$$

where k_1 and k_2 are rate constants for the forward and reverse reactions.

At equilibrium, rate of forward reaction = rate of reverse reaction.

Therefore,

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

or

$$\frac{k_1}{k_2} = \frac{[C][D]}{[A][B]} \quad \ldots (1)$$

Equilibrium Constant : Equilibrium Law

At any specific temperature k_1/k_2 is constant since both k_1 and k_2 are constants. The ratio k_1/k_2 is called **Equilibrium constant** and is represented by the symbol K_c, or simply k. The subscript 'c' indicates that the value is in terms of concentrations of reactants and products. The equation (1) may be written as

Equilibrium constant —— $k_c = \dfrac{[C][D]}{[A][B]}$ —— Product concentrations / Reactant concentrations

This equation is known as the Equilibrium constant expression or Equilibrium law.

Equilibrium Constant : Equilibrium Law

Consider the reaction



Here, the forward reaction is dependent on the collisions of each of two A molecules. Therefore, for writing the equilibrium expression, each molecule is regarded as a separate entity *i.e.*,

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

Then the equilibrium constant expression is

$$k_c = \frac{[C][D]}{[A][A]} = \frac{[C][D]}{[A]^2}$$

Power equal to coefficent of A

As a general rule, if there are two or more molecules of the same substance in the chemical equation, **its concentration is raised to the power equal to the numerical coefficient of the substance in the equation.**

Equilibrium Constant : Equilibrium Law

Equilibrium Constant Expression for a Reaction in General Terms

The general reaction may be written as

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

where a, b, c and d are numerical quotients of the substance, A, B, C and D respectively. The equilibrium constant expression is

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

where K_c is the **Equilibrium constant.** 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.**

Equilibrium Constant : Equilibrium Law

Give the equilibrium constant expression for the reaction

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

$$N_2O_5(g) \rightleftharpoons NO_2(g) + O_2(g)$$

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

Equilibrium Constant : Equilibrium Law

EQUILIBRIUM CONSTANT EXPRESSION IN TERMS OF PARTIAL PRESSURES

When all the reactants and products are gases, we can also formulate the equilibrium constant expression in terms of partial pressure. The relationship between the partial pressure (p) of any one gas in the equilibrium mixture and the molar concentration follows from the general ideal gas equation

$$pV = nRT \quad \text{or} \quad p = \left(\frac{n}{V}\right) RT$$

The quantity $\frac{n}{V}$ is the number of moles of the gas per unit volume and is simply the molar concentration. Thus,

$$p = (\text{Molar concentration}) \times RT$$

The partial pressure of a gas in eq. mixture is directly proportional to its molar concentration at a given temperature.

Equilibrium Constant : Equilibrium Law

Therefore, we can write the equilibrium constant expression in terms of partial pressure instead of molar concentrations. For a general reaction

$$l\,\mathrm{L}(g) + m\mathrm{M}(g) \rightleftharpoons y\mathrm{Y}(g) + z\mathrm{Z}(g)$$

the equilibrium law or the equilibrium constant may be written as

$$K_p = \frac{(p_{\mathrm{Y}})^y (p_{\mathrm{Z}})^z}{(p_{\mathrm{L}})^l (p_{\mathrm{M}})^m}$$

Here K_p is the equilibrium constant, the subscript p referring to partial pressure. Partial pressures are expressed in atmospheres.

Relationship Between K_p and K_c

HOW K_c AND K_p ARE RELATED?

Let us consider a general reaction

$$jA + kB \rightleftharpoons lC + mD$$

where all reactants and products are gases. We can write the equilibrium constant expression in terms of partial pressures as

$$K_p = \frac{(p_C)^l (p_D)^m}{(p_A)^j (p_B)^k} \quad \ldots(1)$$

Assuming that all these gases constituting the equilibrium mixture obey the ideal gas equation, the partial pressure (p) of a gas is

$$p = \left(\frac{n}{V}\right) RT$$

Where $\frac{n}{V}$ is the molar concentration. Thus the partial pressures of individual gases, A, B, C and D are:

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

Relationship Between K_p and K_c

Substituting these values in equation (1), we have

$$K_p = \frac{[\mathrm{C}]^l (RT)^l [\mathrm{D}]^m (RT)^m}{[\mathrm{A}]^j (RT)^j [\mathrm{B}]^k (RT)^k}$$

or

$$K_p = \frac{[\mathrm{C}]^l [\mathrm{D}]^m}{[\mathrm{A}]^j [\mathrm{B}]^k} \times \frac{(RT)^{l+m}}{(RT)^{j+k}}$$

$$K_p = K_c \times (RT)^{(l+m)-(j+k)}$$

$$\therefore \quad K_p = K_c \times (RT)^{\Delta n} \qquad \ldots(2)$$

where $\Delta n = (l+m) - (j+k)$, the difference in the sums of the coefficients for the gaseous products and reactants.

From the expression (2) it is clear that when $\Delta n = 0$, $K_p = K_c$.

Relationship Between K_p and K_c



At 500°C, the reaction between N_2 and H_2 to form ammonia has $K_c = 6.0 \times 10^{-2}$. What is the numerical value of K_p for the reaction?



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

Units of Equilibrium Constant

In the equilibrium expression for a particular reaction, the concentrations are given in units of moles/litre or mol/L, and the partial pressure are given in atmospheres (atm). The units of K_c and K_p, depend on the specific reaction.

(1) When the total 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 K_c or K_p for such a reaction is without units.

Taking example of the reaction

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

$$K_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{(mol/L)^2}{(mol/L)(mol/L)} \qquad \text{(No units)}$$

$$K_p = \frac{(P_{HI})^2}{(P_{H_2})(P_{I_2})} = \frac{(atm)^2}{(atm)(atm)} \qquad \text{(No units)}$$

Units of Equilibrium Constant

(2) When the total number of moles of the 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. Thus for the reaction

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

$$K_c = \frac{[NO_2]^2}{[N_2O_4]} = \frac{(\text{mol/L})^2}{(\text{mol/L})} = \text{mol/L}$$

$$K_p = \frac{(p_{NO_2})^2}{(P_{N_2O_4})} = \frac{(\text{atm})^2}{(\text{atm})} = \text{atm}$$

Thus units for K_c are mol/L and for K_p units are atm. For the reaction

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

the units for K_c and K_p may be found as follows

$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{(\text{mol/L})^2}{(\text{mol/L})(\text{mol/L})^3} = \text{mol}^{-2}\,\text{L}^2$$

$$K_p = \frac{(p_{NH_3})^2}{(p_{N_2})(p_{H_2})^3} = \frac{(\text{atm})^2}{(\text{atm})(\text{atm})^3} = \text{atm}^{-2}$$

Thus units of K_c are $\text{mol}^{-2}\,\text{L}^2$ and units of K_p are atm^{-2}.

Thermodynamic Derivation of Law of Chemical Equilibrium

Van't Hoff reaction Isotherm

Let us consider a general reaction

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

The chemical potential of a substance in a mixture is related to its activity by the expression

$$\mu = \mu^\circ + RT \ln a \qquad \ldots (i)$$

where μ° is the chemical potential of the pure substance in standard state of unit activity, R is gas constant and T the absolute temperature.

For a mole of the substance A we can write using the equation (i)

$$a\mu_A = a(\mu^\circ + RT \ln a_A)$$

and similarly

$$b\mu_B = b(\mu^\circ + RT \ln a_B)$$
$$c\mu_c = c(\mu^\circ + RT \ln a_c)$$
$$d\mu_D = d(\mu^\circ + RT \ln a_D)$$

Thermodynamic Derivation of Law of Chemical Equilibrium

The change in free energy for the reaction is given by

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

On substitution we get

$$\Delta G = (c\mu_c + d\mu_D + \ldots) - (a\mu_A + b\mu_B + \ldots.)$$
$$= [\, c\,\{\mu_c^\circ + RT \ln a_c\} + d\,\{\mu^\circ_D\, RT \ln a_D\}]$$
$$- [a\,\{\mu^\circ_a + RT \ln a_A\} + b\,\{\mu^\circ_B\, RT \ln a_B\}]$$

$$= [\,\{c\,\mu_c^\circ + d\,\mu^\circ_D + \ldots\} - \{a\,\mu^\circ_A + b\,\mu^\circ_B + \ldots\ldots\ldots\}] + RT \ln \frac{a_C^c \times a_D^d \times \ldots}{a_A^a \times a_B^b \times \ldots}$$

$$\Delta G = \Delta G^\circ + RT \ln \frac{a_C^c \times a_D^d \times \ldots}{a_A^a \times a_B^b \times \ldots} \qquad \ldots (ii)$$

where ΔG° is the difference in free energy of the reaction when all reactants and products are in their standard state. It is given by

$$\Delta G^\circ = \{c\mu_c^\circ + d\,\mu_D^\circ + \ldots\} - \{a\mu_A^\circ + b\,\mu_B^\circ + \ldots\}$$

Thermodynamic Derivation of Law of Chemical Equilibrium

In equation (*ii*) the factor A given by

$$\frac{a_C{}^c \times a_D{}^d \times \ldots}{a_A{}^a \times a_B{}^b \times \ldots}$$

stands for the reaction quotient of activities of the product and reactants. It may be denoted by *J*. The equation (*ii*) becomes

$$\Delta G = \Delta G^\circ + RT \ln J \qquad \ldots (iii)$$

The equation (*iii*) is called **van't Hoff reaction isotherm**

For the reaction at equilibrium

$$\Delta G = 0$$

therefore,

$$\Delta G^\circ = -RT \ln J$$

or

$$\Delta G^\circ = -RT \ln \frac{a_C^c \times a_D^d \times \ldots}{a_A^a \times a_B^b \times \ldots}$$

As ΔG° is the free energy of the reaction in the standard state and is constant at a given temperature.

Thermodynamic Derivation of Law of Chemical Equilibrium

Also, the gas constant R and T are constant, the factor

$$\frac{a_C^c \times a_D^d \times \ldots}{a_A^a \times a_B^b \times \ldots} = a \text{ constant} = K$$

It is nothing but the law of chemical equilibrium. Therefore, from equation (*iii*) we have

$$\Delta G^\circ = -RT \ln K \qquad \ldots (iv)$$

or

$$\Delta G^\circ = -2.303\, RT \log K \qquad \ldots (v)$$

The equation (*iv*) is also called van't Hoff Isotherm. It may be used to calculate the change in free energy of a reaction in the standard (ΔG°) from the equilibrium constant and vice-versa.

The sign of ΔG° indicates whether the forward or reverse reaction is spontaneous. Considering the equation (*iv*), we can have three possibilities depending on the sign of ΔG° for the reaction.

(1) If **ΔG° is negative,** $\log K$ must be positive and the reaction proceeds spontaneously in the forward reaction.

(2) If **ΔG° is positive,** $\log K$ must be negative and K is less than one. The reverse reaction is then spontaneous.

(3) If **$\Delta G^\circ = 0$**, $\log K = 0$ and $K = 1$. The reaction is at equilibrium.

Temperature Dependence of Equilibrium Constant

There is appreciable change in the value of equilibrium constant with change in temperature. It can be determined thermodynamically using the relation

$$\Delta G^\circ = -RT \ln K_p \qquad \ldots(i)$$

where ΔG° is the change in standard free energy of the reaction.

Differentiating equation (i) w.r.t. at constant pressure P, we get

$$\left(\frac{\delta(\Delta G^\circ)}{\delta T}\right)_p = -R \ln K_p - RT\left(\frac{\delta \ln K_p}{\delta T}\right)_p$$

Multiplying both sides by T, we get

$$T\left(\frac{\delta(\Delta G^\circ)}{\delta T}\right)_p = -RT \ln K_p - RT^2\left(\frac{\delta \ln K_p}{\delta T}\right)_p$$

From equation (i) we get

$$T\left(\frac{\delta(\Delta G^\circ)}{\delta T}\right)_p = \Delta G^\circ - RT^2\left(\frac{\delta(\ln K_p)}{\delta T}\right)_p \qquad \ldots(ii)$$

Temperature Dependence of Equilibrium Constant

We know that Gibb's Helmholtz equation for a reaction in the standard state can be written as

$$\Delta G^\circ = \Delta H^\circ + T\left(\frac{\delta(\Delta G^\circ)}{\delta T}\right)_p$$

or
$$T\left(\frac{\delta(\Delta G)}{\delta T}\right)_p = \Delta G^\circ - \Delta H^\circ \qquad \ldots (iii)$$

Comparing (*ii*) and (*iii*) we get

$$\Delta H^\circ = RT^2\left(\frac{\delta(\ln K_p)}{\delta T}\right)_p$$

or
$$\frac{\Delta H^\circ}{RT^2} = \frac{\delta(\ln K_p)}{\delta T} \qquad \ldots (iv)$$

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

Temperature Dependence of Equilibrium Constant

It has been found that the enthalpy change does not vary much with change in partial pressures of the reactants or products.
Therefore, ΔH° may be replaced by ΔH. The equation (iv) becomes,

$$\frac{\Delta H}{RT^2} = \frac{d\left(\ln K_p\right)}{dT} \qquad \ldots (v)$$

Integrating equation (v) we get

$$ln\ K_p = -\frac{\Delta H}{RT} + C$$

or

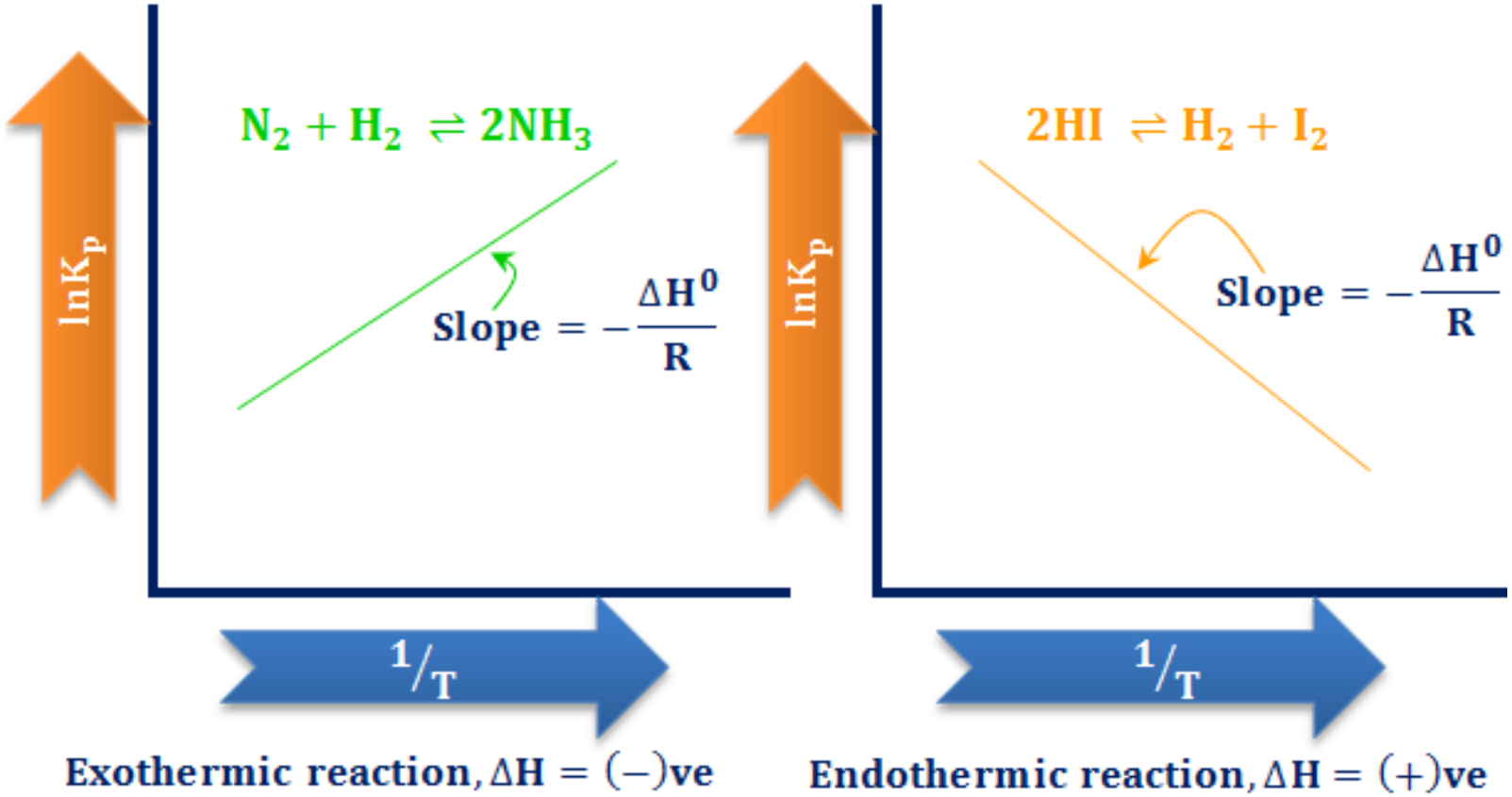
$$\log K_p = -\frac{\Delta H}{2.303\,RT} + C \qquad \ldots (vi)$$

Temperature Dependence of Equilibrium Constant

Van't Hoff equation

$$\ln K_p = \frac{\Delta H^0}{RT} + C$$

where C = integration constant



Exothermic reaction, $\Delta H = (-)ve$

K_p decreases with increase in temperature

Endothermic reaction, $\Delta H = (+)ve$

K_p increases with increase in temperature.

Temperature Dependence of Equilibrium Constant

$$\frac{\Delta H}{RT^2} = \frac{d\left(\ln K_p\right)}{dT} \qquad \ldots (v)$$

Integrating equation (v) within the limits K_{p2} at temperature T_2 and K_{p1} at temperature T_1

$$\int_{K_{p1}}^{K_{p2}} d \ln K_p = \int_{T_1}^{T_2} \frac{\Delta H}{RT^2} dT$$

or

$$\ln \frac{K_{p2}}{K_{p1}} = -\frac{\Delta H}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right]$$

$$= \frac{\Delta H}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

$$\text{In } \frac{K_{p2}}{K_{p1}} = \frac{\Delta H}{R}\left[\frac{T_2 - T_1}{T_1 T_2}\right] \quad \text{or} \quad \log = \frac{K_{p2}}{K_{p1}} = \frac{\Delta H}{2.303\,R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$$

From this equation the heat of reaction can be determined if the values of equilibrium constant Kp_2 and Kp_1 at temperature T_2 and T_1 are known and vice-versa.

Numerical's

1. The equilibrium constant for the reaction,

$$H_2\ (g) + S\ (g) \rightleftharpoons H_2S\ (g)$$

is 20.2 atm at 945 °C and 9.21 atm at 1065 °C. Calculate the heat of reaction

2. The equilibrium constant, K_p for the reaction

$$C_2H_4\ (g) + H_2\ (g) \rightleftharpoons C_2H_6\ (g)$$

is 5.04×10^{17} atm^{-1} at 25 °C. Calculate $\Delta G°$ for this reaction

3. The standard free energy change for the reaction,

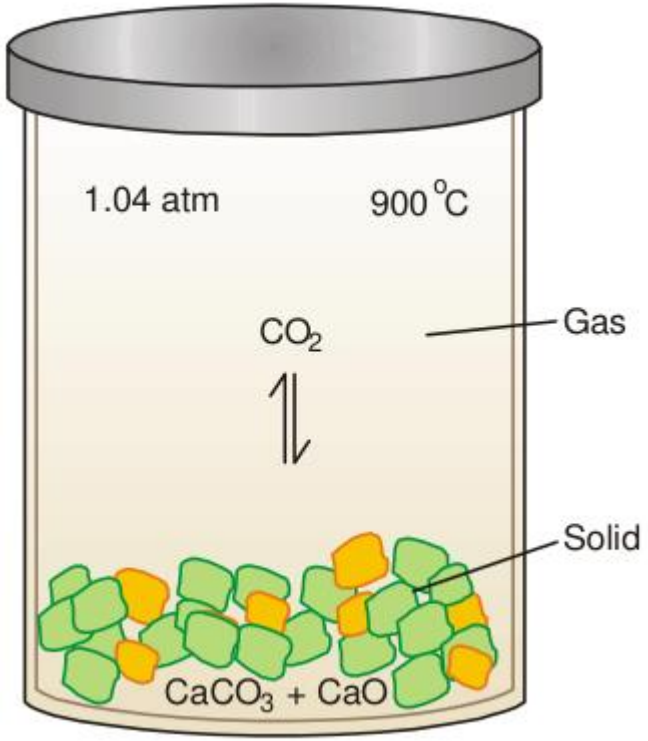
$N_2\ (g) + O_2\ (g) \rightleftharpoons 2NO\ (g)$ is +173.1 kJ. Calculate k_p for the reaction at 25 °C.

HETEROGENEOUS EQUILIBRIA

Heterogeneous equilibria are chemical equilibria in which reactants and products are in different phases, such as solid, liquid, or gas.

The decomposition of calcium carbonate upon heating to form calcium oxide and carbon dioxide is an example of heterogeneous equilibrium. If the reaction is carried in a closed vessel, the following equilibrium is established.

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



When solid $CaCO_3$ is heated in a closed vessel at 900 ^oC, equilibrium is established when the pressure of CO reaches 1.04 atm.

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.

There are three ways in which the stress can be caused on a chemical equilibrium:

(1) Changing the concentration of a reactant or product.

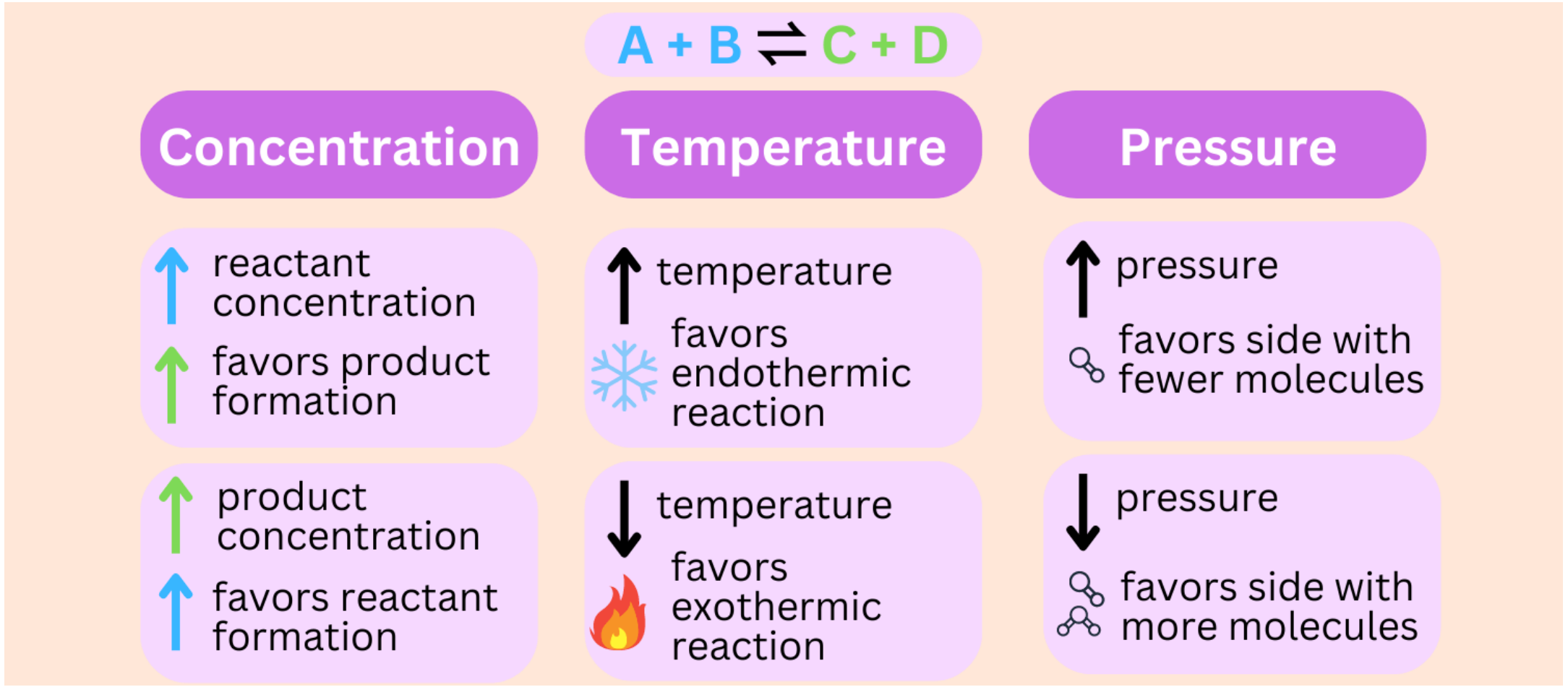
(2) Changing the pressure (or volume) of the system.

(3) Changing the temperature.

Thus when applied to a chemical reaction in equilibrium,

If a change in concentration, pressure or temperature is caused to a chemical reaction in equilibrium, the equilibrium will shift to the right or the left so as to minimize the change.

LE CHATELIER'S PRINCIPLE



LE CHATELIER'S PRINCIPLE

EFFECT OF A CHANGE IN CONCENTRATION

When concentration of any of the reactants or products is changed, the equilibrium shifts in a direction so as to reduce the change in concentration that was made.

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



The addition of an **inert gas** has **no effect** on the position of the equilibrium.

The addition of the inert gas increases the total pressure but the partial pressures of the reactants and products are not changed.

LE CHATELIER'S PRINCIPLE

EFFECT OF A CHANGE IN PRESSURE

When pressure is increased on a gaseous equilibrium reaction, the equilibrium will shift in a direction which tends to decrease the pressure.

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



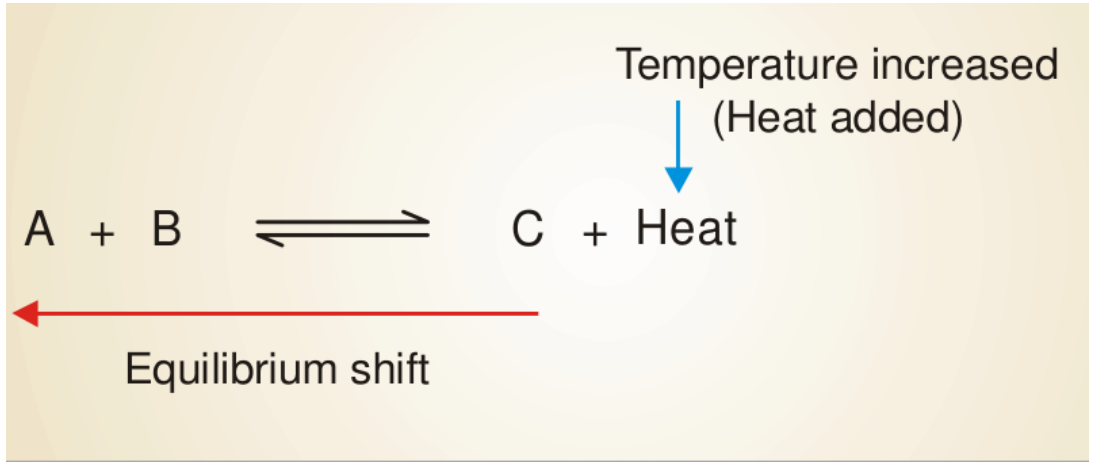
The number of product molecules is equal to the number of reactant molecules are unaffected by pressure changes.

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

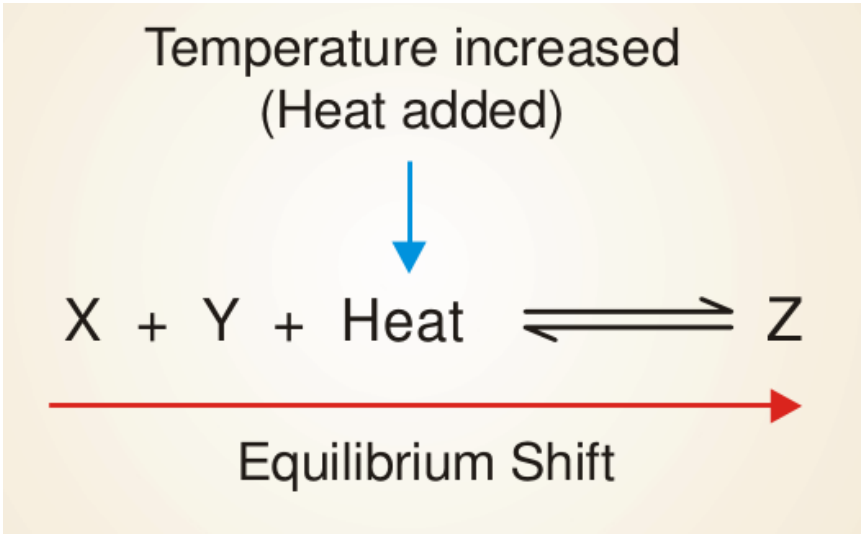
LE CHATELIER'S PRINCIPLE

EFFECT OF CHANGE OF TEMPERATURE

When temperature of a reaction is increased, the equilibrium shifts in a direction in which heat is absorbed.



Exothermic reaction



Endothermic reaction

Synthesis of Ammonia (Haber Process)

The manufacture of ammonia by Haber process is represented by the equation

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) + 22.0\,\text{kcal}$$

A look at the equation provides the following information:

(*a*) the reaction is exothermic

(*b*) the reaction proceeds with a decrease in the number of moles.

(1) **Low temperature.** By applying Le Chatelier's principle, low temperature will shift the equilibrium to the right. This gives greater yield of ammonia. In actual practice a temperature of about 450°C is used when the percentage of ammonia in the equilibrium mixture is 15.

(2) **High pressure.** High pressure on the reaction at equilibrium favours the shift of the equilibrium to the right. This is so because the forward reaction proceeds with a decrease in the number of moles. A pressure of about 200 atmospheres is applied in practice.

(3) **Catalyst.** As already stated, low temperature is necessary for higher yield of ammonia. But at relatively low temperatures, the rate of reaction is slow and the equilibrium is attained in a long time. To increase the rate of reaction and thus quicken the attainment of equilibrium, a catalyst is used. Finely divided iron containing molybdenum is employed in actual practice. Molybdenum acts as a promoter that increases the life and efficiency of the catalyst.

Pure N_2 and H_2 gases are used in the process. Any impurities in the gases would poison the catalyst and decrease its efficiency.