Chemical Equilibrium

■ Reversible Reactions:

→ Not all chemical reactions proceed to completion. In most reactions two or more substances react to form products which themselves react to give back the original substances.

$$A + B \longrightarrow C + D \quad \text{(Forward reaction)}$$

$$A + B \longleftarrow C + D \quad \text{(Reverse reaction)}$$

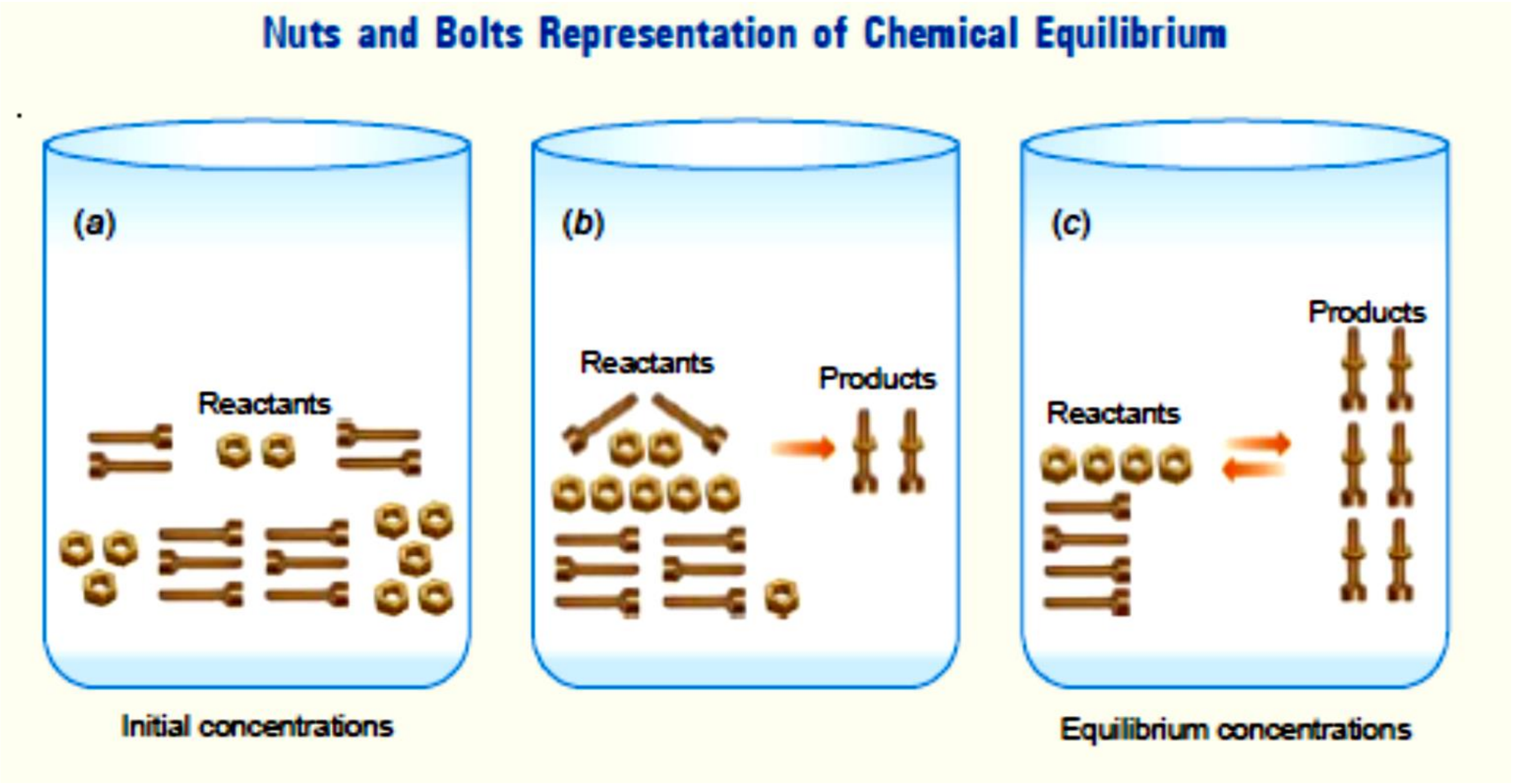
→ **A reaction which can go in the forward and backward direction simultaneously is called a Reversible reaction.**

→ Such a reaction is represented by writing a pair of arrows between the reactants and products.

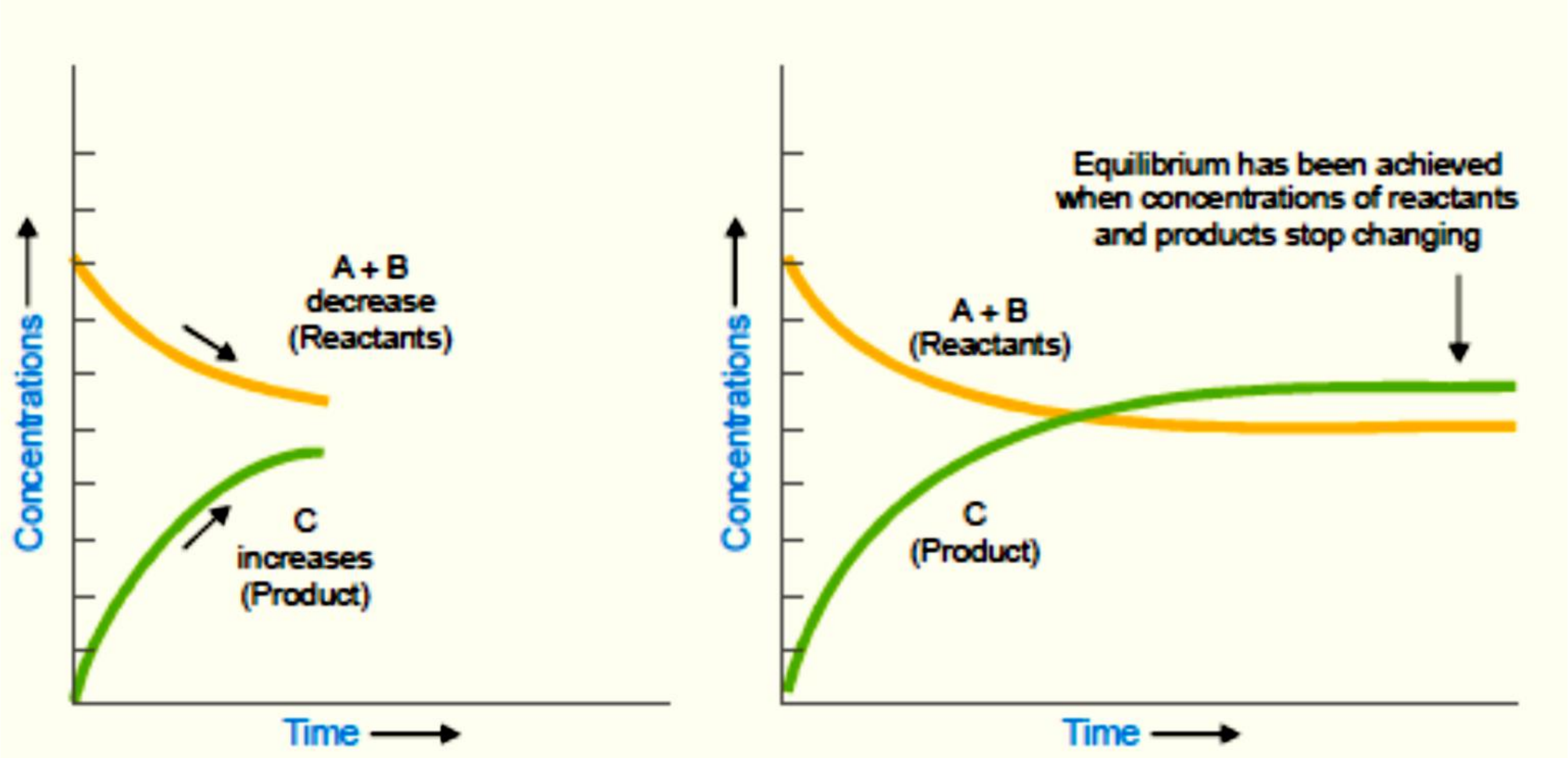
$$PCl_5(s) \rightleftharpoons PCl_3(s) + Cl_2(g)$$

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

Chemical Equilibrium



Chemical Equilibrium

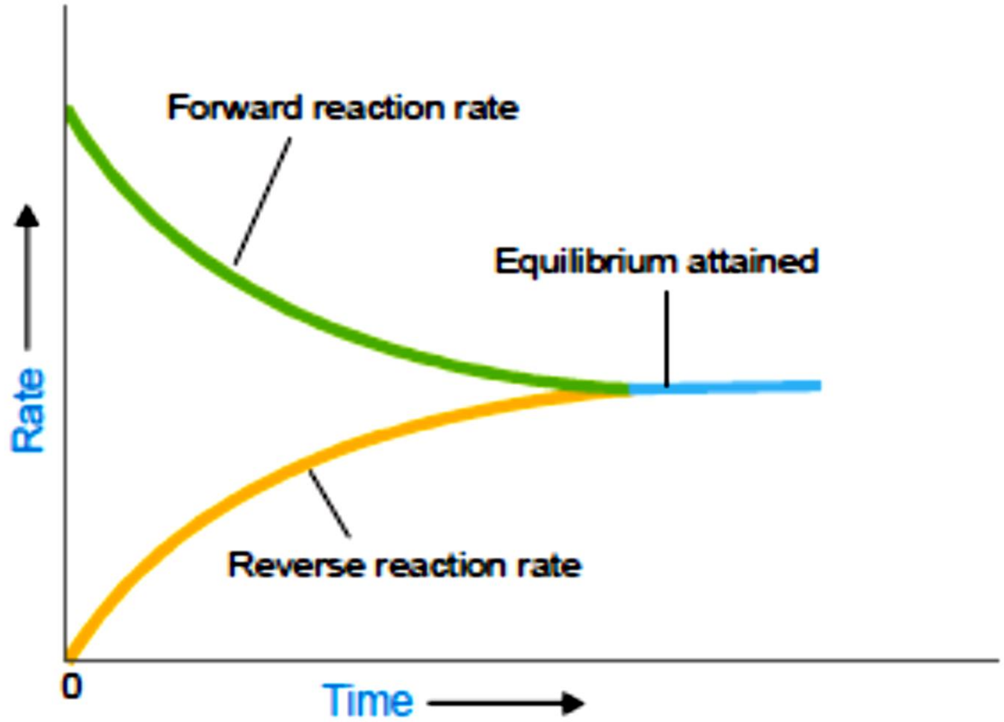


The rate of the forward reaction is equal to the rate of the reverse reaction.

Chemical Equilibrium

■ Nature of Chemical Equilibrium : Its Definition:

→ 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.**



At equilibrium the forward reaction rate equals the reverse reaction rate.

Chemical Equilibrium

■ Characteristics of Chemical Equilibrium:

→ Constancy of concentrations.

→ Equilibrium cannot be Attained in an Open Vessel.

→ A catalyst cannot change the equilibrium point.

→ At Equilibrium $\Delta G = 0$.

■ Equilibrium Constant : Equilibrium Law:

→ Let us consider a general reaction;

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

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.

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

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

Chemical Equilibrium

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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.

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

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

Chemical Equilibrium

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.

Equilibrium constant

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

Product concentrations

Reactant concentrations

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

→ For

Coefficient of A

$$2A \rightleftharpoons C + D$$

Equilibrium constant expression is

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

Power equal to coefficent of A

Chemical Equilibrium

■ Equilibrium Constant Expression for a Reaction in General

Terms:

→ The general reaction may be written as

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

The equilibrium constant expression is;

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

■ Equilibrium Constant (K_c):

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.**

SOLVED PROBLEM 1. Give the equilibrium constant expression for the reaction

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

SOLUTION

(1) The equation is already balanced. The numerical quotient of H_2 is 3 and of NH_3 is 2.

(2) The concentration of the 'product' NH_3 is $[NH_3]^2$

(3) The product of concnentrations of the reactants is $[N_2]\,[H_2]^3$

(4) Therefore, the equilibrium constant expression is

$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

■ 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 partial pressure of a gas in the equilibrium mixture is directly proportional to its molar concentration at a given temperature.**

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

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

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

SOLVED PROBLEM 1. Write the equilibrium constant expression for the synthesis of ammonia,

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

SOLUTION

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

Chemical Equilibrium

■ 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

$$K_p = \frac{(p_C)^l (p_D)^m}{(p_A)^j (p_B)^k} \qquad \text{.................. (1)}$$

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 n/V is the molar concentration.

Chemical Equilibrium

→ 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

Substituting these values in equation (1), we have

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

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

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

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

where Δn = (l + m) – (j + k), the difference in the sums of the coefficients for the gaseous products and reactants.

■ Le Chatelier's Principle:

→ In 1884, the French Chemist Henry Le Chatelier proposed a general principle which applies to all systems in equilibrium.

Le Chatelier's principle may be stated as : **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.

Chemical Equilibrium

■ Le Chatelier's Principle:

→ Thus when applied to a chemical reaction in equilibrium,

Le Chatelier's principle can be stated as: **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 minimise the change.**

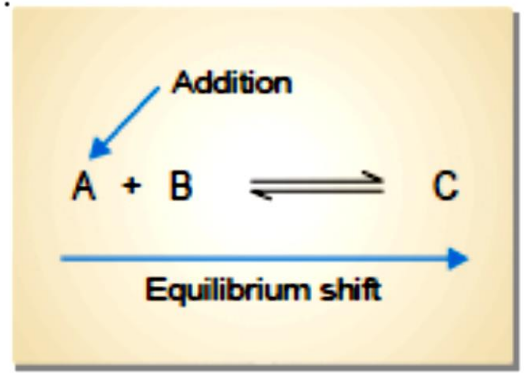
→ **Effect of a Change in Concentration:**

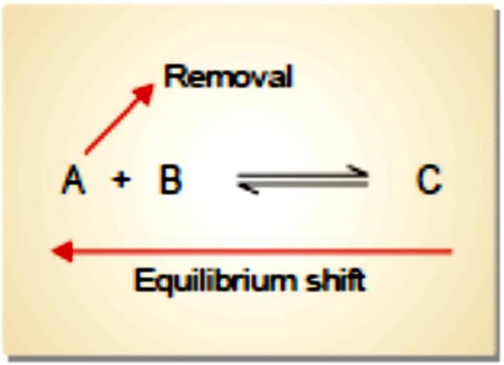
A change in the concentration of a reactant or product can be effected by the addition or removal of that species. Let us consider a general reaction

$$A + B \rightleftharpoons C$$

Chemical Equilibrium

When a reactant, say, **A** is added at equilibrium, its concentration is increased. The forward reaction alone occurs momentarily. According to Le Chatelier's principle, a new equilibrium will be established so as to reduce the concentration of **A**. Thus the addition of **A** causes the equilibrium to shift to right. This increases the concentration (yield) of the product **C**.





A decrease in the concentration of **A** by its removal from the equilibrium mixture, will be undone by shift to the equilibrium position to the left. This reduces the concentration (yield) of the product **C**.

→ Effect of a Change in Pressure:

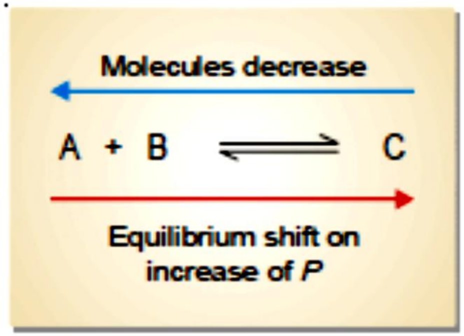
The pressure of a gaseous reaction at equilibrium is determined by the total number of molecules it contains. If the forward reaction proceeds by the reduction of molecules, it will be accompanied by a decrease of pressure of the system and ***vice versa***.

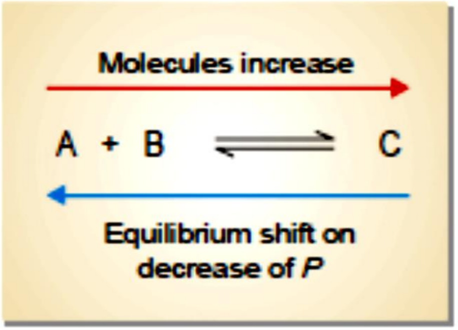
Let us consider a reaction,

$$A + B \rightleftharpoons C$$

The combination of **A and B produces** a **decrease of number of molecules** while the decomposition of **C into A and B results** in the increase of molecules. Therefore, by the increase of pressure on the equilibrium it will shift to right and give more C. A decrease in pressure will cause the opposite effect.

Chemical Equilibrium





→ **Effect of Change of Temperature:**

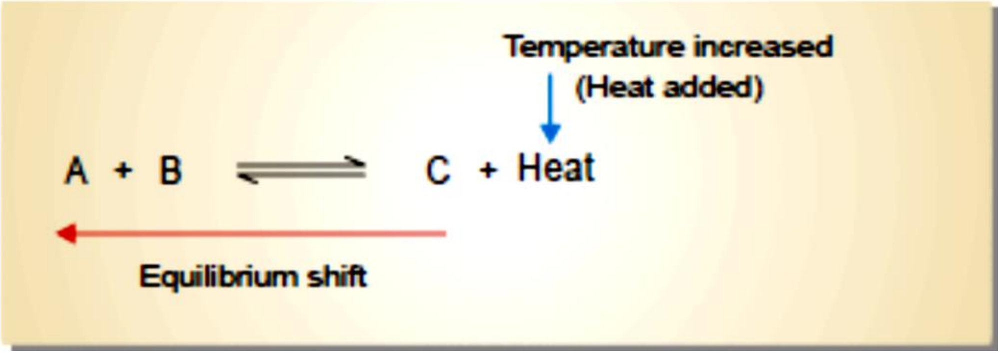
When temperature of a reaction is increased, the equilibrium shifts in a direction in which heat is absorbed.

Let us consider an exothermic reaction

$$A + B \rightleftharpoons C + heat$$

When the temperature of the system is increased, heat is supplied to it from outside. According to Le Chatelier's principle, the equilibrium will shift to the left which involves the absorption of heat.

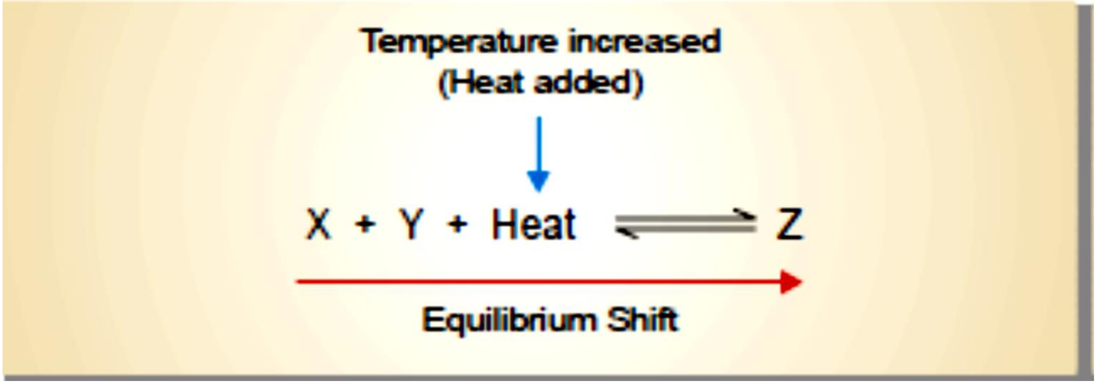
Chemical Equilibrium



→ In an endothermic reaction

$$X + Y + \text{heat} \rightleftharpoons Z$$

the increase of temperature will shift the equilibrium to the right as it involves the absorption of heat. This increases the concentration of the product Z.



Chemical Equilibrium

(1) The value of K_p at 25° C for the reaction

$$2NO(g) + Cl_2\,(g) \rightleftharpoons 2NOCl(g)$$

is 1.9×10^3 atm^{-1}. Calculate the value of K_c at the same temperature.

(2) Manufacture of Sulphuric acid (Contact Process)

The chief reaction used in the process is

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) + 42\text{ kcal}$$

How do you increase the formation of product?

Pressure= ?

Temperature= ?

Concentration= ?

Chemical Equilibrium

(1) At 500^o 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?.

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

(2) Manufacture of Nitric acid (Birkeland-Eyde process)

Nitric acid is prepared on a large scale by making use of the reaction

$$N_2(g) + O_2(g) \rightleftharpoons 2NO(g) - 43.2 \text{ kcal}$$

How do you increase the formation of product?

Pressure= ?

Temperature= ?

Concentration= ?